STRUCTURE AND REACTIONS OF SOME SULPHIDES AND SELENIDES OF PHOSPHORUS AND ARSENIC

By

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SULPHIDES AND SELENIDES OF PHOSPHORUS AND ARSENIC

TO MY WIFE
AND PARENTS

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TITLE: Structure and Reactions of Some Sulphides and Selenides of Phosphorus and Arsenic

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ABSTRACT

A continuation of studies of main group compounds carried out in this laboratory has led to the investigation of the structural and oxidative chemistry of several compounds and mixtures of the elements phosphorus, arsenic, sulfur and selenium. A number of questions and a lack of data regarding known compounds of these elements lead to an examination of the series $P_{4-X}As_XS_{3-Y}Se_Y$, X = 0-4, Y = 0-3. Raman spectra of several members of the series have been recorded. The ^{31}P and natural abundance ^{77}Se nmr spectra of these compounds were also recorded, including a reinvestigation and complete assignment of the ^{31}P nmr spectrum of P_4Se_3. Several trends in the coupling constants and chemical shifts were noted and an empirical equation was devised for the ^{31}P nmr spectral assignments for quaternary members of the series. The compound formerly believed to be $P_2As_2S_3$ was shown to be PAs_3S_3. The crystal structure of an occupationally disordered crystal of stoichiometry $P_2As_2S_3$ is also reported in this thesis.

The compound As_4S_4 and 1:1 As:Se fused mixtures were separately oxidized with the Lewis acids AsF_5 and SbF_5 to produce the new cations $As_3S_4^+$ and $As_3Se_4^+$. The cations were characterized as the salts $As_3S_4(AsF_6)$, $As_3S_4(SbF_6)$, $As_3Se_4(AsF_6)$ and $As_3Se_4(SbF_6)$ by Raman spectroscopy and infrared spectroscopy. The determination of the crystal structures of the first three salts is also reported.

Reactions of As_4S_4 with PF_5, PCl_5, BCl_3, SO_3, NbF_5, TaF_5 and WF_6 were shown to not proceed or, in the case of PF_5, to not produce a stable adduct. The action of AsF_5 on compounds and mixtures of heavy main group elements (e.g., Sb_2Te_3) of groups V and VI produced no new compounds that were identified and generally just gave known homopolyatomic cations of the chalcogens.

Oxidation of As_4S_4 with the halogens (X) chlorine and bromine produced AsX_3 and S_2X_2 while the reaction of $SbCl_5$ with As_4S_4 or 1:1 As:Se fused mixtures produced $SbCl_3$, $AsCl_3$ and the salts $SCl_3(SbCl_6)$ and $SeCl_3(SbCl_6)$, respectively. The crystal structure of $SCl_3(SbCl_6)$ is reported here along with unit cell data for $SeCl_3(SbCl_6)$ and $SBr_{1.2}Cl_{1.8}(SbCl_6)$ and the Raman data for all three compounds. Only AsSI was produced by the oxidation of As_4S_4 by I_2 in SO_2 while a reaction between molten P_4Se_3 and I_2 gave the new compound $\alpha P_4Se_3I_2$. Raman spectra for both AsSI and $\alpha P_4Se_3I_2$ were recorded as well as the ^{31}P nmr spectrum for the latter.

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CHAPTER I

INTRODUCTION

The chemistry of the sulfides and selenides of phosphorus and arsenic has received little attention,[1,2] although there has been considerable interest in recent years in the chemistry of sulfur-nitrogen compounds.[3-6] An interesting development in S-N chemistry has been the preparation of cationic species e.g., $S_4N_4^{+2}$ by the oxidation of S_4N_4 and related compounds with oxidizing agents such as $SbCl_5$, SbF_5 and HSO_3F.[7-9] A related development in the chemistry of the non-metals of Group VI has been the preparation of cations of these elements, such as S_8^{+2}, by the oxidation of the elements with AsF_5, SbF_5 or H_2SO_4.[10] Both the S-N cations and the Group VI non-metal cations have been found to have interesting and often unexpected structures that exhibit unusual types of bonding.

It was of interest and importance therefore to investigate the possibility of cation formation by the oxidation of the sulfides and selenides of phosphorus and arsenic. Any new cations so obtained would add to our knowledge of these compounds and main group cluster atom formation. Also, in view of our meagre knowledge of the P-S and P-Se compounds themselves, some investigations were carried out on the preparation of these compounds.

I-1 Inorganic Chemistry of Group VB Chalconides and Related Species

I-1(i) Preparation of Group VB/VIB Compounds‡

Set out in Tables I-1 and I-2 are the preparations of many of the group VB chalconides. Many are either naturally occurring or are made by heating the elements or another modification of the compound under appropriate conditions. The preparations, which appear to be as varied as the products, include examples of oxidations under extreme conditions, disproportionations, removal and/or removal-replacement of exocyclic atoms and some very complex rearrangements involving potentially interesting intermediates.

There have been few reports of ternary or quaternary VB/VIB compounds. The series $Bi_2Se_XTe_{3-X}$ (X = 0-3)[11] and $P_4O_6E_X$ (E = O, S, Se or some combination of these and X = 0-2, 3 or 4 depending on the series)[12] have been reported. The compounds Sb_2SeTe_2,[13] $P_2As_2S_3$,[14] and P_4O_6SSe[12] are also known. It has been stated[15] that no compounds of the type $P_4S_{3-X}Se_X$ (X = 1,2) could be detected by X-ray powder diffraction or differential thermal analysis in a phase diagram study of mixtures of P_4S_3 and P_4Se_3.

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‡Group VB-group VIB compounds will often be abbreviated VB/VIB. Within this thesis the letter B will refer to main group elements.

TABLE I-1. Preparation of Group VB Chalconides

		ref.
$(PS)_n$	$2nEPX_3+3nMg \xrightarrow[\text{solvent}]{\text{dry}} 3nMgX_2+2(PE)_n$	1
$(PS_X)_n$	$2nH_3PS_4+3nS_YCl_2 \rightarrow 2(PS_X)_n+6nHCl$	1
P_4S_2	$P_4S_3+\frac{1}{2}P_4 \xrightarrow{\Delta} P_4S_2$	16
P_4S_4(II)	$P_4S_3+\alpha P_4S_5 \xrightarrow{350°} P_4S_4$	17
αP_4S_5	$P_4S_3+\frac{1}{4}S_8 \xrightarrow[I_2\text{cat.}]{h\nu} \alpha P_4S_5$	2
αP_4S_4	$\alpha P_4S_3I_2+(Me_3Sn)_2S \xrightarrow{CS_2} \alpha P_4S_4+2Me_3SnI$	18
P_4S_9	$P_4S_{10}+P\phi_3 \xrightarrow{CS_2} P_4S_9+SP\phi_3$	2
As_4S_5	$As_4S_3 \xrightarrow[CS_2]{h\nu}$ small amount of As_4S_5	19
As_2S_5	$2H_3AsO_4+5H_2S \xrightarrow{0°C} As_2S_5+8H_2O$	20
N_4Se_4	$SeBr_4+$excess $NH_3 \xrightarrow{CS_2} N_4Se_4+NH_4Br$	3
N_4Te_4	$TeBr_4+NH_3 \xrightarrow{-15 \text{ to } -70°} N_4Te_4+NH_4Br$	3

General Method for Most M_XE_Y Compounds, M = VB, E = VIB; X = 2 or 4, Y = 3-10.

$XM+YE \xrightarrow{\Delta}$ P_4S_3, P_4S_7, P_4S_{10} 20
P_4Se_3, P_4Se_{10}
As_4S_3, As_4S_4, As_2S_3, As_2S_5,
As_4Se_3, As_4Se_4, As_2Se_3
Sb_2S_3, Sb_2Se_3, etc.

Table I-2. Sulfur-Nitrogen Compounds and Ions

Species	Shape	S-N Bond Lengths	Preparation†
$(SN)_X$	∞ chains	1.593(3)-1.628(7)	$S_2N_2 \xrightarrow[48\ hr]{RT} (SN)_X$
N_2S_2	ring	1.651(1)-1.657(1)	$S_4N_4 \xrightarrow[Ag\ wool]{80°\ vac} 2S_2N_2$
N_2S_4	ring?		$Hg_5(NS)_8+4S_2Cl_2 \xrightarrow{CS_2} 4N_2S_4(\ell)+3HgCl_2+Hg_2Cl_2$
N_2S_{11}	2 fused rings	1.68-1.70	$S_6(NH)_2+S_3Cl_2 \rightarrow N_2S_{11}+2HCl$
$(NS_7)_2S_X$ X=1-5	ring-chain-ring	1.70-1.71	$2S_7NH+S_XCl_2 \rightarrow (S_7N_2)S_X+2HCl$, X = 1-5
N_4S_4	S_4N_4	1.619(2)-1.633(2)	$S_2Cl_2+Cl_2+NH_3 \xrightarrow{CCl_4} S_4N_4$ + other products
N_6S_5	capped S_4N_4	1.536(3)-1.702(3)	$2Br_2+3Bu_4N^+S_4N_5^- \xrightarrow[CH_2Cl_2]{0°} N_6S_5$ + ?
NS^+	chain		$S_3N_3F_2(AsF_6) \xrightarrow{\Delta} SN(AsF_6)+2NSF$
NS_2^+	chain	1.464(3)	$2SbCl_5+S_7NH \xrightarrow{SO_2} S_2N(SbCl_6)+S_8+HCl+SbCl_3$
$N_2S_3^+$	ring	1.564(7)-1.610(3)	$3AsF_5+S_4N_4 \xrightarrow{SO_2} S_3N_2(AsF_6)+AsF_3+?$
$N_3S_4^+$	ring	1.548-1.566	$2S_2Cl_2 + 3S_4N_4 \rightarrow 4(S_4N_3)Cl$
$N_4S_4^{+2}$	ring	1.419(5)-1.778(5)	$3SbCl_5+S_4N_4 \xrightarrow{SO_2} S_4N_4(SbCl_6)_2+SbCl_3$
$N_4S_6^{+2}$	2 rings	1.545(7)-1.610(6)	$S_4N_4+\frac{1}{8}S_8 + 3AsF_5 \xrightarrow{SO_2} S_6N_4(AsF_6)_2+AsF_3$
$N_5S_4^+$	2 fused rings	1.545(4)-1.674(4)	$Me_3SiNSNSiMe_3+S_3N_3Cl_3 \xrightarrow{CCl_4} (S_4N_5)Cl+2Me_3SiCl$

(continued...)

TABLE I-2 (continued).

$N_5S_5^+$	ring	1.465-1.590	$3SbCl_5+S_3N_3Cl_2 \xrightarrow{SOCl_2,S_4N_4} S_5N_4(SbCl_6)$
NS_4^-	branched ring	1.521(5)-1.667(5)	$(\phi_3P_2N)(S_4N_5) \xrightarrow[CH_3CN]{\Delta} (\phi_3P_2N)(NS_4)+S_8+N_2\uparrow$
$N_3S_3^-$	ring	1.580(2)-1.626(12)	$3CsN_3+4S_4N_4 \xrightarrow{MeOH} 3Cs(S_3N_3)+S_8+N_2\uparrow$
$N_5S_4^-$	capped S_4N_4	1.57(2)-1.68(2)	$3NaN_3+4S_4N_4 \xrightarrow{MeOH} 3Na(S_4N_5)+\frac{1}{2}S_8+5N_2\uparrow$

[†] Most equations not balanced, ref. 3-6,9,21-36.

I-1(ii) Reactions of the Elements of Groups VB and VIB and S_4N_4 with Lewis Acids and Oxidizing Agents

No adducts of Lewis acids and main group elements of Group VI have been formed. There have, however, been rather extensive investigations in recent years of the oxidation of the chalcogens with oxidizing Lewis acids and other acidic oxidizing agents.[10] This has lead to the production of a number of interesting cationic species. Most of the cations are stable only in highly acidic media such as HSO_3F-SbF_5, H_2SO_4-SO_3, $AlCl_3$ melts or in very weakly basic and rather unreactive solvents like SO_2. Stable solids usually contain the very weakly basic, singly charged anions of very strong acids, e.g., SO_3F^-, SbF_6^-, $HS_2O_7^-$, or $AlCl_4^-$.

Many of the products and reactions are shown in Tables I-3 and I-4. These preparations include oxidation of an element by oleum or by $S_2O_6F_2$ in HSO_3F; reaction of an element with a chloride of the element in a Lewis acid melt; oxidation of an element, mixture or alloy by AsF_5 or SbF_5 in SO_2; reaction of an element with a polyatomic cation of a different element in SO_2 and reaction between polyatomic cations of two different elements in SO_2. Crystalline salts have most easily been obtained from the melts and SO_2 solutions.

TABLE I-3. Polyatomic Cations of Group VB and the Chalcogens

M_{19}^{+2}	M_{10}^{+2}	M_8^{+2}	M_6^{+2}	M_4^{+2}	M_9^{+5}	M_5^{+3}	M_6^{+4}	Other
								Sb_n^{+n}
		Bi_8^{+2}			Bi_9^{+5}	Bi_5^{+3}		
S_{19}^{+2}		S_8^{+2}		S_4^{+2}				
	Se_{10}^{+2}	Se_8^{+2}		Se_4^{+2}				
				Te_4^{+2}			Te_6^{+4}	
	$Se_8Te_2^{+2}$		$S_3Te_3^{+2}$	Se_3Te^{+2}				
			$Se_3Te_3^{+2}$	$Se_2Te_2^{+2*}$				
			$Se_4Te_2^{+2}$	$SeTe_3^{+2}$				

*Both cis and trans.

TABLE I-4. Examples of Preparations of Polyatomic Cations of Groups VB and VIB

$2n\ Sb + 3n\ AsF_5 \xrightarrow{SO_2} 2Sb_n(AsF_6)_n + n\ AsF_3$

$4Bi + BiCl_3 + 3AlCl_3 \xrightarrow{350°C} Bi_5(AlCl_4)_3$

$8Bi + 2BiCl_3 + 3HfCl_4 \xrightarrow{450°C} Bi^+Bi_9(HfCl_6)_3$

$22Bi + 2BiCl_3 + 6AlCl_3 \xrightarrow[AlCl_3]{270°-320°C} 3Bi_8(AlCl_4)_2$

$19S_8 + 24AsF_5 \xrightarrow{SO_2/SO_2ClF} 8S_{19}(AsF_6)_2 + AsF_3$[a]

$S_8 + 3SbF_5 \xrightarrow{SO_2} S_8(AsF_6)_2 + AsF_3$

$15Se + SeCl_4 + 4AlCl_3 \xrightarrow{\Delta} 2Se_8(AlCl_4)_2$

$4Se + S_2O_6F_2 \xrightarrow{HSO_3F} Se_4(SO_3F)_2$

$Te_4(AsF_6)_2 + S_8(AsF_6)_2 \xrightarrow{SO_2} Te_3S_3(AsF_6)_2$[a]

$2Te + Se_8(AsF_6)_2 \xrightarrow{SO_2} Se_8Te_2(AsF_6)_2$[a]

$1:1\ Se:Te + AsF_5 \xrightarrow{SO_2} Te_2Se_4(AsF_6)_2 + Te_3Se_3(AsF_6)_2 + AsF_3$[a]
alloy or mixture

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[a] Not balanced.

Reaction of antimony metal with large amounts of SbF_5 in SO_2 gives what was first thought to be $SbF_3 \cdot SbF_5$[37] but was later characterized as $Sb_6F_{13}(SbF_6)_5$ by[38] X-ray crystallography.

The reactions of S_4N_4 with Lewis acids leading to the formation of S_4N_4 adducts and several new S-N cations have been extensively studied. There are over forty known adducts[39] of S_4N_4 involving Lewis acids of either transition metals or main group elements and several sulfur-nitrogen cations, most of the latter having been made with a variety of counterions. As noted in Table I-2 most of the cations can be made by the action of Lewis acids on S_4N_4 or related species.

I-1(iii) Lewis Acid Chemistry of Phosphorus Chalconides

The Lewis acid chemistry of phosphorus chalconides has been little studied. It has been demonstrated that transition metal complexes containing P_4S_3 as a ligand can be produced by ligand exchange in solution. Examples of these are: $Mo(CO)_5P_4S_3$, cis-$(P_4S_3)_2M(CO)_4$ [M = Cr, Mo, W] and $Ni(P_4S_3)_4$.[40] Lewis acid complexes of P_4S_3 with CuCl, CuBr and $CuCl_2$ have also been reported.[41] The decasulfide, P_4S_{10}, reacts with $FeCl_3$ to give $SPCl_3$, $FeCl_2$ and FeS_2.[42] There appears to be no information on reactions of any of the heavier group VB chalconides with Lewis acids. No reports have been made of any VB/VIB cations being produced by reaction with Lewis acids or by any other reactions.

I-1(iv) Halogen Chemistry of Group VB Chalconides

A large number of halide derivatives of S-N compounds have been prepared, some of which have been known for some time, e.g., NSF, NSCl, NSF_3, $N_3S_3Cl_3$, $N_3S_3F_3$, $N_4S_4F_4$ and $N_2S_3Cl_2$.[3] Recently the compounds $S_4N_4Cl_2$, $S_4N_4F_2$[43] and $(S_4N_4X_{0.4})_n$ (X = Br, ICl, IBr)[44] have been made.

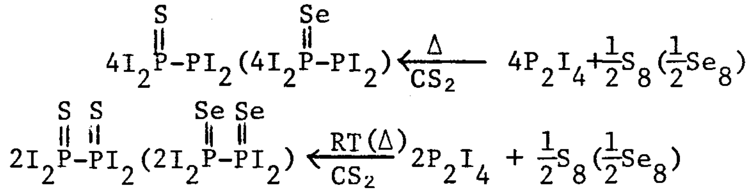
The preparative chemistry of the phosphorus chalcogen halides is summarized in Table I-5. Excluding the well known thiophosphoryl halides SPF_3, $SPCl_3$ and $SPBr_3$, which will not be discussed here, this table summarizes essentially all the known chemistry of the phosphorus chalcogen halides.

The arsenic-chalcogen-halides usually form glasses. However, the polymeric compounds AsSI, AsSeI, $As_4Te_5I_2$ and $As_8Te_7I_5$ have been partially characterized by Russian workers by Mössbauer spectroscopy and X-ray powder diffraction.[45,46] Recently it has been reported that the reaction systems As_2S_3/AsI_3 and $As_4S_4/S/I_2$ also give AsSI.[47] No molecular compounds have been reported.

TABLE I-5. Phosphorous-Chalcogen-Halide Chemistry

$$\left.\begin{array}{l} P_4 + \frac{3}{8}S_8 + I_2 \xrightarrow[CS_2]{RT} \\ 4P_{red} + \frac{3}{8}S_8 + I_2 \xrightarrow{\Delta} \\ P_4S_3 + I_2 \xrightarrow[CS_2]{RT} \end{array}\right\} \alpha P_4S_3I_2 + AgX\ (X=Cl^-, Br^-, CN^-) \rightarrow \alpha P_4S_3X_2$$

$$P_4S_3(P_4Se_3)+I_2 \xrightarrow[CS_2\ (days)]{0°C} \beta P_4S_3I_2(\beta P_4Se_3I_2) \xleftarrow[CS_2]{} P_4S_3+PI_3$$



$$4I_2\overset{S}{\overset{\|}{P}}\text{-}PI_2(4I_2\overset{Se}{\overset{\|}{P}}\text{-}PI_2) \xleftarrow[CS_2]{\Delta} 4P_2I_4+\frac{1}{2}S_8(\frac{1}{2}Se_8)$$

$$P_4 + \frac{1}{2}S_8 + 4I_2 \xrightarrow[CS_2]{RT} 2I_2\overset{S}{\overset{\|}{P}}\text{-}\overset{S}{\overset{\|}{P}}I_2(2I_2\overset{Se}{\overset{\|}{P}}\text{-}\overset{Se}{\overset{\|}{P}}I_2) \xleftarrow[CS_2]{RT(\Delta)} 2P_2I_4 + \frac{1}{2}S_8(\frac{1}{2}Se_8)$$

$$P_4 + \frac{1}{2}S_8 + 6I_2 \xrightarrow[CS_2\,(days)]{0°C} 4SPI_3(4SePI_3) \xleftarrow[CS_2,\ h\nu]{10\text{-}15°C(40°C)} 4PI_3 + \frac{1}{2}S_8(\frac{1}{2}Se_8)$$

$$P_4S_3 + \frac{1}{4}S_8 \xrightarrow[CS_2\ (days)]{h\nu,\ I_2\ cat.} \alpha P_4S_5 + \text{other products}$$

$$5P_4S_3(P_4Se_3) + 12Br_2 \xrightarrow[CS_2]{0° \rightarrow RT} 3P_4S_7(P_4Se_5) + 8PBr_3 + \text{other products*}$$

$$P_4S_3I_2 + \text{excess } I_2 \xrightarrow[CS_2]{} P_4S_7 + PI_3{}^*$$

$$7P_2S_2I_4 \xrightarrow{h\nu} 2P_4S_7 + 6PI_3 + 5I_2$$

$$P_4S_3 + Br_2 \xrightarrow[CS_2]{0°C} P_2S_6Br_2 + P_2S_5Br_4{}^*$$

$$P_4S_{10} + Cl_2 \xrightarrow[CCl_4]{} PCl_5 + S_2Cl_2 + SCl_2{}^*$$

$$P_4S_{10} + SF_4 \xrightarrow{\Delta} PF_5 + S_8{}^*$$

$$P_4S_{10} + NF_3 \xrightarrow{\Delta} (NPF_2)_n,\ n = 3\text{-}9 + PF_3 + PF_5 + SPF_3 + SF_4 + SF_6{}^*$$

$$P_4S_{10} + 3PCl_5(PBr_5) \xrightarrow{\Delta} 5SPCl_3(SPBr_3) + KSO_2F(SbF_5) \rightarrow SPF_3$$

*Not balanced. Ref. 1-3, 43-55.

By fusing the compounds M_2E_3 with the halides MX_3 (M = Sb, Bi; E = S, Se, Te; X = Cl, Br, I) the air stable, unreactive compounds MEX are produced.[3] They are all polymeric with the sulfides and selenides having structures consisting of two interconnected infinite chains $(ME)_n$. The chains are crosslinked by M-E bonds such that each group V atom has three chalcogen neighbours as well as two bromine neighbours outside the chain. A layer structure related to Bi_2Te_3 is noted for BiTeBr and BiTeI.[56]

I-2 Structure and Bonding in Group VB Chalconides and Related Species

Structurally group VB/VIB compounds have been fairly well studied. Listed in Table I-6 are all the known binary Group VA-Group VIA compounds. Most have been characterized by electron diffraction or X-ray crystallography. Generally they can be subdivided into three main structural groups: small molecules with one or two central atoms, molecular rings and cages, and two or three dimensional polymers. These groups correspond roughly to (1) the nitrogen oxides; (2) the nitrogen chalconides, sulfur-nitrogen ions and phosphorus and arsenic-group VIB compounds and (3) the compounds of

TABLE I-6 Binary VB-VIB Compounds

Empirical Formula										
M_2E[a]	M_4E_3	ME	M_4E_5	M_2E_3		M_4E_7	ME_2	M_4E_9	M_2E_5	Others
				molecular	polymer					
N_2O		NO		N_2O_3			NO_2		N_2O_5	NO_3
							N_2O_4			OONO
		N_2S_2					N_2S_4			N_2S_{11}
		N_4S_4								N_2S_X X=15-20
		N_4Se_4								
		N_4Te_4								
				P_4O_6		P_4O_7	P_4O_8	P_4O_9	P_4O_{10}	$(PO)_n$
										$(PO_2)_n$
P_4S_2	P_4S_3[b]	αP_4S_4	αP_4S_5[b]	P_4S_6[c]		αP_4S_7[b]		P_4S_9[b]	P_4S_{10}[b]	$(PS_X)_n$
		βP_4S_4	βP_4S_5							
		P_4S_4II								
						Generally:	Molecular Polymer			
	P_4Se_3[b]	P_4Se_4[b]	P_4Se_5						P_2Se_5	
					P_2Te_3					
				As_4O_6	As_2O_3I+II					
	As_4S_3[b]	As_4S_4[b]	As_4S_5		As_2S_3				As_2S_5	As_4S
		As_4S_4II								
	As_4Se_3[b]	As_4Se_4			As_2Se_3					
		AsTe[d]			As_2Te_3					
				Sb_4O_6	Sb_2O_3		Sb_2O_4		Sb_2O_5	Sb_6O_{13}
					Sb_2S_3					
					Sb_2Se_3					
					Sb_2Te_3					
					Bi_2O_3[b]					
					Bi_2S_3		BiS_2			
					Bi_2Se_3		$BiSe_2$			
	Bi_4Te_3	BiTe			Bi_2Te_3					

---

[a] M = Group VB, E = Group VIB

[b] Two or more crystallographic forms

[c] As a mixed crystal with P_4S_7 - known as βP_4S_7

[d] Not molecular

antimony and bismuth. Recent discussions[57-58] on the basic structural relationships of main group rings, cages and clusters have helped to increase interest in the second broad group mentioned above as well as the previously discussed investigations of group VIB cations.

I-2(i) Structures of the Elements and Ions of Groups VB and VIB

Before discussion of the basic structures of VB/VIB compounds, it is appropriate to briefly review the structures of the individual elements[3] and their ions to lay a foundation for comparison (Figure I-1). Nitrogen and oxygen molecules and chalconide ions are simple unbranched chains while elemental sulfur and Se_3S_5[59] exist as eight membered crown-shaped rings (A), although smaller and larger rings are known for sulfur. There is also a thermodynamically unstable eight-membered selenium ring. Catenasulfur, a metastable polymer; grey selenium and tellurium all consist of helical chains with weak interchain bonding.

The chalcogen cations S_4^{+2}, Se_4^{2+}, Te_4^{+2}, $Te_{4-n}Se_n^{+2}$ (n = 0-4)[57] and the isoelectronic anion Bi_4^{-2}[60] have square planar structures with some multiple bond character. The cations S_8^{+2} and Se_8^{+2} are eight membered rings like the elements but with an exo-endo conformation (B).[37,38] A six

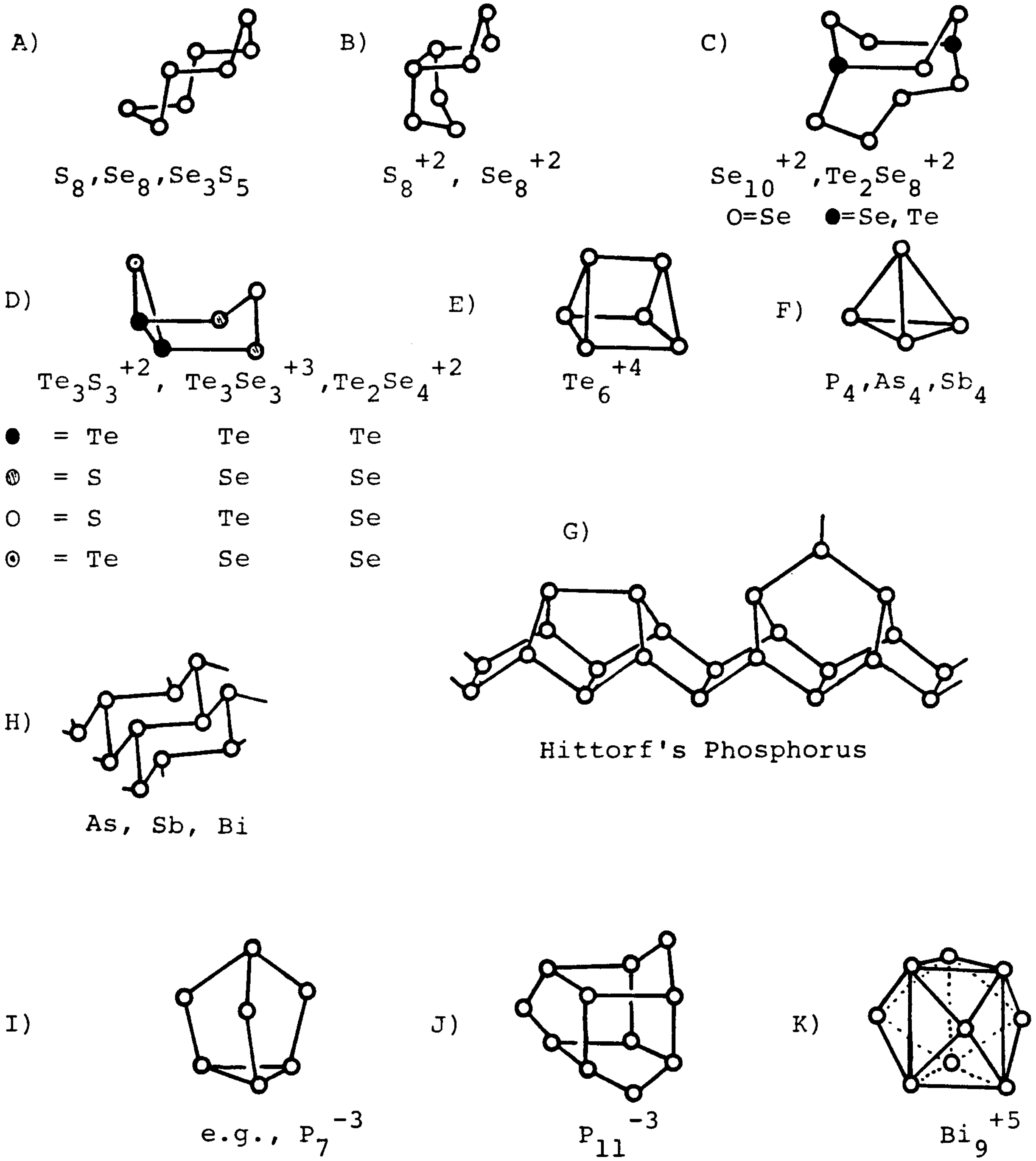


FIGURE I-1. Structures of Group VB and Group VIB Elements and Ions.

membered boat-shaped ring can be discerned in the[57] structures of Se_{10}^{+2}, $Te_2S_8^{+2}$, $Te_3S_3^{+2}$, $Te_2Se_4^{+2}$ and Te_6^{+4} (C) & (D). The first two have the ring bridged by a four atom chain to produce an eight membered ring while the last ion has a bond between the upturned ends of the ring to form a trigonal prism (E). Finally, S_{19}^{+2} consists of two seven membered rings joined by a five atom chain.[57]

Condensation of the vapours of phosphorus, arsenic and antimony produce tetrahedral molecules (F) of decreasing stability. Hittorf's phosphorus, a form of red phosphorus, consists of infinite chains of P_8 cuneane units with two phosphorus bridges between each unit and every other unit having an additional phosphorus atom spanning it (G).[61] Black phosphorus and the common forms of arsenic, antimony and bismuth consist of layers of fused six atom rings (H) such that each atom has three directly bonded neighbours and three farther away. The cations and anions of Group VB have not been as extensively characterized with only P_7^{-3},[62] As_7^{-3},[63] Sb_7^{-3},[64] P_6^{-4},[65] P_{11}^{-3},[66] and Bi_9^{+5} [67] having been structurally determined by X-ray crystallography. However, others are known to exist on the basis of solution studies, analysis and spectroscopic measurements. The first three anions can be considered as either end-capped trigonal prisms with the capped face expanded or tetrahedra with all the edges of a common apex bridged (I). The anion P_6^{-4} is a flat, regular ring. The structure of P_{11}^{-3} can be derived by bridging three non-adjacent edges of a cube so as to maintain three-fold symmetry around a body diagonal (J). The cation Bi_9^{+5} is a slightly distorted tricapped trigonal prism (K).

I-2(ii) Structures of the Group VB/VIB Compounds

a) S_4N_4 Structure

The molecular structure of realgar (As_4S_4) was first determined by electron diffraction studies of the vapour by Lu and Donahue in 1944.[68] Realgar is a cage of point group symmetry D_{2d} with the sulfur atoms occupying the corners of a square and the arsenic atoms forming an intermeshing tetrahedron. It can also be considered to be a saddle-shaped 8-membered ring of alternating elements with transannular bonds (Figure I-2). This is known as the S_4N_4 structure. X-ray structural determinations have shown that the molecular unit is[69,70] maintained in both the α and β forms of the solid. Figure I-2 shows the similarity in structure of As_4S_4 with S_4N_4.[24] The compounds αP_4S_4,[71] As_4Se_4,[72-75] N_4Se_4 [76] As_4S_4(II)[77] and βP_4S_4 [71] also have this same basic shape (Figure I-3). Usually the most electronegative element is in the square but for As_4S_4(II) and βP_4S_4 this is not strictly followed.

TABLE I-7 Bond Lengths in S_4N_4-shaped Molecules

Molecule	M-E Bonds	Σ Single Covalent Radii	M-M or E-E Bonds	Σ Single Covalent Radii
S_4N_4	1.619(2)-1.633(2)	1.73	2.590(1) 2.595(1)	2.06
Se_4N_4	1.77(3)-1.80(2)	1.87	2.748(9)	2.34
αP_4S_4	2.106(1)-2.112(1)	2.23	2.350(1)	2.20
αAs_4S_4	2.228(2)-2.247(2)	2.24	2.566(1) 2.571(1)	2.42
βAs_4S_4	2.238(9)-2.252(9)	2.24	2.593(6)	2.42
As_4S_4(II)	2.199(4)-2.269(4)	2.24	2.510(3) 2.550(3)	2.42

M = VB atom, E = VIB atom.

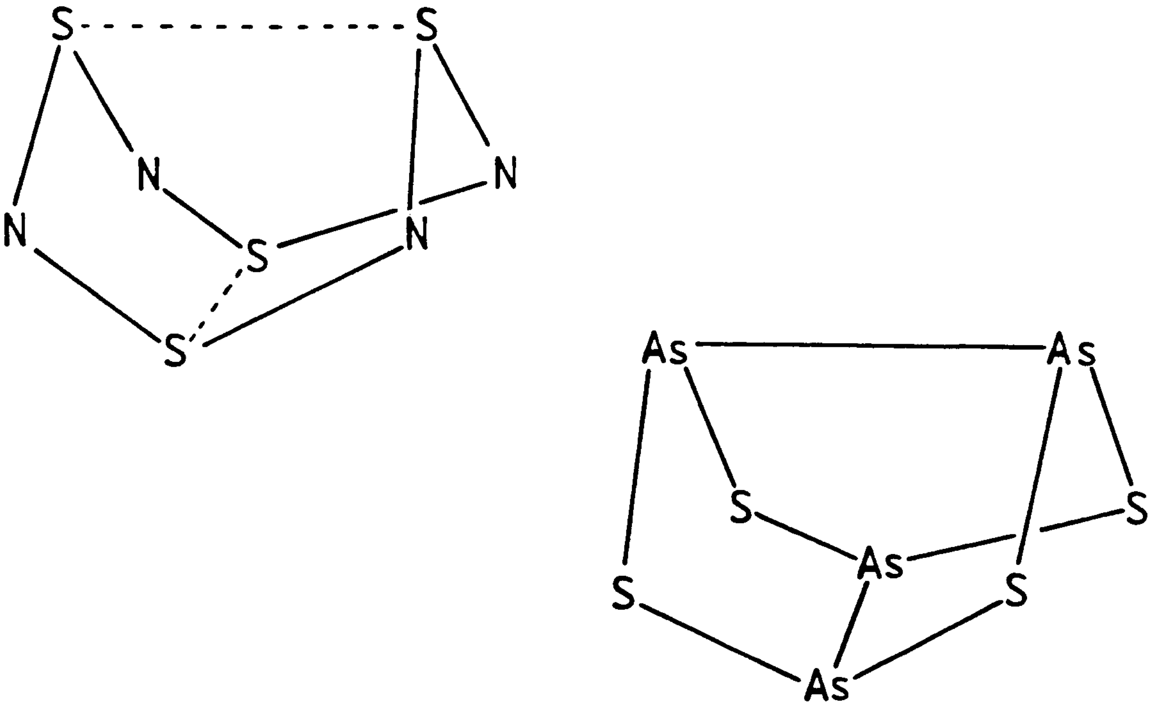
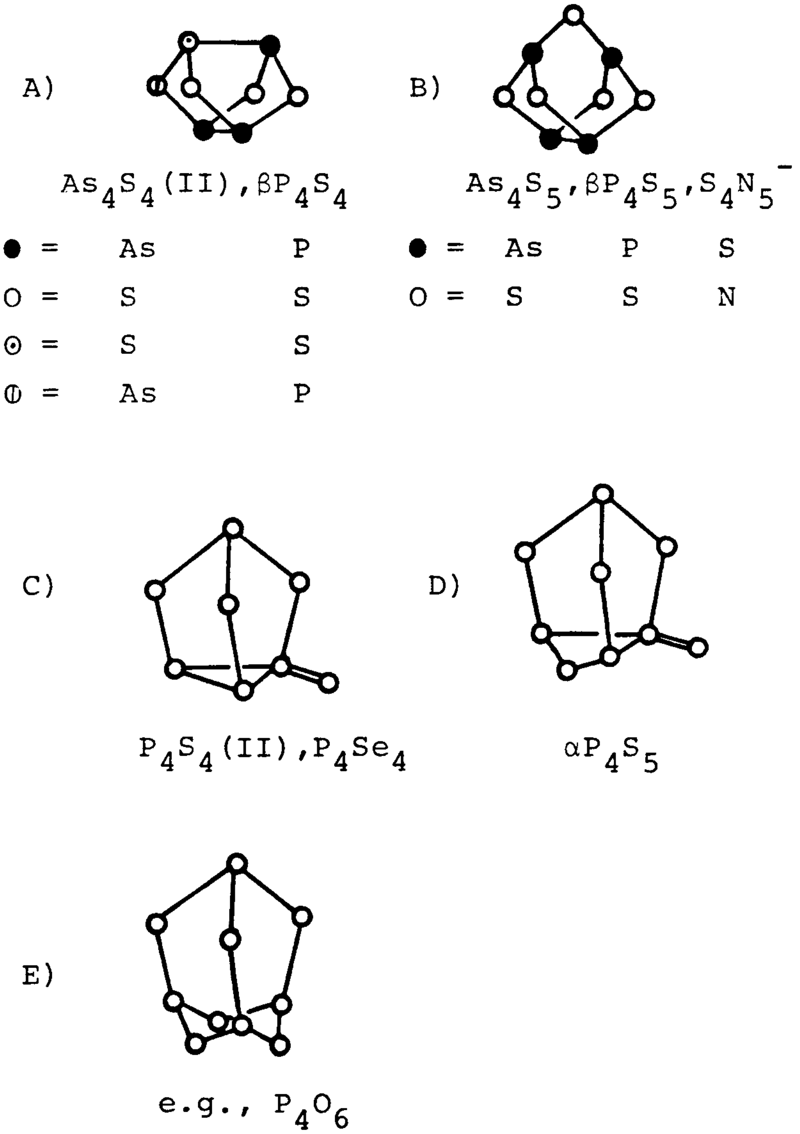


FIGURE I-2. Structures of S_4N_4 and αAs_4S_4.



A) As_4S_4(II), βP_4S_4

● = As P

○ = S S

⊙ = S S

⦶ = As P

B) As_4S_5, βP_4S_5, $S_4N_5^-$

● = As P S

○ = S S N

C) P_4S_4(II), P_4Se_4

D) αP_4S_5

E) e.g., P_4O_6

FIGURE I-3. Molecular Structures of Some Group VB-Group VIB Compounds.

In Table I-7 are listed the bond lengths of the molecules exhibiting the structure of S_4N_4. It appears that N_4Se_4 may also have some multiple bond character like S_4N_4 (Table I-2). On comparison with other phosphorus-sulfur molecules the P-S bonds of αP_4S_4 appear to be quite normal. Note the relative length of the transannular chalcogen linkages in S_4N_4 and Se_4N_4 compared to the corresponding bonds between two arsenic atoms in As_4S_4. The trivalent atoms are generally in the three coordinate positions in the isomers of As_4S_4 while this is not the case for S_4N_4. This results in some considerable differences in reaction chemistry.

The compounds $MPbP_{14}$ (M = Zn, Cd and Hg), KP_{15}[78,79] and Hittorf's phosphorus as mentioned previously have networks based on the S_4N_4 structure. Beta P_4S_5[80] and As_4S_5[19] have one M-M linkage of the S_4N_4 structure bridged by a sulfur atom. The molecule N_6S_5 and the anion $N_5S_4^-$ have the S_4N_4 structure with bridges of NSN and N^-, respectively.

b) Birdcage Structure

Another structural type found in VB/VIB compounds is the "bird-cage" formed by the bridging of all the edges of a common apex of the parent tetrahedron (Fig. I-3). Examples of this "bird-cage" structure are quite limited, and usually involve group VB elements. Besides the previously mentioned homopolyatomic anions P_7^{-3}, As_7^{-3} and Sb_7^{-3}, isostructural molecules are P_4S_3,[81] P_4Se_3,[82] α[83] and β[84] As_4S_3, α and βAs_4Se_3,[85] P_7R_3,[86] As_7R_3[87] (R = $SiMe_3$), $P_4(SiMe_2)_3$[86] and $CH_3C(CH_2As)_3$.[88] The structures of the related compounds P_4S_4II, P_4Se_4[89] and αP_4S_5 are shown in Figure I-3.

c) Adamantane Structure

The last main basic molecular shape is that of P_4O_6. In this molecule all phosphorus-phosphorus bonds of the P_4 tetrahedron have been replaced by oxygen bridges (Fig. I-3). All the structures of more highly oxidized, chalcogen-rich, polymeric molecules have the exocyclic double bonds mentioned earlier. The molecule P_4O_{11} is believed[90] to have one intramolecular peroxide linkage. The P_4O_6, adamantane or, the urotropinic structure is more widespread than the others previously mentioned with examples either proven or suggested for molecules involving Groups IIIB and IVB elements as well as Group VB. Some of these are: $(BSH)_4S_3(NR_2)_3$, $(AlCl)_4(NMe_2)_6$, $C_{10}H_{16}$, $(SiR)_4(NH)_6$, $(Si\phi)_4(P\phi)_6$, $(SiR)_4O_6$, $(SiR)_4S_6$, $(SiR)_4Se_6$, $(Ge\phi)_4(P\phi)_6$, $(GeR)_4S_6$, $(SnR)_4S_6$, $N_4(CR_2)_6$, $P_4(NR)_6$, $(PS)_4(NR)_6$, $As_4(NR)_6$, As_4O_6, Sb_4O_6, and $Sb_4(NR)_6$; (R = organic moiety).[91]

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d) Polymeric Structures and Poorly Defined Species

The compounds Claudetite I[92] and II;[93] (forms of As_2O_3), As_2S_3,[69] As_2Se_3[94,95] and orthorhombic Sb_2O_3[96] (valentinite) consist of MX_3 pyramids sharing the group VIB atoms at the corners to form infinite spirals linked into pairs. In arsenic telluride, although there are linked spirals, half the arsenic atoms are octahedrally coordinated by tellurium.[97] Alternating group VB/VIB spirals are also seen in Sb_2S_3,[98] Sb_2Se_3,[99] and Bi_2S_3.[3] These short spirals VIB-VB-VIB-VB-VIB have a coordination number for the group VB atoms ranging from three to five and two or three for the chalcogen. The exact nature of the coordination depends on the orientation of the spiral units with respect to each other. The structures of Sb_2Te_3,[100] Bi_2Se_3,[11] and Bi_2Te_3[11] consist of infinite sheets having five distinct layers each of one element such that the sequence of layers in the sheet is, again, VIB-VB-VIB-VB-VIB. All atoms have coordination number six.

It has been suggested[101] that AsTe has an NaCl type structure. There is also mention in the literature of P_2Te_3[102] and As_2S_5[20] but there is no evidence for these compounds other than analytical data. For P_4Se_{10} Russian workers[103] have inferred on the basis of solid state ^{31}P NMR that phosphorus is in the +5 oxidation state.

Mössbauer spectroscopy has shown that Sb_2S_5 contains no Sb(V).[104] A close scrutiny of a paper[105] claiming the formation of As_3S_2 shows that the formula is better written as $As_4S_{2.7}$. All the major X-ray powder pattern lines can be indexed to As_4S_3.

I-2(iii) Observations on the Structure and Bonding of Group VB-Group VIB Compounds

The important structural features of the elements that appear fairly regularly in the structures of the VB/VIB compounds are the tetrahedron of the group VB elements and the spiral chain of group VIB elements. Short spiral lengths can even be seen in the structure of the molecule As_4S_4 (Figure I-4). It would appear that high chalcogen content in conjunction with the greater tendency of the heavier elements to establish metal-like close packing structures results in the diagonal division between molecular and polymeric species seen in Table I-6. Few of any of the compounds have dichalcogen bonds.

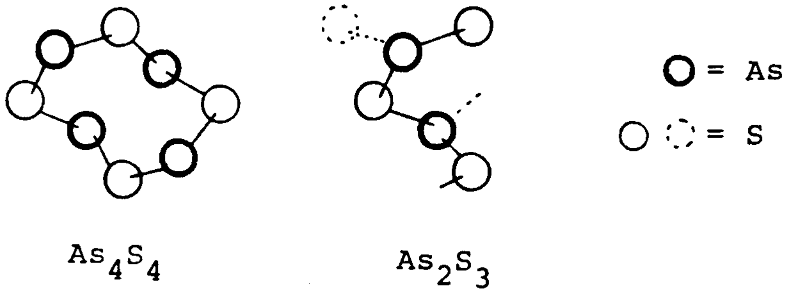


FIGURE I-4. Sprial Structure Common to VB/VIB Compounds.

Nitrogen readily forms multiple bonds in contrast to its heavier congeners. This multiple bonding is prevalent with its near neighbours carbon and oxygen because of their similar size and therefore good orbital overlap. Tabulated[106] values of N-O single and double bonds show the latter to have a bond energy three times that of an NO single bond. It is therefore not surprising to find the nitrogen oxides to be small molecules showing a great deal of multiple bond character. There is also ample evidence for multiple bonding in sulfur-nitrogen compounds as evidenced by the data in Table I-2. This table also shows that many S-N species are flat rings which allow for better π overlap.

For the rest of the VB/VIB compounds multiple bonds are limited to the formation of exocyclic double bonds ($P = O$, $P = S$, $P = Se$). Sulfur is observed to form exocyclic double bonds more readily than oxygen. These exocyclic double bonds are not observed until at least three edges of a common apex of the "parent" group VB tetrahedron are bridged first. No double bonds have been found in the binary arsenic oxides or heavier VB/VIB compounds although double bonds are found in the alkyl and aryl arsine oxides[107] and sulfides.[108,109]

I-3 Aims of the Present Work

This introduction has been a review of various aspects of the chemistry of the VB/VIB compounds. The sections dealing with the chemistry and structure of the VB and VIB elements and S-N compounds illustrate many possible parallel areas of investigation for the chalconides of phosphorus and arsenic. The primary aim of the present work was to study the oxidation of the sulfides and selenides of phosphorus and arsenic with the hope of producing new cationic forms of these compounds and also new halides. As it became apparent that there were a number of unanswered problems relating to the various sulfides and selenides binary, ternary and quarternary systems of the elements phosphorus, arsenic, sulfur and selenium were also studied. In studying systems containing phosphorus considerable use was made of ^{31}P nmr.

It was hoped in this work to extend our knowledge of cage and cluster systems and to contribute to an understanding of the factors determining the formation and stability of such compounds.

CHAPTER II

EXPERIMENTAL

II-1 Preparation and Purification of Materials

II-1 (i) Group VB-VIB Compounds

Tetraphosphorus Trisulfide (P_4S_3)

Tetraphosphorus trisulfide (Research Organic/ Inorganic Corp.) was dried under vacuum and dissolved in air-free dry carbon disulfide. The solution was filtered, the solvent distilled off and the solid sublimed under vacuum. Its purity was checked by N.M.R. and Raman spectroscopy.

α Tetraphosphorus Pentasulfide (αP_4S_5)

Tetraphosphorus pentasulfide was made by leaving a dry, air-free carbon disulfide solution of P_4S_3 and sulfur (1:2 ratio) and a catalytic amount of iodine in sunlight for a week. The product was washed several times with dry carbon disulfide.

α Tetraphosphorus Trisulfur Diiodide ($\alpha P_4S_3I_2$)

Stoichiometric amounts of the elements heated in an evacuated tube or equimolar amounts of P_4S_3 and iodine added to dry, air-free carbon disulfide at room temperature produced $\alpha P_4S_3I_2$. The products from both reactions were recrystallized from dry, air-free carbon disulfide.

Tetraphosphorus Triselenide (P_4Se_3)

Tetraphosphorus triselenide was prepared by heating the stoichiometric amounts of red phosphorus and grey selenium in an evacuated tube to about 420°C for several days with occasional shaking. The solidified melt was then crushed and extracted with dry carbon disulfide in a Soxhlet apparatus fitted with a drying tube. After a vacuum distillation to remove the solvent the crystals were vacuum sublimed and their identity confirmed by NMR and Raman spectroscopy.

α Realgar (αAs_4S_4)

Alpha realgar resulted from the vacuum sublimation of the beta modification.

α Tetraarsenic Trisulfide (αAs_4S_3)

A few crystals of α tetraarsenic trisulfide were obtained from carbon disulfide extractions of quickly quenched arsenic-sulfur melts.

β Tetraarsenic Trisulfide (βAs_4S_3)

Beta tetraarsenic trisulfide was obtained by the vacuum sublimation of amorphous As_4S_3.

β Realgar (βAs_4S_4)

Beta realgar was simply made by adding the dry weighed elements to Pyrex tubes which were evacuated, sealed and heated to 360-450°C for at least four days.

Arsenic-Selenium and Other Melts

Arsenic-selenium and other melts were prepared in the same fashion as βAs_4S_4.

II-1 (ii) Other Materials

Arsenic

Arsenic metal powder (Alfa Inorganics, 99.5%) was heated at 200°C under vacuum to remove As(III) oxide by sublimation.

Fluorine

Fluorine (Matheson, 98%) was passed through sodium fluoride before use.

Chlorine

Chlorine (Canadian Liquid Air, 99.5%) was purified by passage through calcium oxide, two sulfuric acid (95%) traps and a P_4O_{10} trap before being distilled through traps at -78.5, -96.7, -130 and -196°C. The fraction in the trap at -130°C was used.

Niobium Pentafluoride

Niobium pentafluoride (Alfa Inorganics) was purified by vacuum sublimation at 220°C.

Tantalum Pentafluoride

Tantalum pentafluoride (Alfa Inorganics) was purified by vacuum sublimation onto a water-cooled cold finger in an evacuated glass apparatus.

Arsenic Trifluoride

Arsenic trifluoride (City Chemical Co.) was vacuum distilled onto dried sodium fluoride. It was also prepared by an alternative method[110] given in Inorganic Synthesis. Large scale preparations were done by direct fluorination of the metal at -196°C in a nickel can.

Arsenic Pentafluoride

Arsenic pentafluoride was also directly prepared from the elements by the addition of excess fluorine to powdered arsenic at -196°C in a nickel can, followed by heating to 150°C for 12 hours and subsequent removal of excess fluorine at -196°C by pumping under vacuum.

Antimony Pentafluoride

Antimony pentafluoride (Ozark Mahoning Co.) was doubly distilled in a Pyrex still in an atmosphere of dry nitrogen. It was then distilled under vacuum and stored in an F.E.P. bottle in a dry box. Subsequent batches were of better quality and the first step was omitted.

Fluorosulfuric Acid

Fluorosulfuric acid (J.T. Baker Co.) which had been purified by standard procedures[111] was kindly donated by Dr. J.E. Vekris.

Sulfuryl Chlorofluoride

Sulfuryl chlorofluoride (Research Inorganics) which had been purified by standard procedures,[112] was kindly donated by Dr. G.J. Schrobilgen.

Anhydrous Hydrogen Fluoride

Anhydrous hydrogen fluoride (Harshaw Chemicals) was kindly provided by Dr. Schrobilgen. It had been subjected to a pressure of 100 lb/sq. in. of fluorine to react with any traces of water followed by removal of the fluorine and any resulting OF_2 by exposing the frozen acid to a high vaccum.

$S_8(AsF_6)_2$

The compound $S_8(AsF_6)_2$ was prepared according to the method of Dean, Gillespie and Ummat.[113]

Aluminium Trichloride

Aluminium trichloride (McArthur Chemical Co.) was vacuum sublimed through a layer of aluminium pellets and/or foil to remove any iron chlorides.

Sulfur Dioxide

Anhydrous sulfur dioxide (Canadian Liquid Air, 99.98%) was stored as a liquid over P_4O_{10} prior to use.

Sulfur Trioxide

Sulfur trioxide (Baker and Adamson) was distilled under vacuum into a dry glass storage vessel.

Phosphorus Pentachloride

Phosphorus pentachloride (B.D.H., 99%) was vacuum sublimed at 160°C prior to use.

Acetonitrile

Acetonitrile (Fisher Scientific Co., ACS reagent) was vacuum distilled onto dried molecular sieves for storage.

Several materials were stored over anhydrous calcium chloride and then distilled onto and stored over P_4O_{10}. These substances included:

bromine (Fisher Scientific Co., ACS reagent)
carbon disulfide (J.T. Baker Co., 100%)
methylene chloride (Fisher Scientific Co.)

The following were vacuum distilled and then cooled and exposed to vacuum to remove any HCl:

phosphorus trichloride (J.T. Baker Co.)
arsenic trichloride (B.D.H.)
boron trichloride (Matheson)
phosphorus oxychloride (J.T. Baker Co.)
thionyl chloride (J.T. Baker Co.)
antimony pentachloride (J.T. Baker, analyzed)

Many materials were exposed to vacuum and heated where appropriate before use:

antimony (Fischer Scientific Co., 99.8%)
antimony selenide (K & K Laboratories Inc.)
antimony telluride (K & K Laboratories Inc.)
bismuth Selenide (K & K Laboratories Inc.)
bismuth telluride (K & K Laboratories Inc.)
iodine (B.D.H., 99.9%)
phosphorus, red (B.D.H.)
phosphorus, white (Source unknown)
phosphorus pentoxide (Fisher Scientific Co.)
selenium (Alfa Inorganic, 99.9%)
sulfur (B.D.H. sublimed)
tellurium (Alfa Inorganic, 99.5%)
triphenyl phosphine (B.D.H.)

The following were used as received:

sulfuric acid (Fisher, ACS reagent)
hydrochloric acid (Fisher, ACS reagent)
nitric acid (Fisher, ACS reagent)
phosphorus pentafluoride (Ozark Mahoning)
selenium tetrachloride (Alfa Inorganics)
tungsten hexafluoride (Ozark Mahoning)

Several common organic solvents usually of analytical grade from a variety of sources, e.g., methanol, acetone, 1,4-dioxane, formaldehyde, petroleum ether, dimethyl sulfoxide, nitrobenzene, pyridine, N,N-dimethylformamide and carbon tetrachloride.

II-2 General Experimental Techniques

II-2 (i) Dry Box

For all the moisture sensitive compounds studied manual operations were carried out in a very good dry box (S. Blickman) constantly flushed with nitrogen passed through an electrodryer. The nitrogen initially came from the boil off of a large liquid nitrogen tank. The box was equipped with an evacuable ante-chamber and an analytical balance.

II-2 (ii) Handling of Chemicals

Most gases were transferred in a calibrated Pyrex vacuum line fitted with Rotoflow valves and a mercury manometer. Gas cylinders were connected to the line via Swagelok Teflon unions and Teflon tubing. Reactions involving fluorine were done in nickel cans fitted with high pressure Autoclave Engineering valves. In this case the vacuum line was constructed of Monel with the fluorine cylinder attached by seasoned copper tubing. Transfers of HF were also done in metal vacuum lines. The Kel-F and F.E.P. plastic equipment is described elsewhere.[114] Liquids with a reasonable vapour pressure were distilled on the vacuum line. Other organic and inorganic liquids were transferred in a glove bag and the dry box, respectively. Antimony pentafluoride required the use of an all-glass syringe. Almost all solids were transferred in the dry box.

II-2 (iii) Reaction Vessels

Typical reaction vessels are shown in Figure II-1. The two arms of the vessels were separated by a medium glass frit. The vessels were attached to the vacuum line by means of Teflon valves. Reactants and/or products that were moisture sensitive required the vessels be flame-dried under vacuum before use. If desired the vessels could be flame sealed.

II-2 (iv) Crystal Mounting

Air-sensitive crystals for X-ray crystallography were handled in a dry box equipped with a microscope. Each crystal was transferred to a thin-walled quartz capillary tube which was sealed with Halocarbon grease. The capillary was flame sealed with a micro-burner outside the dry box. Crystals stable in air and moisture were glued to the end of a pyrex filament.

II-3 Instrumentation

II-3 (i) Infrared Spectroscopy

Routine preliminary spectra were recorded on a Perkin Elmer Grating Infrared spectrometer Model 283. Final spectra were recorded with a Nicolet 7199 FT-IR system fitted with the appropriate beam splitter for the

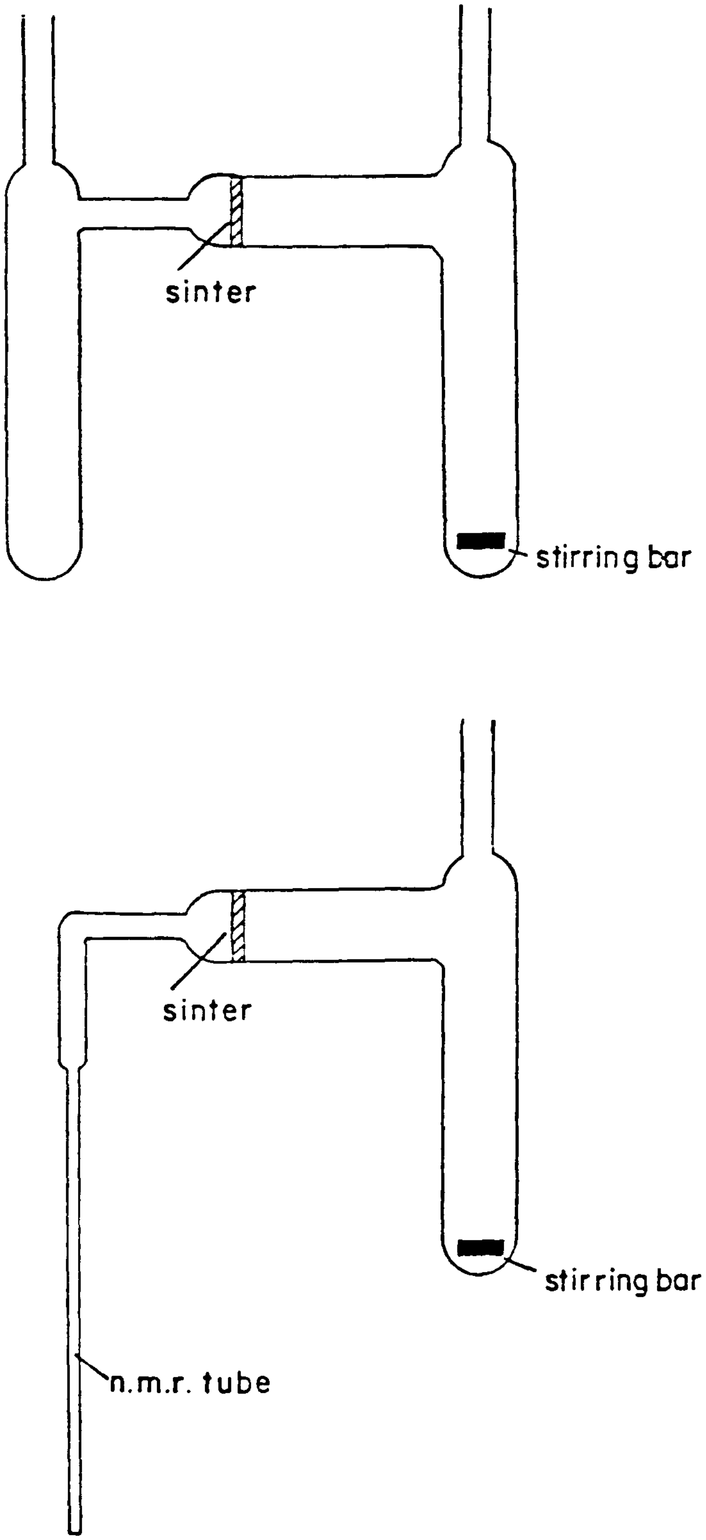


FIGURE II-1. Typical Reaction Vessels.

region of interest. The entire spectrometer was constantly flushed with dry nitrogen for far IR spectra. Solid samples were prepared as Nujol mulls in the dry box using sodium dried Nujol. For the 4000 cm^{-1} to 200 cm^{-1} range CsI windows were used and polyethylene packets for the 400 cm^{-1} to 60 cm^{-1} region. Solution spectra were run using molded polyethylene cells (Barnes Engineering Co.) of varying path length.

II-3 (ii) Laser Raman Spectroscopy

A Spectra Physics Model 164 argon ion laser giving up to 900 mW at 5145 Å or a Spectra Physics Model 125 Helium-Neon gas laser giving up to 65 mW at 5328 Å were used to excite the Raman spectra. The spectrometer was a Spex Industries Model 14018 double monochromator equipped with 1800 grooves/mm Holographic gratings. An RCA C31034 phototube detector in conjunction with a pulse count system consisting of pulse amplifier, analyzer and ratemeter (Hamner NA-11, NC-11 and N-780A, respectively) and a Texas Instruments FSOZWBA strip character recorder were used to record the spectra. The spectrometer was periodically calibrated by recording the discharge lines from an argon lamp over the spectral range of interest; the Raman shifts quoted are estimated to be accurate to ± 1 cm^{-1}. Slit widths depended on the scattering efficiency of the sample, laser power, etc., with 100 μ being typical.

Cylindrical sample tubes were mounted vertically. The angle between the incident laser beam and the sample tube was 45° and Raman scattered radiation was observed at 45° to the laser beam or 90° to the sample tube direction. Samples were capable of being spun up to 1000 rpm by means of a variac-controlled electric motor.

Low temperature spectra were recorded at -196° by mounting the sample vertically in an unsilvered Pyrex glass Dewar filled with liquid nitrogen. High temperature spectra were recorded up to 250°C by mounting the sample vertically in a similar Dewar fitted with an inlet near the bottom for introducing heated air. The air was heated by passing it through a resistance heater, the temperature being controlled by flow rate, a Varian power source and judicious insulating of the heater and Dewar. The temperature was monitored with a copper-constantan thermocouple connected to a Leeds and Northrup temperature potentiometer.

II-3(iii) Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance spectra were obtained with the following spectrometers: Bruker WH-90, Bruker WH-200 (University of Alberta, Edmonton, Alberta), Bruker WH-250 (Bruker Spectrospin Ltd., Mississauga, Ontario) and a Bruker WH-400 (University of Guelph, Guelph, Ontario). The WH-90 was equipped with a Nicolet 1080 computer while the rest were equipped with Aspect 2000 computers.

Sulfur dioxide, SO_2ClF or a mixture of these were used for all ^{19}F NMR samples. Unless noted otherwise all ^{31}P and ^{77}Se samples were dissolved in dry, air-free CS_2. Spectral simulations were carried out using the Nicolet program ITRCAL[115] or the program NUMARIT.[116] Low temperature ^{19}F and ^{31}P NMR spectra were obtained using a Bruker temperature controller. Temperatures were measured using a copper-constantan thermocouple inserted directly into the sample region of the probe and were accurate to ±1°C. The IUPAC conventions were used for reporting chemical shifts, positive shifts being to low field.

a) ^{19}F NMR Spectra

Spectra were recorded on the WH-90 spectrometer using a fixed frequency transmitter and probe operating at 84.66 MHz. Spectral widths of 20,000-50,000 Hz were employed with resulting software resolution of 2.4-6.1 Hz/point. All samples were in sealed 5 mm o.d. medium wall NMR tubes locked to an external D_2O capillary in the probe-head housing. The reference compound was external $CFCl_3$.

b) ^{31}P NMR Spectra

A WH-90 spectrometer equipped with a fixed frequency transmitter and probe (36.43 MHz) or with a broad band multinuclear NMR probe set at 36.44 MHz was used to record several spectra. Spectra were accumulated with a spectral width of 5,000 to 20,000 Hz giving a software resolution of 0.6-2.4 Hz/point. All samples were in sealed 8 mm o.d. precision round bottom NMR tubes placed inside similar unsealed 10 mm o.d. tubes. The annular space contained the external ^{2}H lock substance. At ambient temperature D_2O was used and d_6-acetone for low temperatures.

All other ^{31}P NMR samples were run unlocked in 10 mm o.d. NMR tubes using the WH-200, WH-250 or WH-400 spectrometers with software resolutions of 0.5-0.9, 0.1-2.5 and 1-3 Hz/point, respectively.

c) ^{77}Se NMR Spectra

Some preliminary spectra were recorded using the Bruker WH-90 spectrometer equipped with a broad band multinuclear NMR probe set at 17.19 MHz. Spectra were accumulated with a spectral width of 30,000-50,000 Hz giving a software resolution of 3.7-6.1 Hz/point. All other spectra were recorded on the WH-250 and WH-400 with software resolution of $\leqslant$ 1 Hz/point. Samples were in sealed 10 mm o.d. tubes. The IUPAC sign convention was again used and the reference compound was external saturated selenous acid.

II-3(iv) UV-Visible Absorption Spectroscopy

Absorption spectra were recorded from 320 to 1500 mm on a Cary 14 spectrometer. Spectra of solutions of compounds dissolved in SO_2 were obtained in one centimeter path length cells (Hellma Ltd.) with a graded seal to a rotoflow valve and a Pyrex reaction vessel equipped with a magnetic stirrer (Figure II-2).

II-3(v) X-ray Crystallography

The mounted crystals were attached to standard goniometer heads. Usually preliminary crystal alignment was achieved with a Beurger precession camera using a low precession angle ($\mu = 10°$) and unfiltered Mo radiation. The space group was normally determined from the systematic absences characteristic of the space group by examination of the zero and first layer precession photographs obtained using Mo K_α ($\lambda = 0.71069$ Å) radiation and the appropriate screen.

Intensity data were collected on a Syntex $P2_1$ four-circle diffractometer using graphite monochromated Mo K_α radiation. Unit cell parameters were found by least

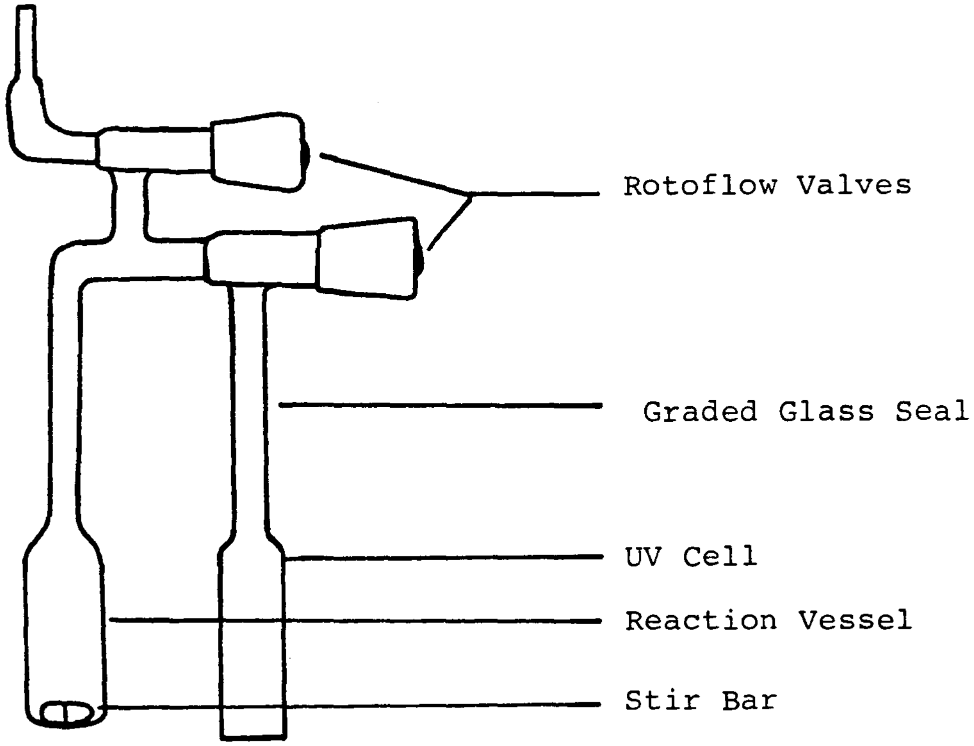


FIGURE II-2. High Pressure UV Cell

squares refinement of the Bragg angle and crystal orientation for 15 reflections with θ in the range 23-33°. The θ-2θ scan technique was used with scan rates varying from 2 to 24°/min (in 2θ) so that the weaker reflections were counted more slowly to minimize counting errors. The scan ranges were in the order of $K\alpha_1$ - (0.60 to 1.1) to $K\alpha_2$ + (0.6 to 1.1). Stationary background counts with a time equal to one quarter of the scan time for each reflection were made at each end of the scan range. Three standard reflections were recorded at least every 100 measurements to monitor crystal stability and orientation. The recorded intensities were corrected for background, Lorentz and polarization factors. The atomic scattering factors were taken from International Tables.[117] Specific details of absorption corrections and other conditions for the crystal structures done by this researcher are included in the discussion of the individual crystal structures. All calculations were done on a CDC 6400 computer using SHELX[118] and the X-ray 76 system.[119]

X-ray powder patterns were recorded by Mrs. Lynne Soderholm using a Phillips automatic X-ray powder diffractometer equipped with a copper radiation source and a graphite monochromator.

II-3(vi) Analyses

Analyses were done by Butterworths, 41 High Street, Teddington, Middlesex TW11 8ET, England. The results of these analyses are presented at the end of Chapter V.

CHAPTER III

CAGE MOLECULES CONTAINING PHOSPHORUS

III-1 Introduction

It was necessary to prepare and study several phosphorus containing cages to provide background data before oxidative studies could be undertaken. These studies included investigating the previously recorded ^{31}P NMR spectra of P_4Se_3[120] and αP_4S_5[79] and the Raman spectra of P_4S_3 and P_4Se_3.[121]

Ternary and quaternary mixtures of the Group VB and Group VIB elements were also investigated in an attempt to produce novel cage compounds and extend our knowledge of such cages. Ternary mixtures of the Group VB and Group VIB elements were studied in the early part of this century[122] but no further work was done until the early seventies. Recently what was believed to be $P_2As_2S_3$[14] was extracted from a P_4S_3/As_2S_3 melt. The investigation of a P_4S_3/P_4Se_3 melt[15] by X-ray powder photography and thermal analysis, however, revealed no new species. Existence of the phosphorus-arsenic-sulfur compound as well as, for example, Se_3S_5[59] and As_2Se_2S[95] suggested that other VB/VIB compounds of tertiary and quaternary elemental combinations might be produced under the appropriate conditions.

III-2 ^{31}P and ^{77}Se NMR Spectroscopy of the $P_4S_{3-X}Se_X$, (X = 0-3) System

III-2(i) P_4S_3 and P_4Se_3

The ^{31}P NMR spectrum of P_4S_3[120] consists of a high-frequency quartet for the apical phosphorus and a low-frequency doublet for the three basal phosphorus atoms. The ^{31}P NMR spectrum of P_4Se_3 shows the same basic AX_3 pattern with additional ^{77}Se satellites (^{77}Se, I = 1/2, 7.5% natural abundance). The chemical shifts of the basal atoms occur at rather low frequency compared to the resonances of most tricoordinated phosphorus compounds.[123] The values recorded for the phosphorus chemical shifts and $^2J_{PP}$ are in agreement with previously reported values. Chemical shifts for the apical and basal phosphorus atoms of P_4S_3 are 67.8 ppm and -119.4 ppm while those of P_4Se_3 are 38.3 ppm and -103.8 ppm, respectively. The phosphorus-phosphorus coupling constants in these two molecules are essentially the same (P_4S_3: $^2J_{PP}$ = 70.3 Hz and P_4Se_3: $^2J_{PP}$ = 70.8 Hz).

The natural abundance ^{77}Se NMR spectrum and the ^{77}Se satellites observed in the ^{31}P NMR spectrum of P_4Se_3 were both recorded in the present study. These spectra could not be fitted using the previously[120] reported P-Se coupling constants and the associated P-P coupling constants and chemical shifts. The P-Se coupling constants were calculated from the ^{77}Se satellites seen in a nuclear electron Overhauser enhanced ^{31}P NMR spectrum. The previous workers were probably limited in their observation of the ^{77}Se satellites by the signal-to-noise capabilities of their available continuous wave instruments.

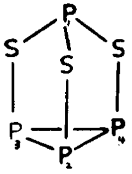
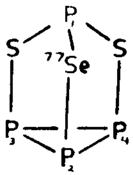
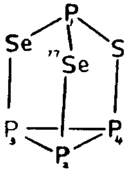
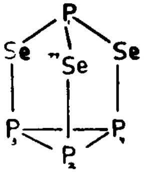
The natural abundance ^{77}Se NMR spectrum of P_4Se_3 (Figure III-1) appears to exhibit a first order pattern due to splitting by the apical phosphorus atom (256.6 Hz), by the directly bonded basal phosphorus atom (316 Hz) and by what appears to be a long range coupling of 116 Hz to the two remaining basal phosphorus atoms. However, the spectrum actually arises from a $AM_2M'X$ spin system (Fig. III-1) with the coupling constants listed in Table III-1.

The ^{31}P NMR spectrum of the apical region of P_4Se_3 is shown in Figure III-2. Superimposed on the quartet arising from coupling with the basal phosphorus atoms are the satellite doublets due to ^{31}P-^{77}Se coupling (256.6 Hz). The four very weak satellites are due to the isotopic isomer containing two ^{77}Se atoms (1.56%). The recorded and calculated ^{77}Se satellite spectra for the basal phosphorus atoms of P_4Se_3 are illustrated in Figure III-3.

III-2(ii) $\underline{P_4S_2Se \text{ and } P_4SSe_2}$

The ^{31}P NMR spectra of CS_2 extractions of 4:2:1 and 4:1:2 P:S:Se melts are quite complex. In both spectra

TABLE III-1 ^{31}P and ^{77}Se Chemical Shifts and Coupling Constants for $P_4S_{3-x}Se_x$, X=0-3

				
δP_1	67.8	60.8	50.9	38.3
δP_2	-119.4	-128.5	-116.0	-103.8
δP_3		-106.2		
δP_4			-93.8	
$\delta^{77}Se$		-646.8	-591.0	-534.9
${}^2J_{P_1P_2}$	70.3^{a}	61.4^{a}	65.4^{b}	70.8^{b}
${}^2J_{P_1P_3}$		75.4		
${}^2J_{P_1P_4}$			81.9	
${}^1J_{P_2P_3}$		143.9	-142.9	-150.0
${}^1J_{P_2P_4}$			-151.0	
${}^1J_{P_3P_4}$		-		-
J_{P_1Se}		265.2	261.0	256.6
J_{P_2Se}		331.1	-323.7	316.5
J_{P_3Se}		7.3	-2.4	0.8
J_{P_4Se}		7.3	-6.5	0.8

a) From spectra. b) From calculations. No exhaustive study made of possible sign combinations that would produce the expt. spectra.

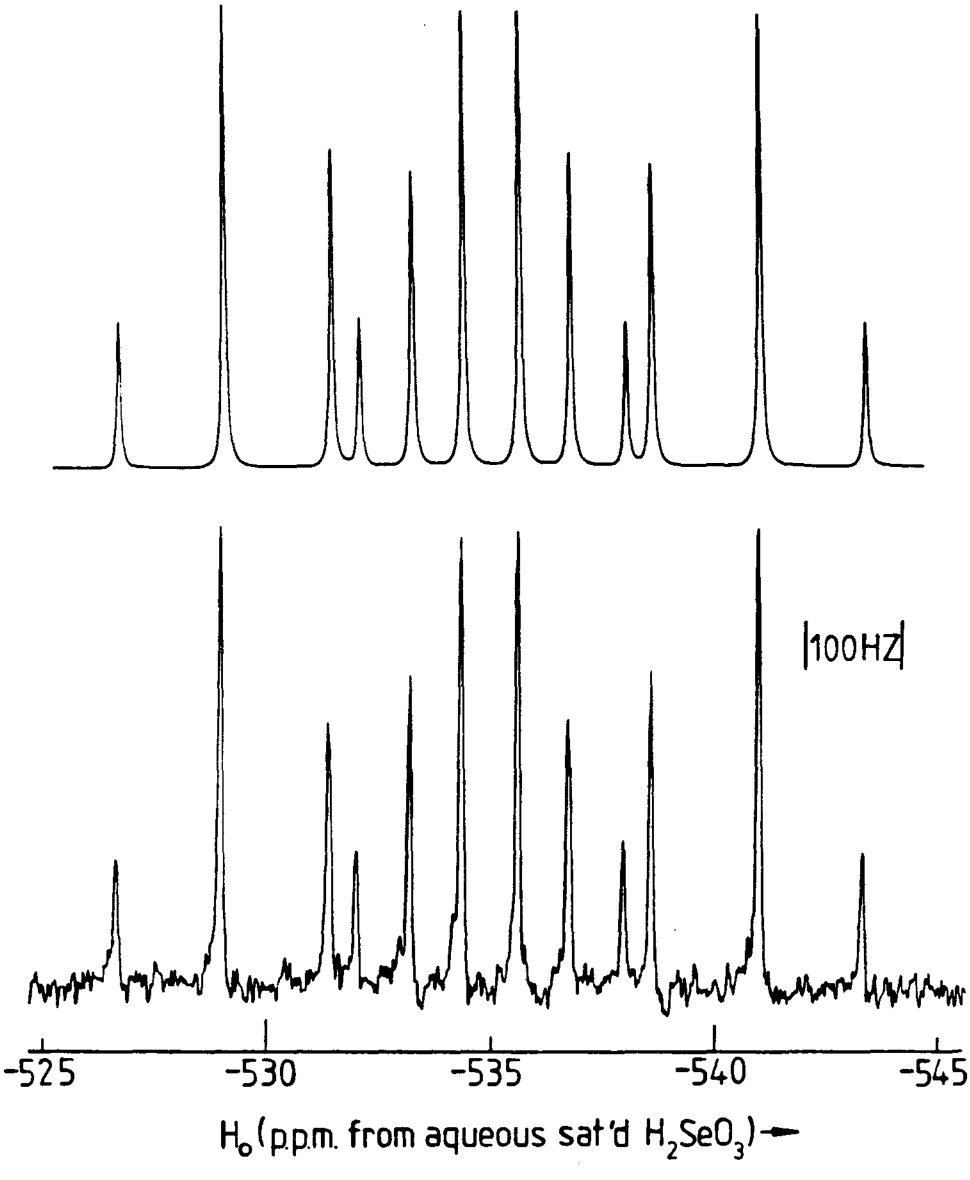


FIGURE III-1. Natural Abundance ^{77}Se NMR Spectrum of P_4Se_3 and the Simulated Spectrum.

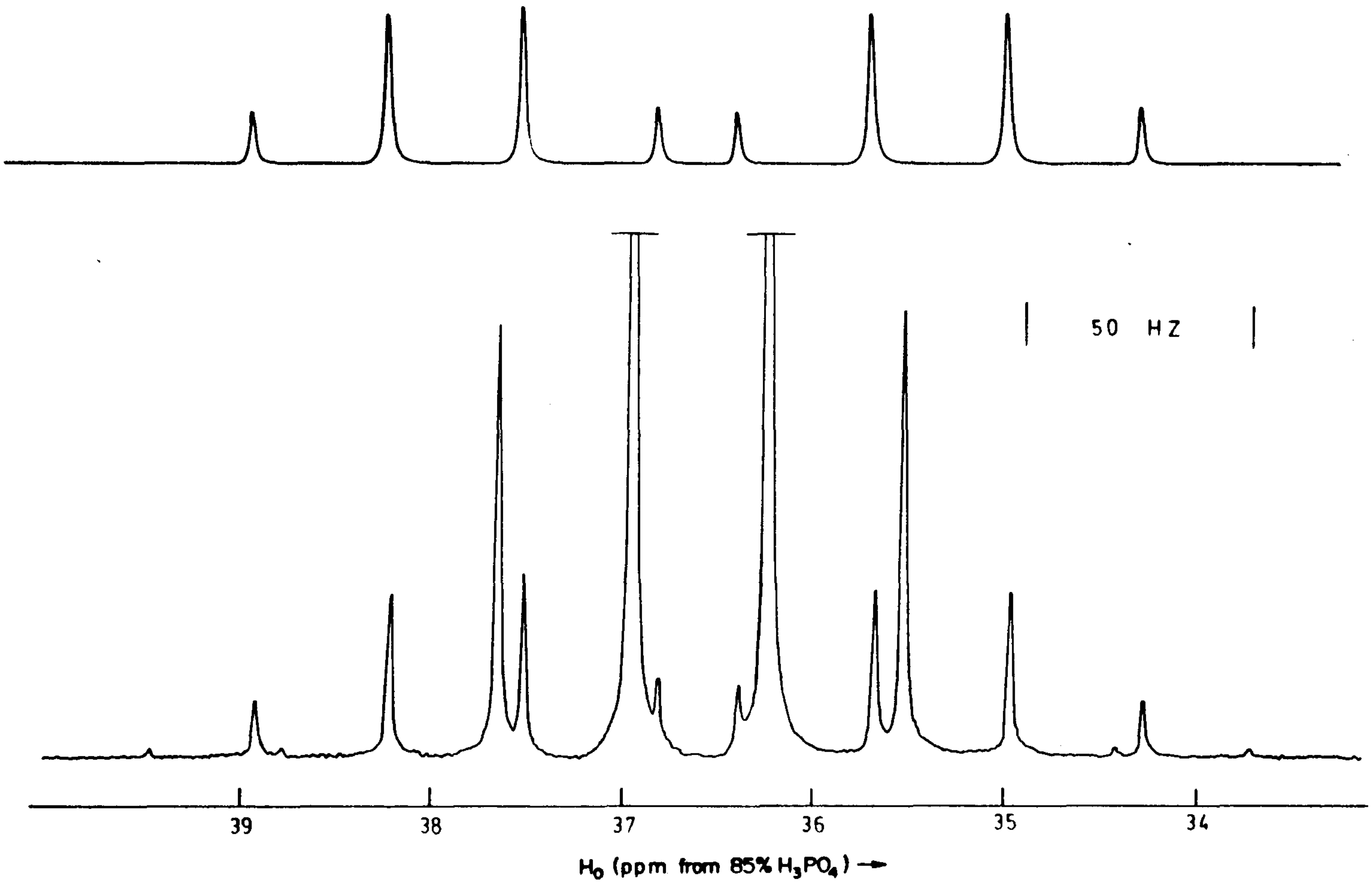
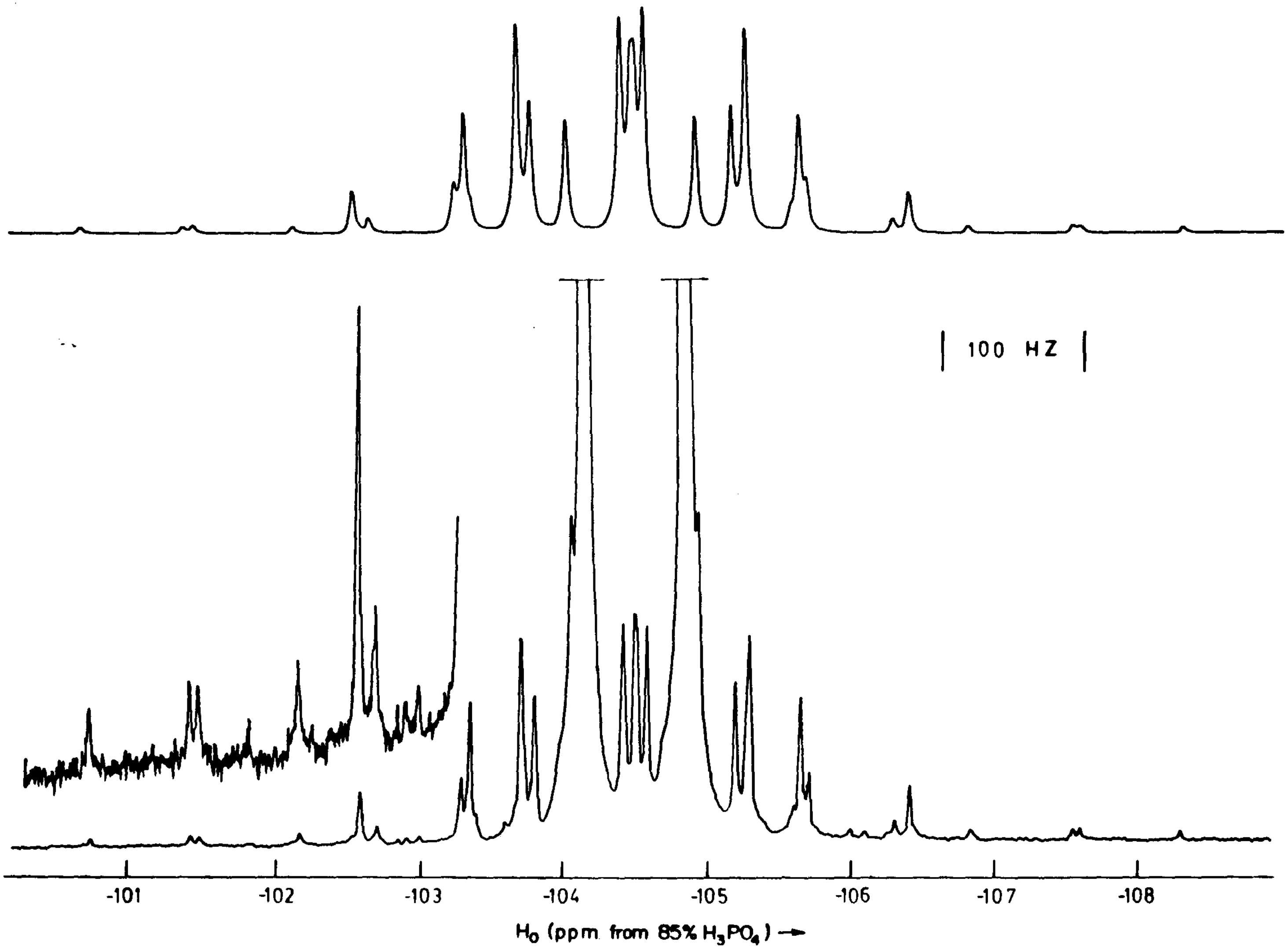


FIGURE III-2. ^{31}P NMR Spectrum of the Apical Region of P_4Se_3 and the Simulated Spectrum of the ^{77}Se Satellites.



<u>FIGURE III-3</u>. ^{31}P NMR Spectrum of the Basal Region of P_4Se_3 and the Simulated Spectrum of the ^{77}Se Satellites.

peaks for P_4S_3 and P_4Se_3 were present as well as peaks due to two new species. The peaks for the new species are assigned to P_4S_2Se and P_4SSe_2. The phosphorus NMR spectra for the ternary compounds arise from AY_2Y and AXY_2 spin systems in contrast to the binary chalconides which arise from the AX_3 spin system. The observed and calculated ^{31}P NMR spectra for P_4S_2Se and P_4SSe_2 obtained at 36.44 MHz for a 4:2:1 P:S:Se sample are illustrated in Figures III-4 and III-5. Relative intensities of the peaks in the spectra of samples of different sulfur-selenium ratios were used to make the assignments for the phosphorus atoms.

Considering the similarity of $^2J_{PP}$ in P_4S_3 and P_4Se_3 it is somewhat surprising that the corresponding coupling constants for the ternary compounds vary from 61.4 to 81.6 Hz (see later discussion). The ^{77}Se satellites observed in a phosphorus NMR spectrum of P_4SSe_2 recorded at 81.015 MHz are illustrated in Figures III 6 - 8 along with the calculated spectra. The observed and calculated ^{77}Se spectra of P_4SSe_2 are shown in Figure III-9. The corresponding selenium NMR spectrum for P_4S_2Se is given in Figure III-10.

The ^{31}P NMR spectrum of a CS_2 solution of P_4S_3 and P_4Se_3 stirred for one hour showed no other species present. In addition a ^{31}P NMR spectrum for a solution

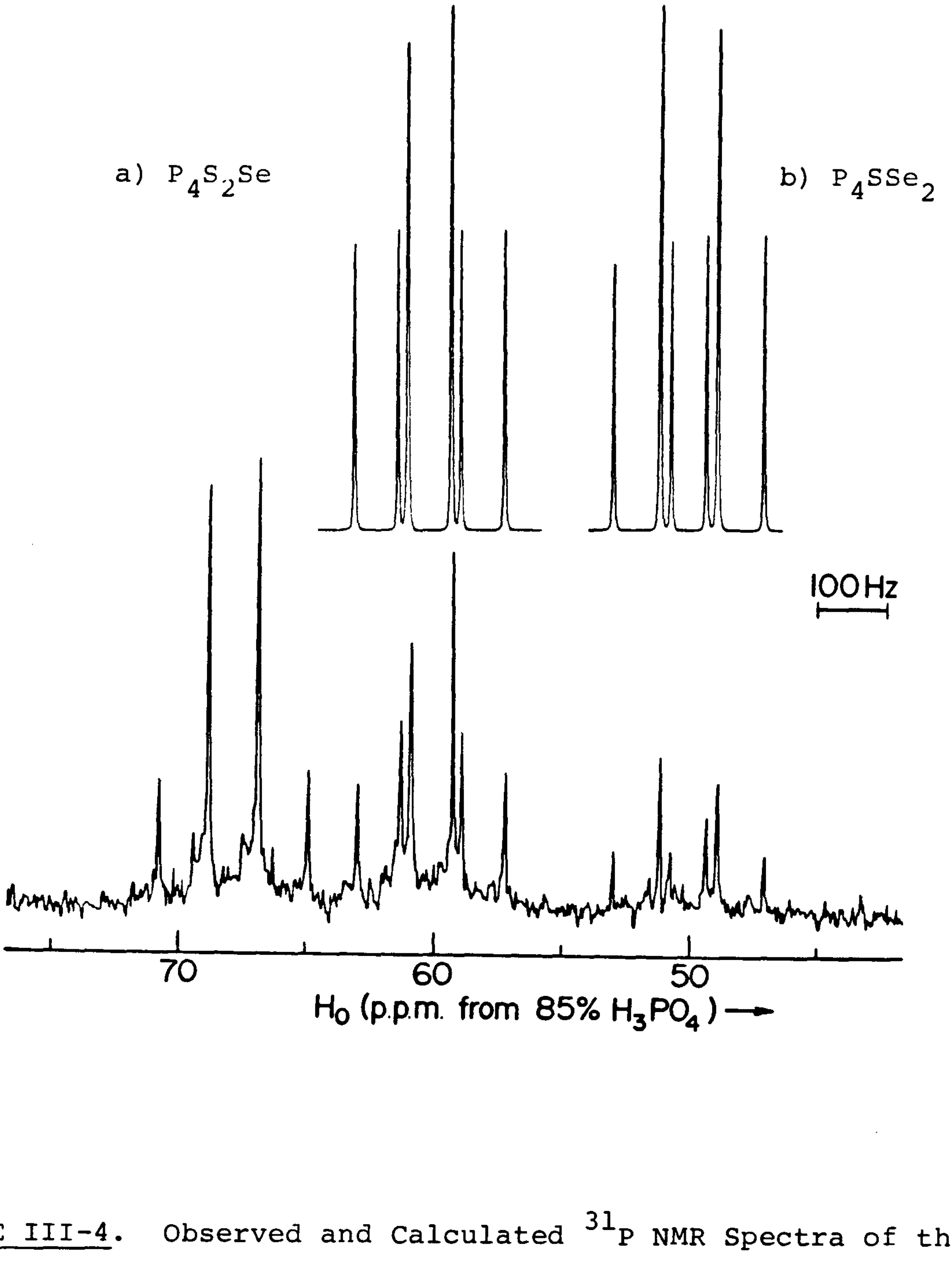


FIGURE III-4. Observed and Calculated ^{31}P NMR Spectra of the Apical Region of the P/S/Se System.

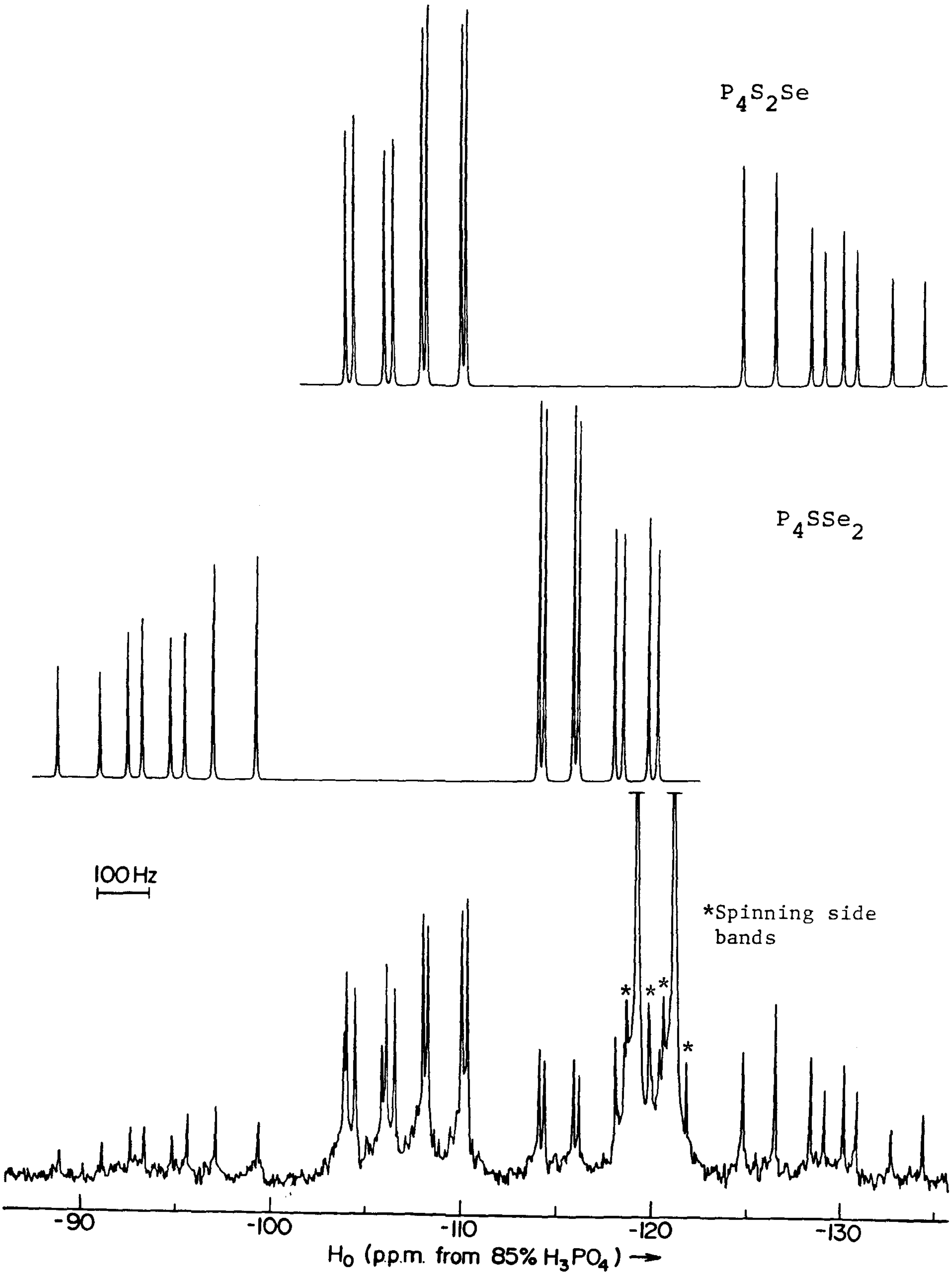


FIGURE III-5. Observed and Calculated ^{31}P NMR Spectra of the Basal Region of the P/S/Se System.

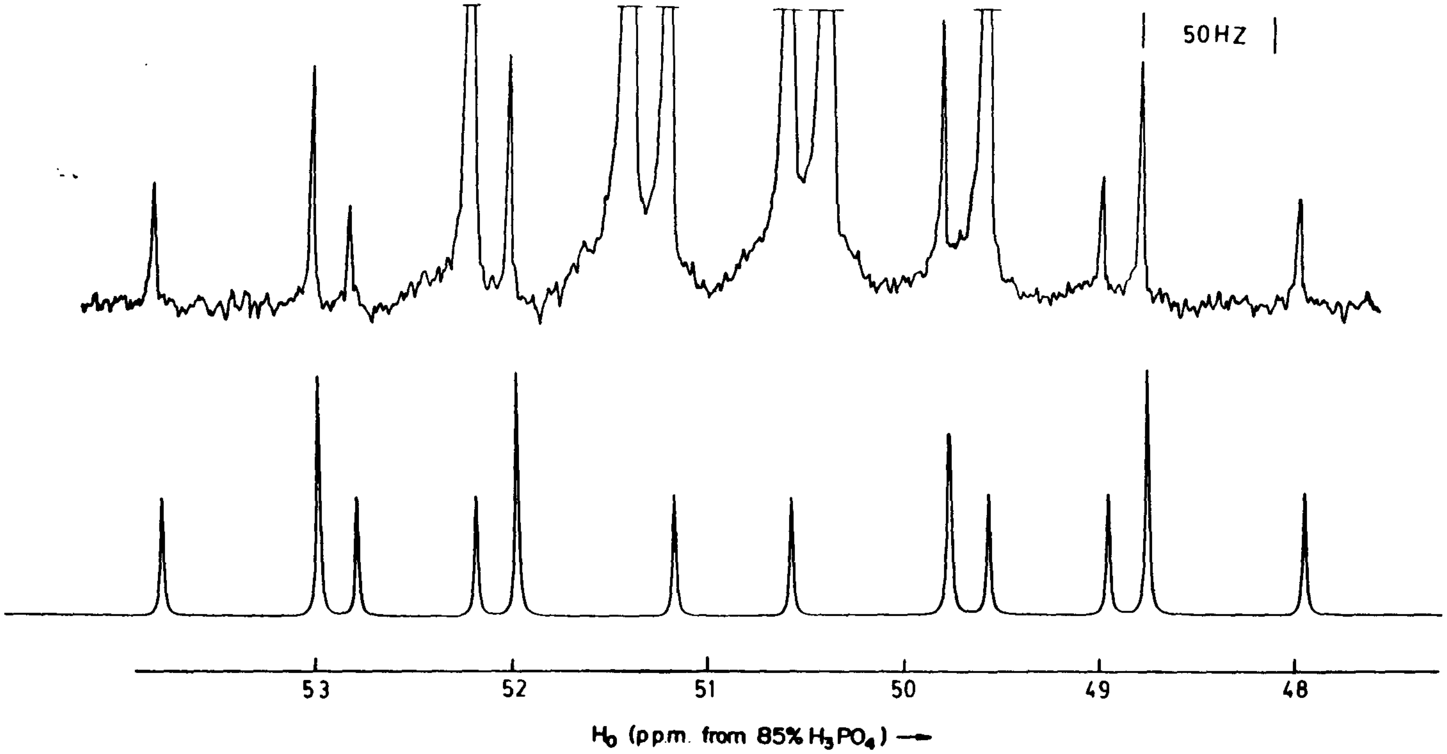


FIGURE III-6. ^{31}P NMR spectrum of the Apical Region of P_4SSe_2 and the Simulated Spectrum of the ^{77}Se Satellites.

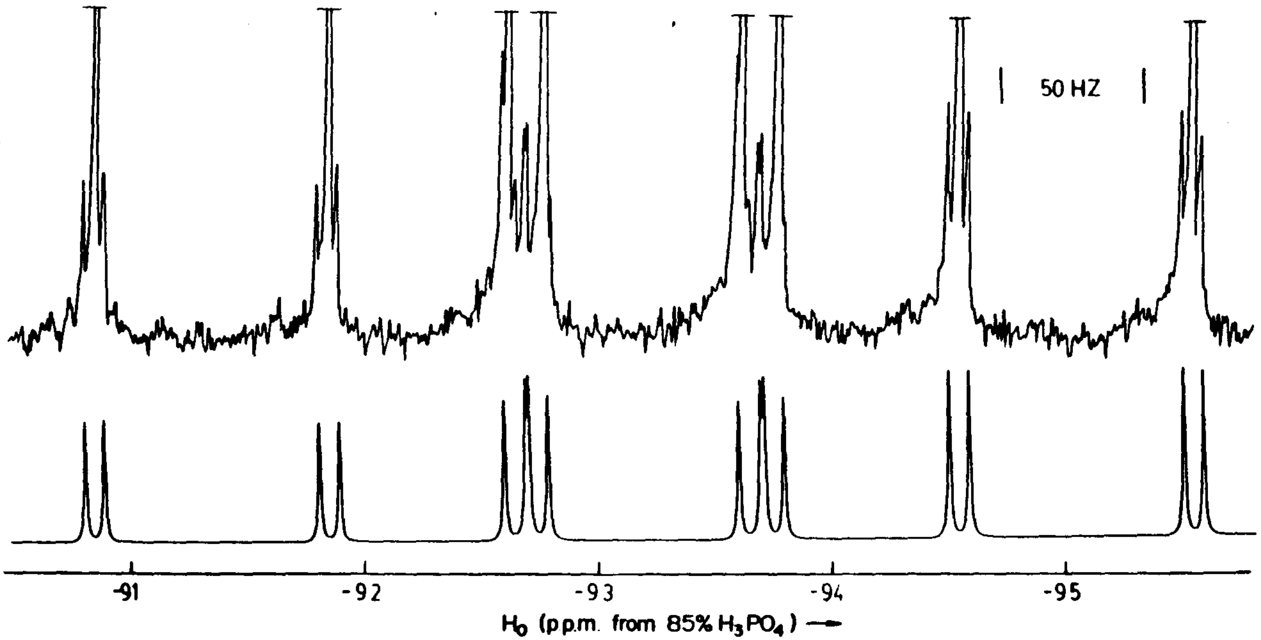


FIGURE III-7. ^{31}P NMR Spectrum of the High Frequency Portion of the Basal Region of P_4SSe_2 and the Simulated Spectrum of the ^{77}Se Satellites.

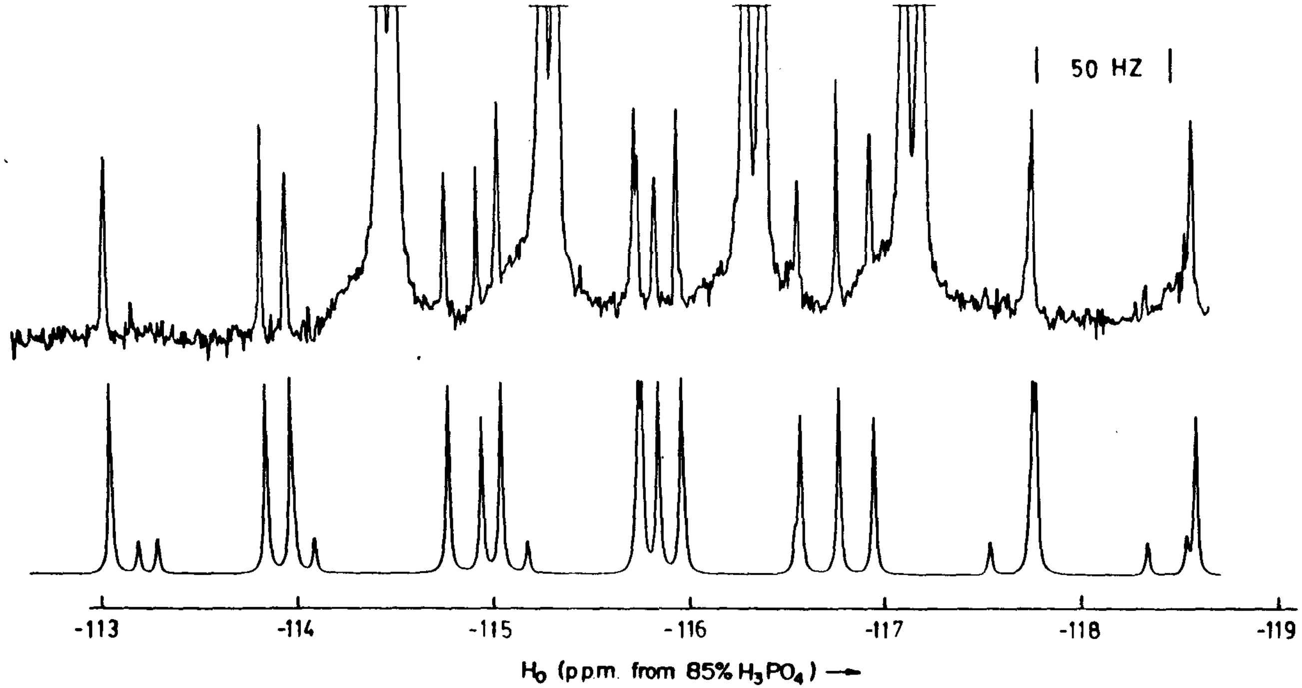


FIGURE III-8. ^{31}P NMR Spectrum of the Low Frequency Portion of the Basal Region of P_4SSe_2 and the Simulated Spectrum of the ^{77}Se Satellites.

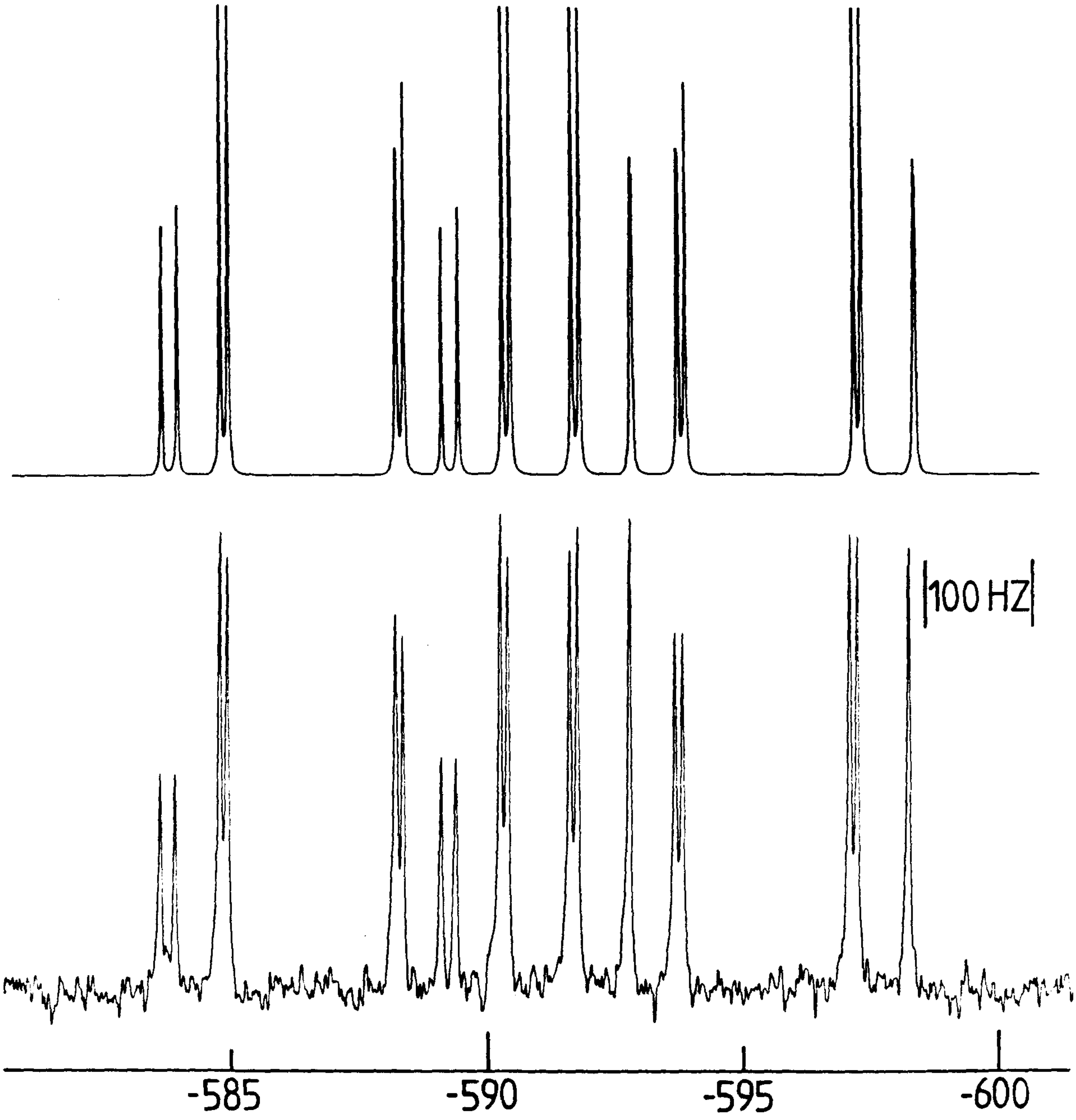


FIGURE III-9. Natural Abundance ^{77}Se NMR Spectrum of P_4SSe_2 and the Simulated Spectrum.

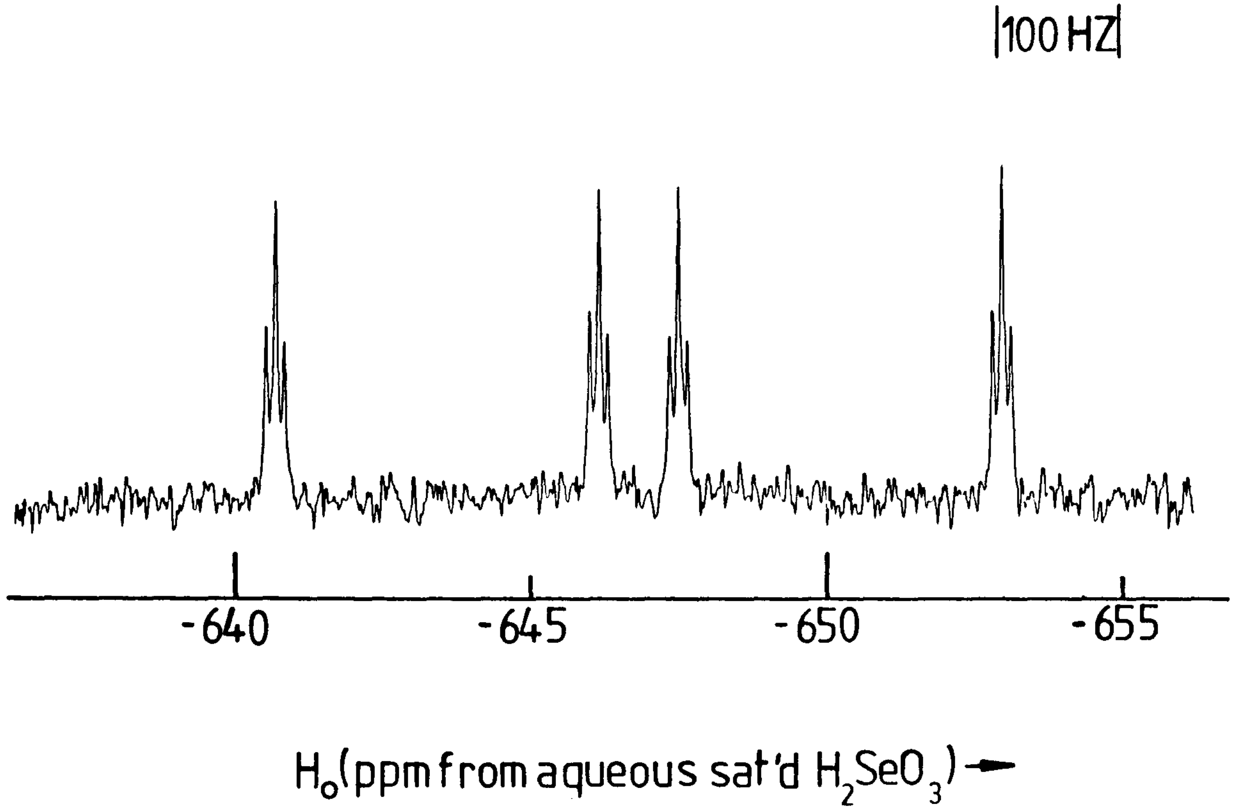


FIGURE III-10. Natural Abundance ^{77}Se NMR Spectrum of P_4S_2Se.

formed by the CS_2 extraction of a 1:1 P_4S_3:P_4Se_3 melt also showed peaks only due to the P_4S_3 and P_4Se_3. This is the same conclusion obtained from X-ray powder photography[15] of the products in solidified P_4S_3/P_4Se_3 melts. The compounds must have high thermal stability with respect to molecular rearrangements.

III-3 ^{31}P and ^{77}Se NMR Spectroscopy of $P_{4-X}As_XS_3$ and $P_{4-X}As_XSe_3$ (X = 0-3) Systems

In an attempt to obtain crystals of $P_2As_2S_3$ a melt having the stoichiometric ratio of elements was extracted with dry, air-free CS_2. A ^{31}P NMR spectrum of the sample showed many more peaks than the two doublets expected for the two non-equivalent phosphorus atoms in $\alpha P_2As_2S_3$[‡] (Figure III-11,12). The detection of P_4S_3 and

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[‡] All ternary and quaternary species with a phosphorus atom in the apex will be referred to as the alpha (α) form while those with an apical arsenic as the beta (β) form.

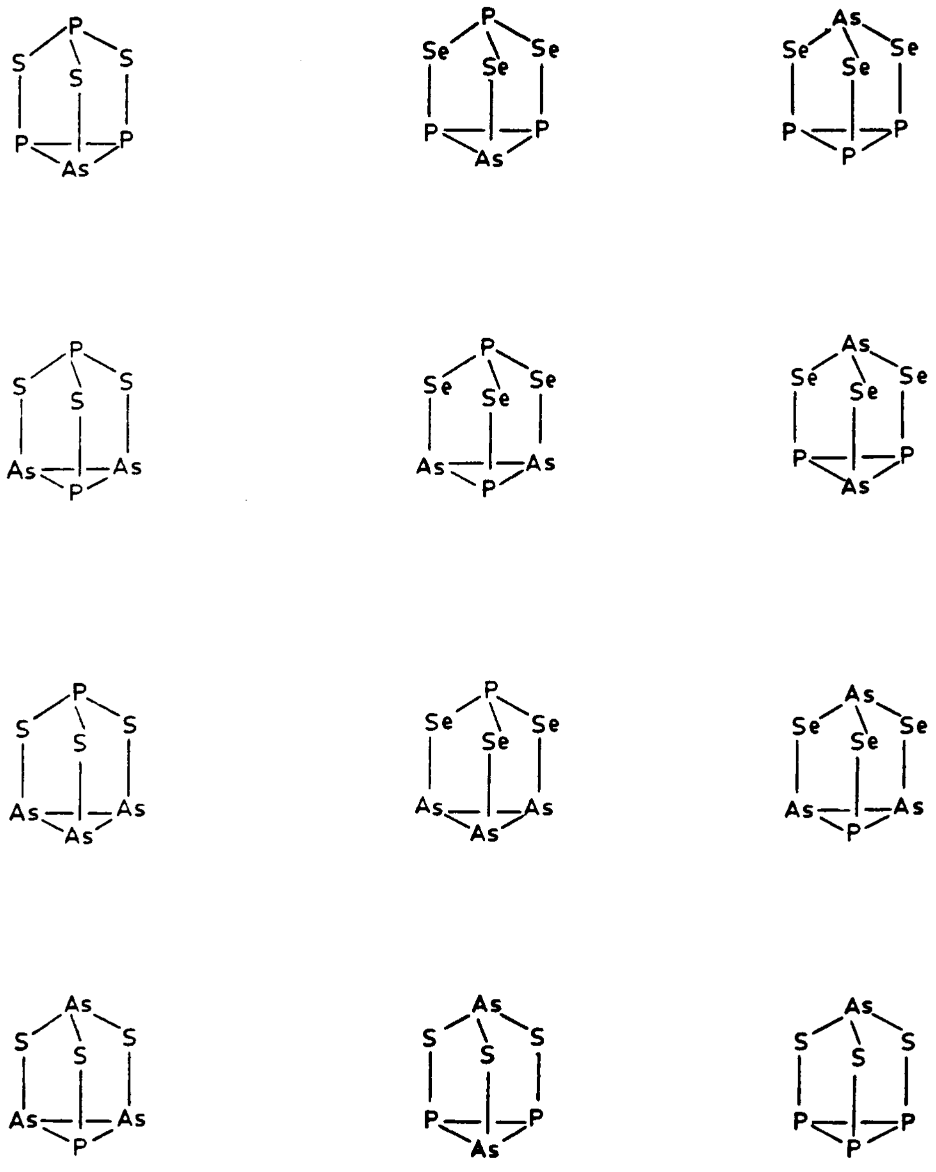


FIGURE III-11. Tertiary Members of the Series $P_{4-x}As_xS_3$, X = 0-3.

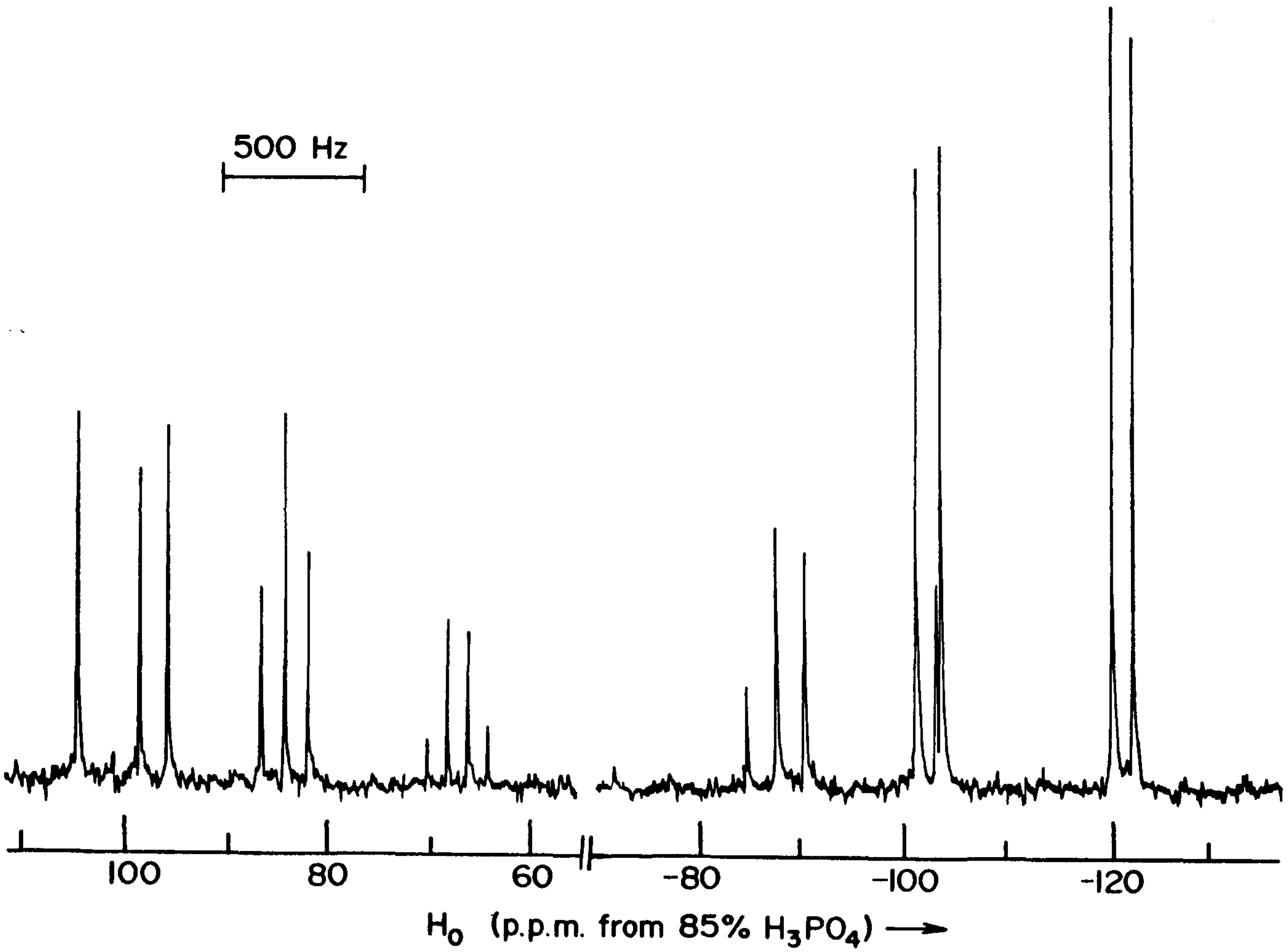


FIGURE III-12. ^{31}P NMR Spectrum of the $P_{4-x}As_XS_3$, X = 0-3 System.

signals with similar shifts and coupling constants leads to the conclusion that the series of birdcage molecules $P_{4-X}As_XS_3$, X = 0-4 is formed. Any As_4S_3 produced would of course not be detected by ^{31}P NMR.

The high frequency region is assigned to those phosphorus atoms in apical environments and the low frequency region to the basal phosphorus atoms. The apical region clearly displays a singlet, a doublet, a triplet and a quartet ranging from high to low frequency. These resonances may be assigned to αPAs_3S_3, $\alpha P_2As_2S_3$, αP_3AsS_3 and P_4S_3, respectively.

The basal region consists of doublets and singlets; each doublet splitting is due to an apical phosphorus. A total of three singlets and three doublets is observed. As already mentioned for P_4S_3 tricoordinated phosphorus signals usually occur at higher frequencies than recorded here for these basal phosphorus atoms. The doublets, in order of decreasing frequency, are assigned to $\alpha P_2As_2S_3$, αP_3AsS_3 and P_4S_3 on the basis of the coupling constants measured in the apical region and the apical-basal integrated intensity ratios. The singlets, again in order of decreasing frequency are assigned to βPAs_3S_3, $\beta P_2As_2S_3$ and βP_3AsS_3.

Integration of the spectrum of a saturated solution for the 2:2:3 P:As:S melt gave a ratio of 1:2:2:1 for αPAs_3S_3 : $\alpha P_2As_2S_3$:αP_3AsS_3:P_4S_3. This does not necessarily reflect the constitution of the solid because of the expected different solubilities. The product ratio for a 3:1:3 P:As:S sample slightly favoured the phosphorus-rich compounds.

Interestingly, the ^{31}P NMR spectra for CS_2 extractions from 1:3:3 melts show only the apical singlet due to αPAs_3S_3. This would indicate a definite preference of the phosphorus for the apical position. This could account for the large percentage of the α compounds present in the solutions of the mixtures, if solubility differences are not the major factor. The positioning of the phosphorus may be due to a greater stability of a homonuclear basal triangle.

Crystals grown by vacuum sublimation from P:As:S melts of composition 1:3:3, 2:2:3 or 1:3:4 gave a Raman spectrum essentially the same as that recorded for what was believed to be $\alpha P_2As_2S_3$.[14] However, a ^{31}P NMR spectrum of a CS_2 solution of the crystals again showed only an apical singlet assignable to αPAs_3S_3. A Raman spectrum of the solid recovered from the solution was similar to that recorded previously but also contained several additional peaks as well as small shifts of the others. This can be explained by the formation of different crystal forms for αPAs_3S_3. This has been observed for P_4S_3,[17] P_4Se_3,[15] As_4S_3[83,84] and As_4Se_3.[85] Redissolution of the solid and repetition of the ^{31}P NMR spectrum showed only the apical singlet.

The ^{31}P NMR spectrum obtained for a CS_2 solution of an extract from a 3:1:3 P:As:Se melt exhibits the same pattern as for the P/As/S system (Figure III-13). The peaks for the compounds αPAs_3Se_3 and βPAs_3Se_3 could not be detected for the 3:1:3 P:As:Se sample but were easily seen in the ^{31}P NMR spectrum of a 1:3:3 P:As:Se sample. In fact, signals for αPAs_3Se_3 and the β compounds were dominant for the latter sample. This greater proportion of β compounds in the selenium system may be related to the expected decrease in strain for a phosphorus atom in a basal ring attached to selenium ($\angle$EPP = 103° in P_4S_3, 105° in P_4Se_3, E = chalcogen).

A ^{77}Se NMR spectrum for the 3:1:3 P:As:Se sample clearly indicates the presence of P_4Se_3 in the sample. Signals due to two and possibly more species could be detected after 100,000 scans. On the basis of peak ratios in the ^{31}P NMR spectrum one would expect that the sets of peaks at -614 and -523 ppm could be due to two of the following three molecules: βP_3AsSe_3 and the isotopic

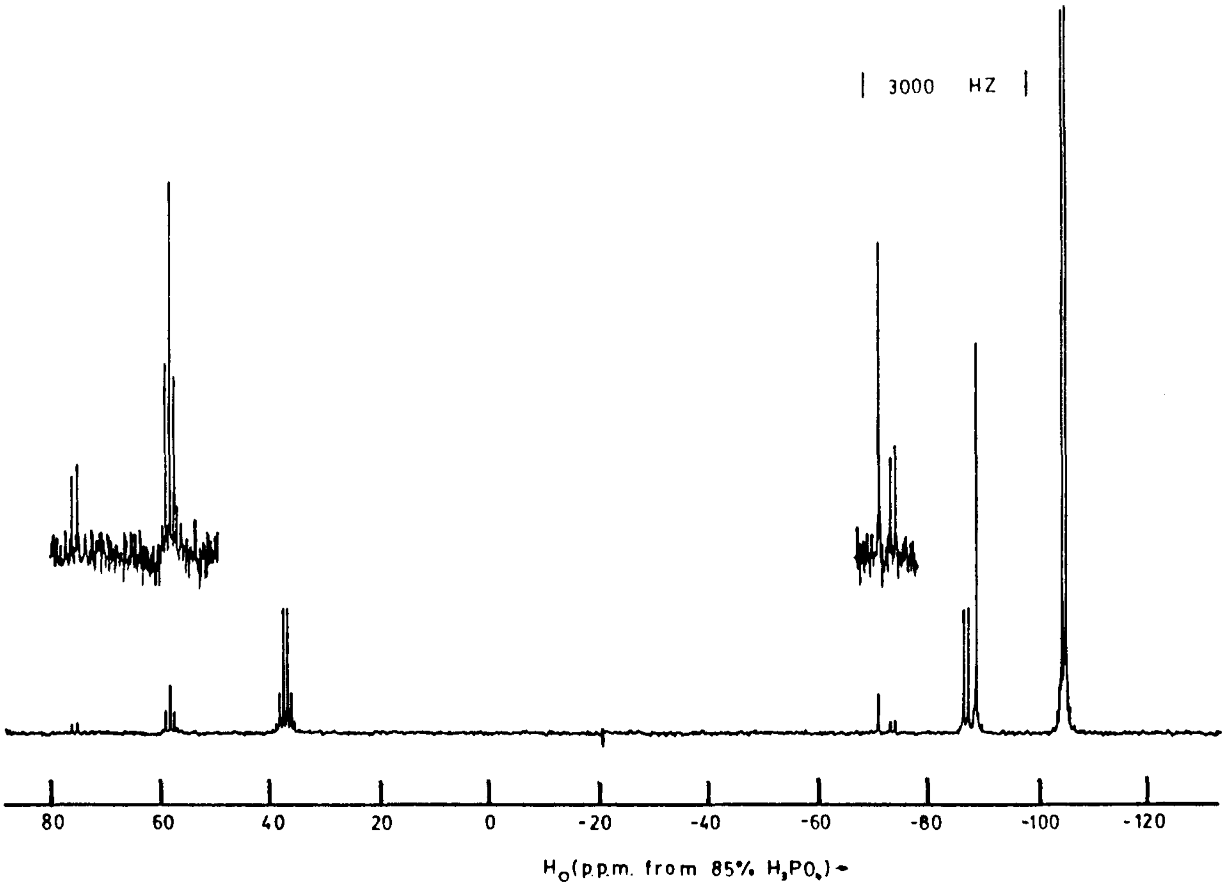


FIGURE III-13. ^{31}P NMR Spectrum of the $P_{4-X}As_XSe_3$, X = 0-3 System.

isomers of αP_3AsSe_3. The isomers would be present in equal amounts. One isomer would have the ^{77}Se atom attached to a basal phosphorus atom while in the other isomer it would be bonded to arsenic.

At -614 ppm there appears to be a triplet (216 Hz) of doublets (99 Hz). If this is due to a birdcage molecule this would require the indirect coupling to be the larger of the two. At -523 ppm a doublet of doublet of doublets may be discerned with coupling constants of 88, 212 and 396 Hz. This might correspond to the unsymmetrical form of αP_3AsSe_3.

III-4 Chemical Shifts, Coupling Constants and Empirical Correlations

The magnitude and direction of the ^{31}P NMR shift differences between P_4S_3 and P_4Se_3 are not consistent with the similarity of the electronegativities of sulfur (2.58) and selenium 2.55). This indicates that other factors must also be considered. The chemical shifts of tri- and tetra-coordinated phosphorus environments have been accounted for[123] in terms of bond angle changes, π-bonding effects and electronegativity effects. Rotameric equilibrium and changes in oxidation state are also important but are not relevant here.

It is commonly believed that the large negative shift of the basal atoms in P_4S_3 (-119.4 ppm) and P_4Se_3 (-103.8 ppm) is related to the strain present in the basal plane. As well as the birdcage molecules studied here similar shifts have been observed (-45 t0 -169 ppm) in the homo and heterocyclic three-membered phosphorus ring compounds studied extensively by Baudler and co-workers.[124] An examination of the data for the homocyclic phosphorus ring compounds generally shows deshielding of the phosphorus atoms with an increase in the RPP angle on addition of larger organic moieties (R) of similar electronegativity with no π-bonding capability. It is believed that RPP angles less than 109.5° together with the small PPP angles produce lone pair orbitals of greater s character and electron density on the phosphorus atoms and this in turn leads to more shielding of these atoms. This would seem to apply for the basal chemical shift ordering for P_4S_3 and P_4Se_3 where the corresponding EPP (E = S, Se) angles are 103.0(5)° and 105.3(1.0)°, respectively.[81,82] However, this does not explain why the basal phosphorus atom attached to selenium in P_4S_2Se has a chemical shift of -129.0 ppm which is more negative than that of the basal phosphorus atoms of P_4S_3.

Lack of theoretical data precludes any quantitative analysis of π-bonding effects. However, Van Wazer and

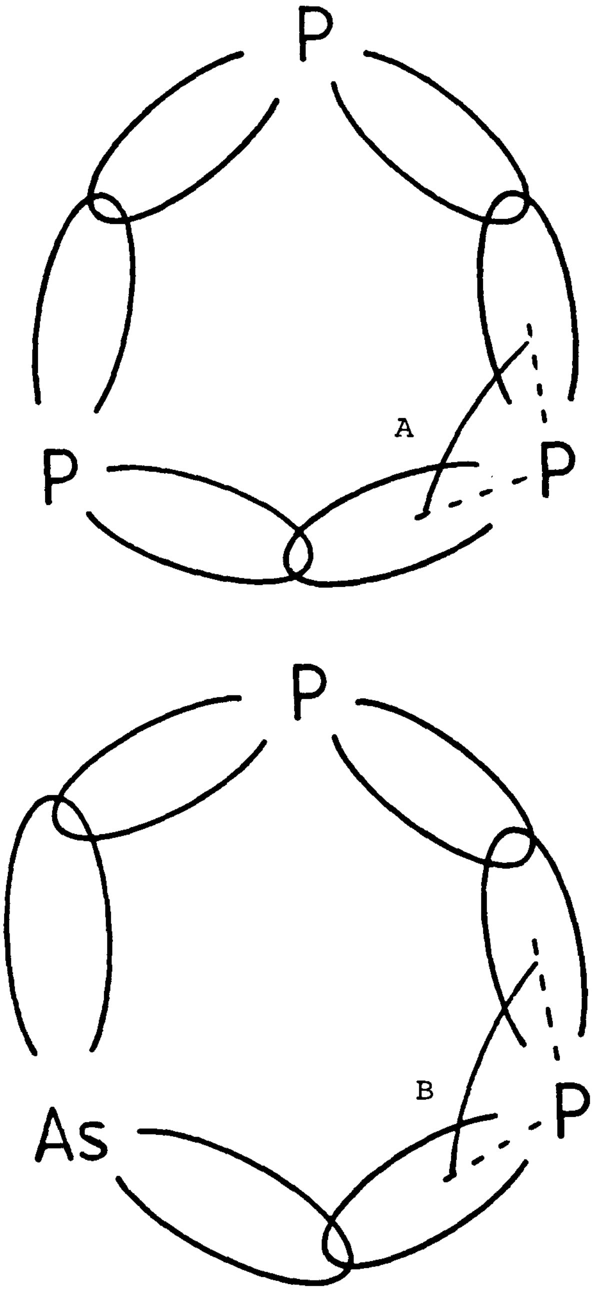
Letcher[123] have calculated values for the σ bonding contribution to the chemical shifts of P(III)homotricoordinated molecules PX_3 using the XPX bond angles and the electronegativities of the substituents as variables. Plotting these σ bonding values against experimental chemical shifts a straight line was obtained for molecules exhibiting no π bonding. Both P_4S_3 and P_4Se_3 lie off this line indicating a π bonding effect on the chemical shift. The point for P_4S_3 is farther from the line than that for P_4Se_3 indicating more π bonding which is not unreasonable considering greater possibility of good overlap in P_4S_3 because valence orbitals of the same principle quantum number are involved.

Their data also show that the π bonding has a deshielding effect. Therefore, the chemical shift decrease for P_4S_2Se mentioned above may be due to a combination of the very slight difference in electronegativity of sulfur and selenium and the decrease in π bonding in P_4S_2Se compared to P_4S_3 because of the third row atom bonded to the basal phosphorus atom in question. Further replacement of sulfur atoms by selenium atoms results in a deshielding effect (Table III-1). The reason for this remains unclear at this time.

The atoms attached to the basal triangle for the P/As/S and P/As/Se systems do not change within each series and the EPP angle should not change very much. On the basis of electronegativity one would expect with more arsenic in the basal triangle there would be greater shielding of the basal phosphorus but this is not the case. One possible explanation is that in the P_2As and PAs_2 basal triangles the larger size of the arsenic bonding orbitals allow the phosphorus bonding orbitals to extend out from the basal triangle, alleviating the angle strain, and still maintain sufficient overlap. However, the orbitals must be closer to the basal triangle to allow bonding in P_4S_3. This gives the lone pair orbitals of P_4S_3 more s character and thus more shielding ability (Figure III-14).

An empirical equation for the prediction of basal chemical shifts could be formulated from the chemical shift data for the binary and tertiary systems: Basal Chemical Shifts = -119 - 10a + 12b + 16c + d, a = 0, 1 (number of Se atoms attached to the P atom), b = 0, 1, 2 (number of other Se atoms), c = 0, 1 (number of apical As atoms), d = 0, 18, 31 (for 0, 1 or 2 basal As atoms). This equation was subsequently used for assignment of ^{31}P NMR peaks of the quaternary members of the series. The third row atoms not directly bonded to the basal phosphorus atom in question have a deshielding effect.

The chemical shifts of the apical phosphorus atoms (Tables III-1 and 2 and Figure III-15) also cannot be



The larger bonding orbitals of arsenic compared to those of phosphorus perhaps result in $\angle B > \angle A$ and therefore less angle strain at the phosphorus atoms attached to arsenic atoms in the basal plane resulting in less s character of each phosphorus lone pair and therefore less shielding.

FIGURE III-14. Possible Orbital Geometries in the Basal Triangles $P_{3-X}As_X$, X = 0-3.

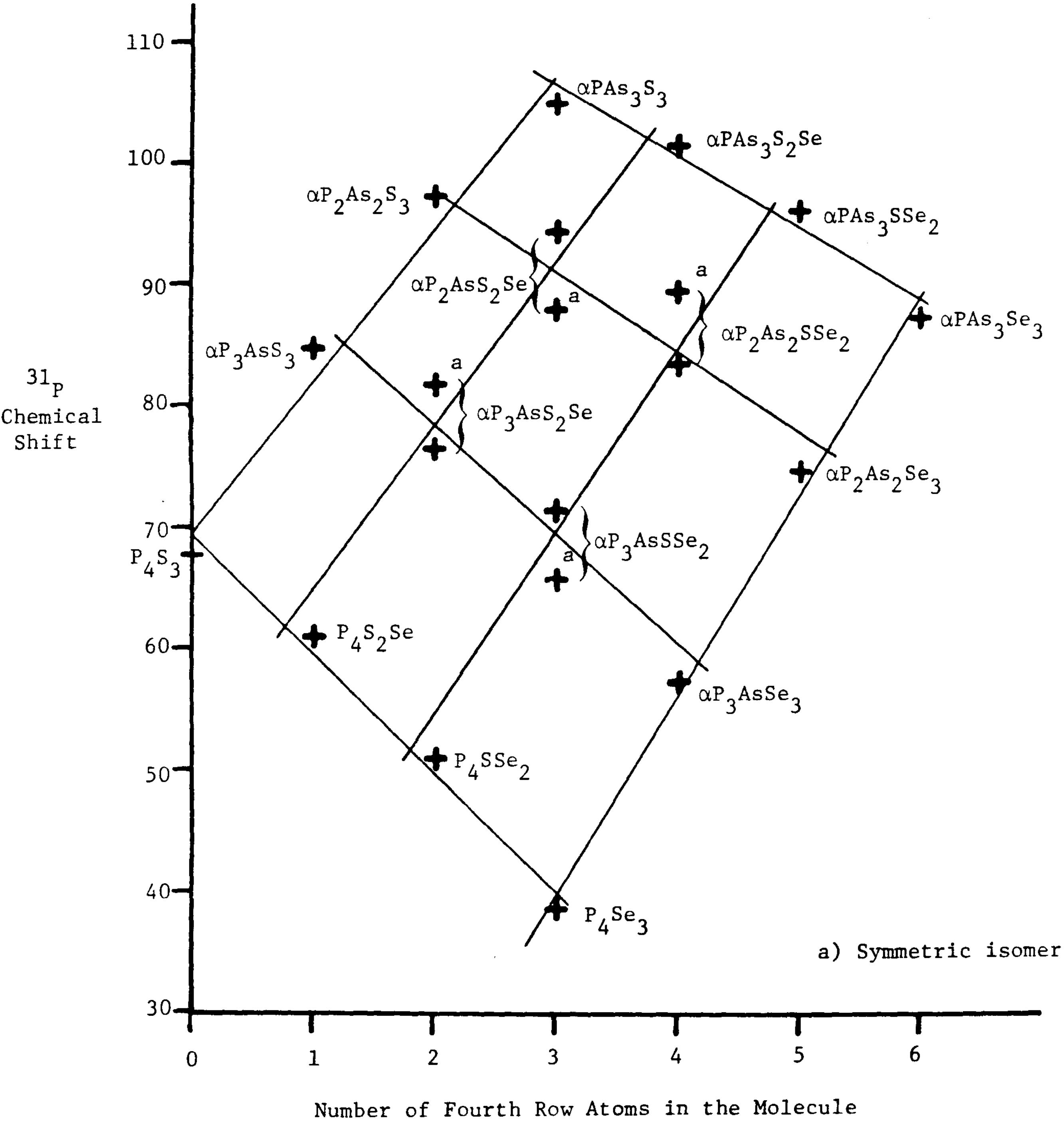


FIGURE III-15. Chemical Shift of the Apical Phosphorus vs. the Number of Fourth Row Atoms in the Molecule for the $P_{4-x}As_xS_{3-y}Se_y$; X,Y = 0-3 System.

explained in terms of bond angles. With increasing selenium content, and presumably bigger apical angles, the chemical shifts become less positive showing that there is more shielding not less. Like the basal atoms the slight electronegativity difference between sufur and selenium and π bonding effects may be considered possible reasons for the trend observed for sulfur-selenium content. Why increasing arsenic content results in deshielding is not clear but is typical of heavy atom paramagnetic effects.

Finer and Harris[125] have observed that, assuming that the Fermi contact term is dominant for P-P coupling, more s character in P-P bonds leads to more positive values. The following trends may then be discerned:

1) The larger the electronegativity of the substituents on the phosphorus atoms the more phosphorus s character in the P-P bond and the more positive the coupling constants and
2) The bigger the substituents on phosphorus the less s character in the P-P bond and the more negative the coupling constant.

Only four $^1J_{PP}$ values were determined so little can be said. Usually $^1J_{PP}$ values are negative where the sign has been determined. The two bond P-P couplings reported here also fit the observations if they are negative. This can be seen by examining the columns in Figure III-16. No attempt has been made to experimentally determine the absolute values of coupling constants here.

The chemical shifts and coupling constants have been satisfactorily discussed in terms of the s and p orbital character of the bonds and lone pairs. It should be noted, however, that Xα molecular orbital calculations for P_4S_3[126] show that the molecular orbitals composed mainly of 3s atomic orbitals are dominant in the multi-center bonding principally responsible for holding the molecule together. The molecular orbital consisting of mostly 3p orbitals are more directed and are involved in the bent bonds and have a high electron density in the conventional lone pair directions. In addition, the molecular orbital about the apical phosphorus atom with the greatest "lone pair character" has more calculated s character than comparable molecular orbitals situated about the basal phosphorus atoms. This is born out experimentally in the phosphorus electron Overhauser effect experiments. This s and p orbital distribution is opposite to that used as a basis for the previous discussion of chemical shifts and coupling constants. A more detailed

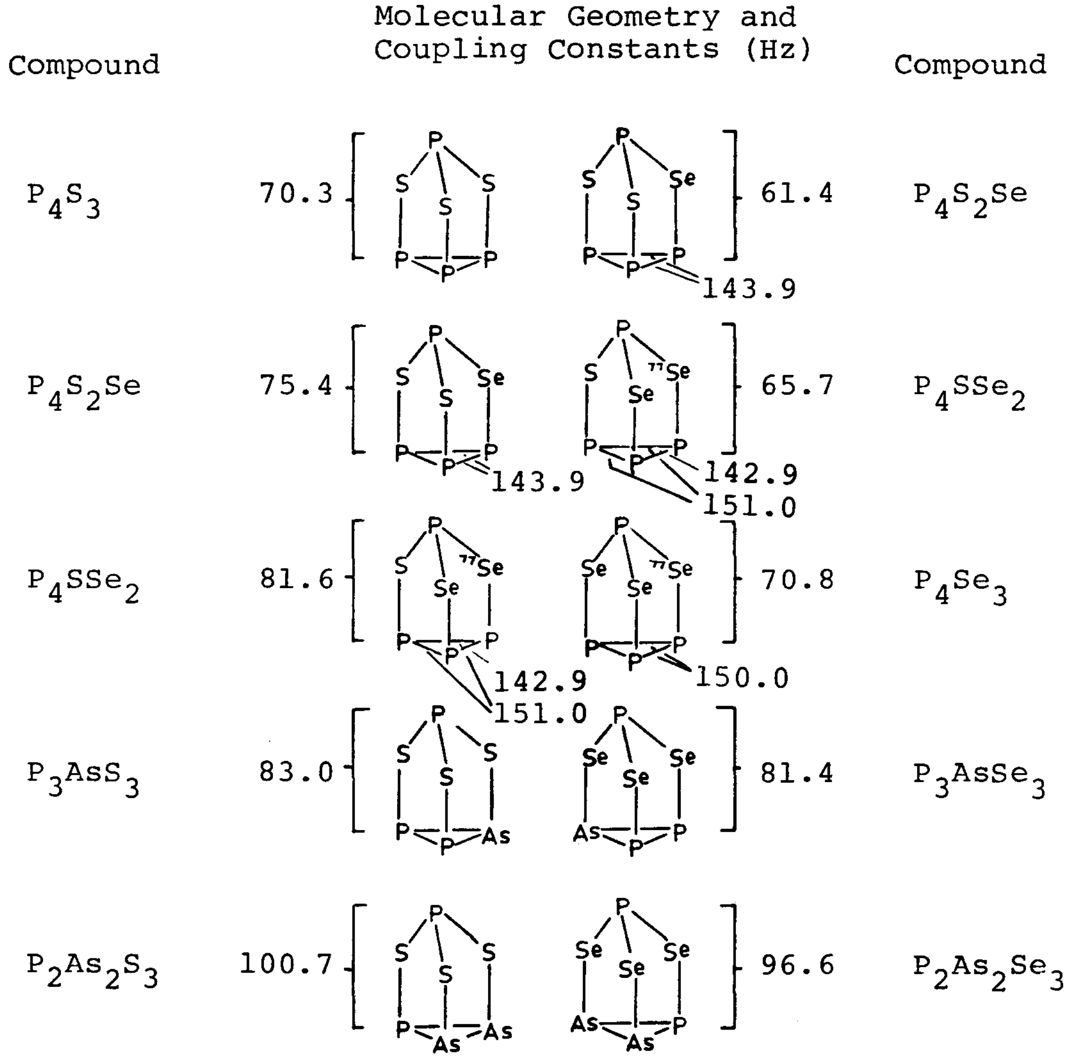


FIGURE III-16. Phosphorus-Phosphorus Coupling Constants ($|^1J_{PP}|$ and $|^2J_{PP}|$) of the Binary and Ternary Birdcage Molecules.

examination of this area is needed.

The theoretical calculations also show two other important facts. Both CNDO and Xα calculations show that d orbitals contribute only a small amount to the bonding (CNDO ~11%, Xα 2-5%). Finally, Xα calculations indicate that the highest occupied orbitals of P_4S_3 protrude into the solvent. Perturbations caused by different solvents would appreciably affect the charge distribution of these orbitals and thus affect the chemical shifts, as observed for P_4 and P_4S_3 by Fluck and Heckmann.[127,128] Charge distribution changes might also account for the small variations in the chemical shifts of compounds in different solutions noted in the present work. All ^{31}P NMR spectra were recorded using CS_2 as solvent but differing proportions of compounds in the solid samples resulted in varying solute ratios which might result in different charge distributions.

III-5 The Quarternary System $P_{4-X}As_XS_{3-Y}Se_Y$; X,Y = 0-3

Of the total of forty possible isomorphous molecules of the birdcage series $P_{4-X}As_XS_{3-Y}Se_Y$ (X = 0-4, Y = 0-3) there are twenty phosphorus-containing cages that have not been discussed. The empirical correlations noted above can be used to make probable assignments for the quarternary members of the series that can be observed.

The molecules that are most likely to be observed, on the basis of data in previous sections, are those that contain an apical phosphorus and/or are sulfur rich. The ^{31}P NMR spectrum obtained at high field (161.95 MHz) for a solution formed from a 4:4:3:3 P:As:S:Se melt extracted with CS_2 is shown in Figures III-17 and III-18. Chemical shifts, assignments and coupling constants are given in Tables III-2 to III-4.

In the apical region of the ^{31}P NMR spectrum new singlets are seen at 101.2 and 96.0 ppm. As shown in Figure III-15 these are assigned to αPAs_3S_2Se and αPAs_3SSe_2, respectively. There are also four new apical doublets at 94.3, 89.4, 87.8 and 83.4 ppm which are due to the two forms of $\alpha P_2As_2S_2Se$ and the two forms of $\alpha P_2As_2SSe_2$. Definite assignments are more difficult for these. However, keeping in mind the dominance of the sulfur rich compounds, the apparent affinity of arsenic for selenium and phosphorus for sulfur and using Figures III-15 and III-16 the new doublets are tentatively assigned, in order of decreasing frequency, to $\alpha P_2As_2S_2Se$(I)[‡] (with a P-S-P linkage), $\alpha P_2As_2SSe_2$(I) (with a P-S-P linkage), $\alpha P_2As_2S_2Se$(II) (with a P-Se-P linkage) and $\alpha P_2As_2SSe_2$(II) (with a P-Se-P linkage) (see Figure III-19).

For the six α compounds with a 3:1 P:As ratio one expects apical signals for four triplets and two

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[‡] I, mirror plane in molecule, II, no mirror plane.

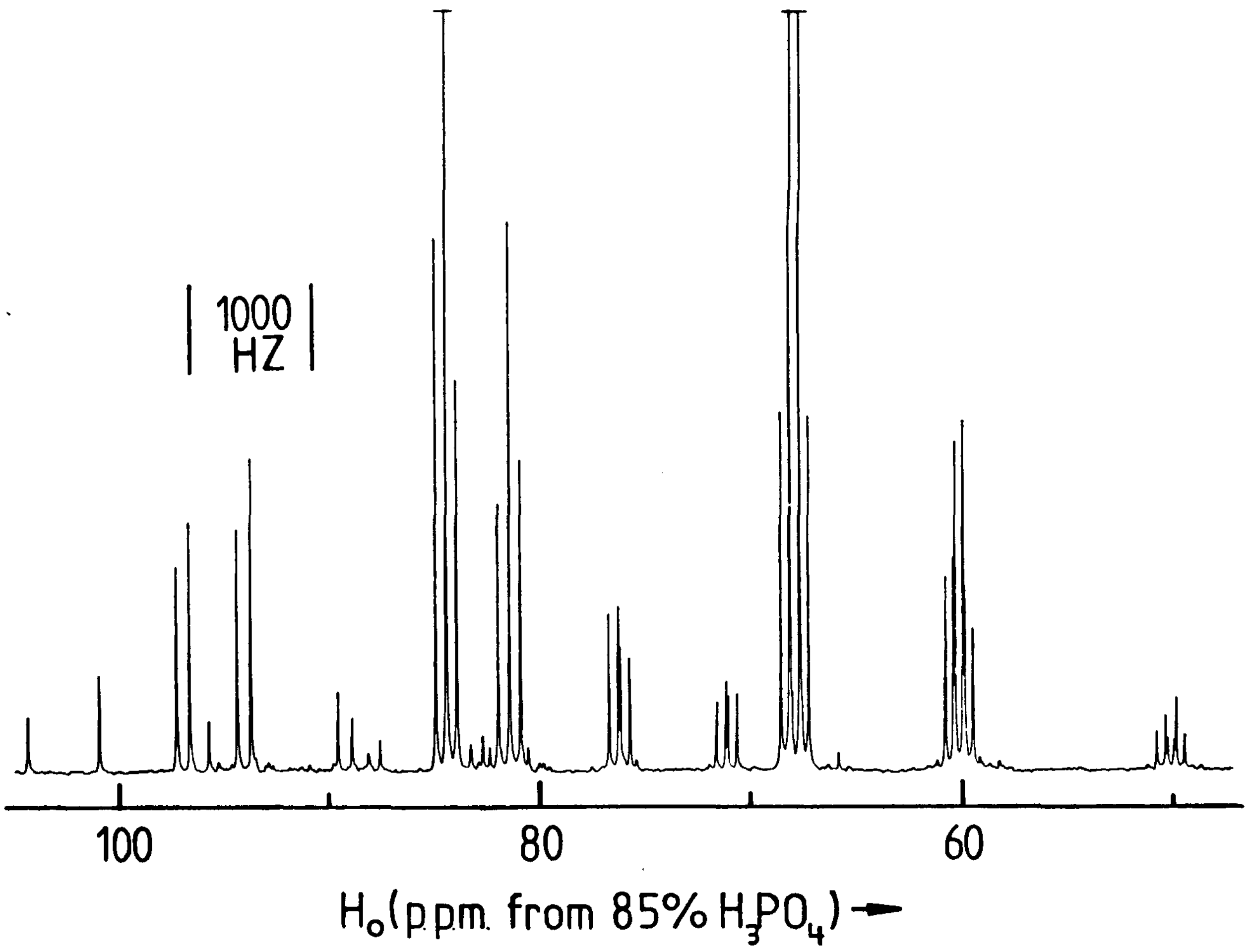


FIGURE III-17. ^{31}P NMR Spectrum of the Apical Region of the $P_{4-X}As_{X}S_{3-Y}Se_{Y}$; X,Y = 0-3 System.

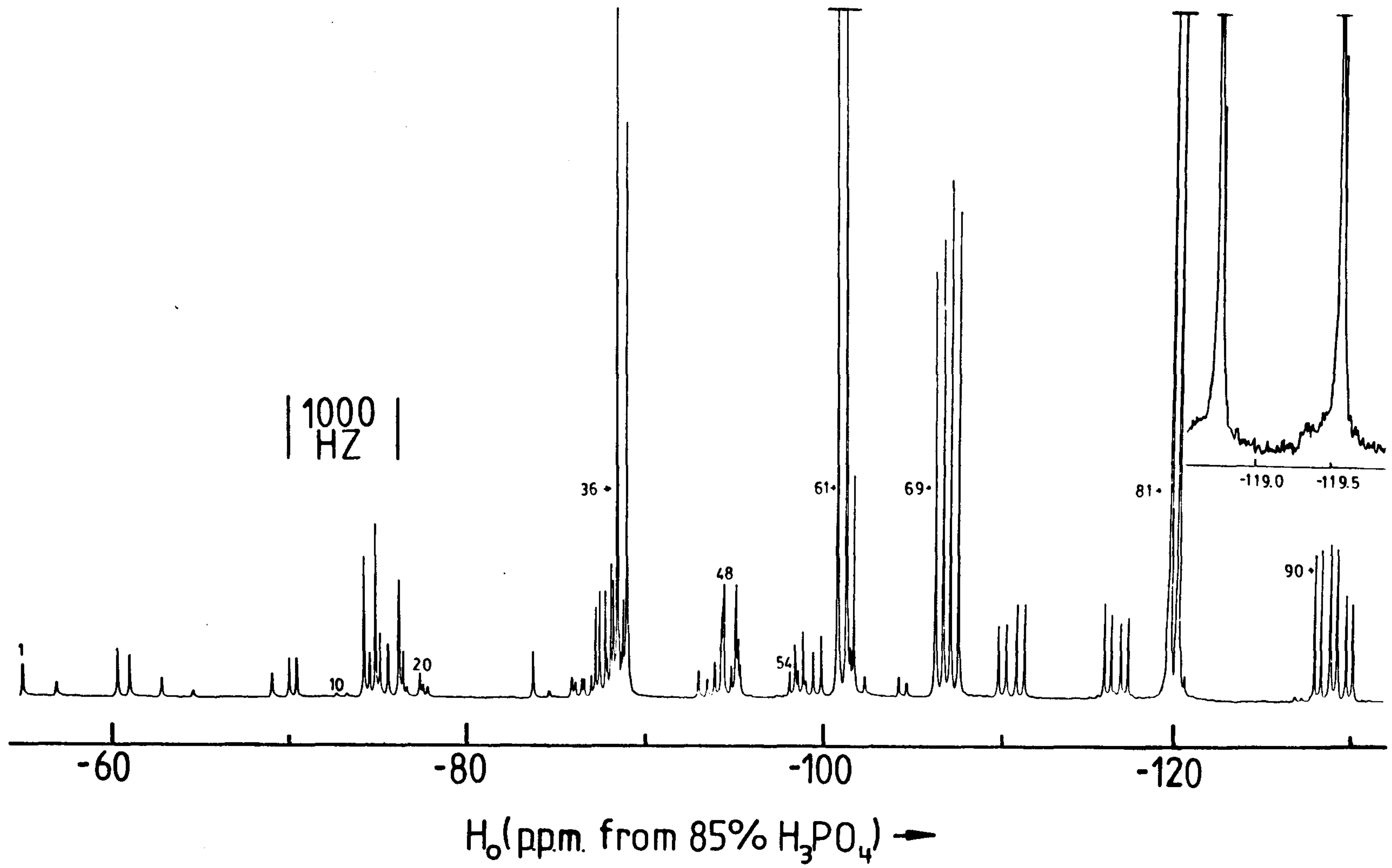
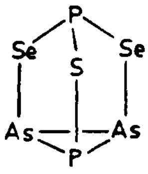
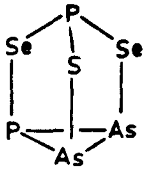


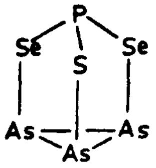
FIGURE III-18. ^{31}P NMR Spectrum of the Basal Region of the $P_{4-X}As_XS_{3-Y}Se_Y$; X,Y = 0-3 System.



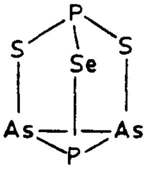
$\alpha P_2As_2SSe_2$(I)



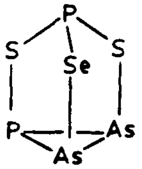
$\alpha P_2As_2SSe_2$(II)



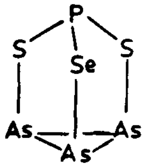
αPAs_3SSe_2



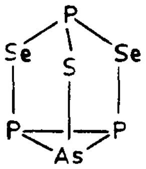
$\alpha P_2As_2S_2Se$(I)



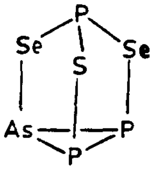
$\alpha P_2As_2S_2Se$(II)



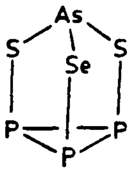
αPAs_3S_2Se



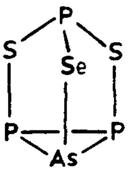
αP_3AsSSe_2(I)



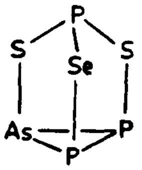
αP_3AsSSe_2(II)



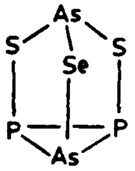
βP_3AsS_2Se



αP_3AsS_2Se(I)



αP_3AsS_2Se(II)



$\beta P_2As_2S_2Se$(I)

FIGURE III-19. Some Quaternary Members of the Series $P_{4-x}As_xS_{3-y}Se_y$; X,Y = 0-3.

TABLE III-2 ^{31}P NMR Chemical Shifts and Assignments for the Apical Phosphorus Atoms of the Binary, Tertiary and Quarternary Systems $P_{4-X}As_XS_{3-Y}Se_Y$; X,Y=0-3.

Chemical Shifts		Assignments
Binary/Tertiary Systems	Quaternary Systems	
104.3	104.7	αPAs_3S_3
	101.2	αPAs_3S_2Se
	96.0	αPAs_3SSe_2
88.4	87.4	αPAs_3Se_3
96.8	97.2	$\alpha P_2As_2S_3$
	94.3	$\alpha P_2As_2S_2Se$(II)
	89.4	$\alpha P_2As_2SSe_2$(I)
	87.8	$\alpha P_2As_2S_2Se$(I)
	83.2	$\alpha P_2As_2SSe_2$(II)
75.8	74.7	$\alpha P_2As_2Se_3$
84.2	84.6	αP_3AsS_3
	81.6	αP_3AsS_2Se(I)
	76.4	αP_3AsS_2Se(II)
	71.3	αP_3AsSSe_2(II)
	65.6	αP_3AsSSe_2(I)
58.3	57.3	αP_3AsSe_3
67.8	68.0	P_4S_3
60.8	60.2	P_4S_2Se
50.9	50.2	P_4SSe_2
38.3	36.2	P_4Se_3

TABLE III-3 Phosphorus-Phosphorus Coupling Constants for the Birdcage Molecules

Compound	$^2J_{PSP}$	$^2J_{PSeP}$	$^1J_{PP}$
$\alpha P_2As_2SSe_2$(I)	110.6		
$\alpha P_2As_2S_2Se$(II)	104.4		
$\alpha P_2As_2S_3$	100.7		
$\alpha P_2As_2Se_3$		96.6	
$\alpha P_2As_2SSe_2$(II)		95.0	
$\alpha P_2As_2S_2Se$(I)		76.3	
αP_3AsSe_3		81.4	
αP_3AsSSe_2(II)	94.4	74.4	166.8
αP_3AsS_2Se(II)	87.7	72.5	163.0
αP_3AsS_2Se(I)	84.2		
αP_3AsS_3	83.0		
P_4Se_3		70.8	
P_4S_2Se	81.6	65.7	150.0
P_4SSe_2	75.6	61.4	143.9
P_4S_3	70.3		

TABLE III-4 Experimental and Empirically Calculated ^{31}P NMR Chemical Shifts and Assignments for the Basal Phosphorus Atoms of the Binary, Tertiary and Quaternary Systems $P_{4-X}As_XS_{3-Y}$; X,Y = 0-3

Peak Numbers Figures III-17&18	Chemical Shifts			
	Binary/ Tertiary Systems	Quaternary System	Empirically Calculated	Assignments
1		-55.0	-47	βPAs_3SSe_2(I)
2	-57.5	-56.9	-59(-57)	βPAs_3S_2Se(II) (or βPAs_3Se_3)
3,4		-60.7	-64	$\alpha P_2As_2SSe_2$(I)
5,6		-63.9,-64.7		?
7		-69.1	-69	βPAs_3SSe_2(II)
8	-66.7	-70.0	-72	βPAs_3S_3
9	-71.0	-70.5	-70	$\beta P_2As_2Se_3$
10,11	-73.6	-73.0	-74	$\alpha P_2As_2Se_3$
12,14		-74.6	-76	$\alpha P_2As_2S_2Se$(II)
13,15,16,17		-75.4	-77	αP_3AsSSe_2(II)
18		-76.5	-76	$\beta P_2As_2S_2Se$(I)
19-22		-76.7 to -77.9		?
23	-84.4	-83.8	-85	$\beta P_2As_2S_3$
24		-84.7	-81	βPAs_3S_2Se
25-29		-85.9 to -87.0	-86	$\alpha P_2As_2SSe_2$,(II)
	-86.8		-86	αP_3AsSe_3,?

(continued...)

TABLE III-4 (continued)

30,32,35,39		-88.0	-89	$\alpha\mathrm{P_3AsS_2Se}$(II)
31,34	-88.5	-87.8	-88	$\alpha\mathrm{P_2As_2S_3}$
33	-88.6	-87.9	-88	$\beta\mathrm{P_3AsSe_3}$
36,40		-88.7	-89	$\alpha\mathrm{P_3AsS_2Se}$(I)
37,38,41		-88.6,-88.7,-89.1		?
42-44,48 49,53	-93.8	-94.2	-95	$\mathrm{P_4SSe_2}$
45-48		-94.3 to -94.4	-95	$\beta\mathrm{P_2As_2SSe_2}$(I)+?
50-52		-95.2 to -95.3		
55,57 59,60		-99.2	-98	$\alpha\mathrm{P_3AsSSe_2}$(II)
54,56		-98.4	-97	$\alpha\mathrm{P_2As_2S_2Se}$(I)
61,62	-101.8	-101.1	-101	$\alpha\mathrm{P_3AsS_3}$
58,63,64		-99.0,-101.6,-101.7		?
65	-102.5	-101.8	-103	$\beta\mathrm{P_3AsS_3}$
66		-102.5		?
67,68	-103.6	-105.9	-105	$\mathrm{P_4Se_3}$
69-72	-106.2	-107.0	-107	$\mathrm{P_4S_2Se}$
73-76		-110.9	-111	$\alpha\mathrm{P_3AsS_2Se}$(II)
77-80	-116.0	-116.8	-117	$\mathrm{P_4SSe_2}$
81,85	-119.4	-119.5	-119	$\mathrm{P_4S_3}$
82,86		-119.18		$\mathrm{P_4{}^{32}S_2{}^{34}S}$
83,84,87		-119.9,-120.0,-120.4		?
88-97	-128.5	-129.0	-129	$\mathrm{P_4S_2Se}$

doublets of doublets, assuming no second order effects. No signals due to αP_3AsSe_3 are present but there are two triplets, the first due to αP_3AsS_3, two doublets of doublets and possibly a fifth signal at 65.6 ppm. Assignments for the quarternary species with a 3:1 P:As ratio, in order of increasing field strength, are αP_3AsS_2Se (I) (P-Se-As linkage), αP_3AsS_2Se (II) (P-S-As linkage), αP_3AsSSe_2 (II) (P-Se-As linkage) and αP_3AsSSe_2 (I) (P-S-As linkage). All apical peaks to higher field are due to the P/S/Se system.

The assignment of the second triplet to the symmetrical αP_3AsS_2Se is further strengthened by noting the coupling constant trends in Figure III-16 They indicate that the αP_3AsS_2Se in question should have an indirect coupling constant for the phosphorus atoms joined by sulfur atoms greater than 83.0 Hz while the symmetrical αP_3AsSSe_2 should have the corresponding indirect coupling constant for the phosphorus atoms joined by selenium less than 81.4 Hz. The triplet has a coupling constant of 85.4 Hz. The assignments for the unsymmetrical αP_3AsS_2Se and αP_3AsSSe_2 molecules are also consistent with the data in Figure III-16 which show that an increase in selenium content results in larger corresponding coupling constants (Table III-3). An example is the increase in the indirect coupling constants associated with the sulfur atoms for the series P_4S_3, P_4S_2Se and

P_4SSe_2.

Assignments for the basal portion of the spectrum were based on apical:basal intensity ratios, coupling constants found in the apical portion of the spectrum and the empirical equation derived in the previous section. Assignments for the basal phosphorus atoms are given in Table III-3. Some peaks have not been assigned. These plus other obscured peaks may be due to the unsymmetical molecules $\beta P_2As_2S_2Se$, $\beta P_2As_2SSe_2$, βP_3AsS_2Se and βP_3AsSSe_2 and the symmetrical molecule αP_3AsSSe_2.

Peaks 82 and 86 have been assigned to the 11.43%[129] of the P_4S_3 molecules that have the isotopic formula $P_4{}^{32}S_2{}^{34}S$. This is a primary isotopic shift of 0.3 ppm to low frequency of $P_4{}^{32}S_3$. No observable chemical shift difference for the apical phosphorus was detected.

III-6 Crystal Structure of the Occupationally Disordered Crystal $P_2As_2S_3$

Yellow needle-shaped crystals grown during a high temperature (~400°C) vacuum sublimation of a 2:2:3 P:As:S melt gave a Raman spectrum similar to that previously reported for what was thought to be $\alpha P_2As_2S_3$. Precession photographs of most of these crystals showed that they were twinned. For a small pentagonal plate, however, the cell parameters were found to be a = 10.98, b = 9.93 and c = 6.58 (Å). Systematic absences of $h + \ell = 2n + 1$ for $0k\ell$ and $h = 2n + 1$ for $h0\ell$ were consistent with the space groups Pnma and $Pn2_1a$ (a non-standard setting of $Pna2_1$). Comparison with the cell parameters of other group VB chalconides indicated that the crystals were probably isomorphous with βAs_4S_3 and the volume of the cell was consistent with the formulation $P_2As_2S_3$.

Intensities were measured as described in Chapter II. The unit cell dimensions were obtained from a least-squares refinement of 2θ, W and χ for 15 high angle ($27° < 2\theta < 33°$) reflections. Data were collected for θ-2θ scans over a scan range ($K\alpha_1$ -0.90°) to ($K\alpha_2$ +0.90°) with variable scan rates of 3-29.3°/min depending on the intensity of a preliminary 2 second count. Stationary background counts were recorded at each end of the scan, each for one quarter of the scan time. The intensities of three standard reflections monitored after every 67 reflections showed no significant changes over the period of the data collection. A total of 3102 reflections (including standards) in the quadrants h, ±k, ±1 with $2\theta < 55°$ were collected. Lorentz and polarization corrections were applied to all data.

The initial positions of the atoms of $\alpha P_2As_2S_3$ were assumed to be those of the atoms of βAs_4S_3. The program

SHELX[118] two cycles of least-squares gave an R factor of 0.1953 for 6σ data consisting of 2966 reflections. Scrutiny of the isotropic temperature factors indicated that a formulation αPAs_3S_3 might be more reasonable because of the very small isotropic temperature factor of the basal phosphorus situated on the crystallographic mirror plane. Two further cycles of least squares then gave an R factor of 0.1423. With anisotropic temperature factors R dropped to 0.0754 and the temperature factors of the remaining phosphorus atoms dropped significantly. The population parameters of all the group VB atoms were then allowed to refine and R conveyed to 0.0370 after 4 cycles of least squares. The composition calculated from the population parameters was $P_{2.0}As_{2.0}S_3$. A single crystal Raman spectrum recorded at this point confirmed that the crystal chosen contained other members of the series $P_{4-X}As_XS_3$, X = 0-4.

The crystal was a pentagonal plate bound by the plane {100} and the faces (00-1), (-101), (101), (0-10) and (05-1). The latter two were 0.00875 cm from an origin in the crystal while all other faces and planes were 0.01125 cm from the origin. The linear absorption coefficient was calculated to be 110 cm^{-1}. The absorption correction was calculated by the program ABSORB from the X-ray 76 system.[119] After averaging equivalent reflections, excluding reflections which were systematically absent or have zero structure amplitudes, a final data set of 864 reflections was obtained.

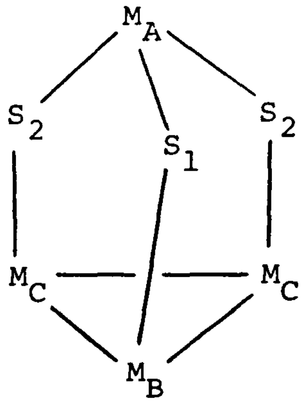
Dispersion correction factors and scattering curves were then constructed using the population parameters obtained at the point of the convergence of R in the SHELX program. Two cycles of least squares using the X-ray 76 program CRYLSQ gave R_1 and R_2 values for 2σ data of 0.060 and 0.061, respectively. With a weighting scheme of $W = 1.0/(4.0\sigma F_o^2 + 3.5 \times 10^{-3} F_o^2)$ for the 565 reflections with $F/\sigma F>6$ two further cycles of least squares converged to final agreement indices $R_1 = 0.028$ and $R_2 = 0.035$ (40 parameters refined). In the final cycle of least squares no parameters shifted by more than 10% of its standard error. A final difference Fourier map showed some residual electron density (0.59 e/$\mathring{A}^3$) at the position of the two basal atoms related by the mirror plane. The maximum trough was 0.76 e/$\mathring{A}^3$.

The final population parameters for the composite Group VB atom positions showed that there was no significant change in the cell composition during the calculations involving the hybrid scattering curves. The final composition was $P_{2.0}As_{2.0}S_3$. A definite preference for phosphorus occupying the apical position is evident (Table III-5). This is consistent with the

TABLE III-5 Unit Cell Data and Final Atomic Positional (x 10^4), Site Population and Thermal Parameters (x 10^3) for $P_2As_2S_3$ with e.s.d.'s in Parentheses.

$P_2As_2S_3$, orthorhombic, Pnma, a = 10.976(2), b = 9.930(3),
c = 6.582(2), U = 717.4 Å^3,
z = 4, D_c = 2.85 gm/cc.

ATOM	M_A	M_B	M_C	S(1)	S(2)
x	6796(1)	4144.8(8)	5689.1(7)	4880(2)	6994(1)
y	2500	2500	1278.5(7)	2500	865(1)
z	1699(2)	-1026(2)	-2802.1(10)	2072(3)	- 355(2)
%As	11	59	66	-	-
%P	89	41	34	-	-
U11	25.6(9)	27.1(5)	58.3(5)	31.3(9)	44.9(8)
U22	73.4(13)	57.6(7)	39.0(4)	72.9(14)	51.8(9)
U33	32.4(9)	38.3(6)	33.4(4)	28.4(9)	50.6(9)
U12	0.0	0.0	1.9(3)	0.0	15.8(7)
U13	-4.6(6)	-7.2(4)	-2.6(3)	3.6(8)	4.5(6)
U23	0.0	0.0	-6.6(3)	0.0	10.5(7)



observation that the ^{31}P NMR spectrum of the P/As/S melt extracts show a greater proportion of molecules in solution have an apical phosphorus atom. The bond lengths calculated are as expected for composite values of As-S/P-S and As-As/P-P bond lengths (Table III-6). The bond angles in the apex are slightly bigger than expected and those in the base are generally smaller than expected. The final structure factors are listed in Appendix I.

III-7 Vibrational Spectra of P_4S_3, P_4Se_3 and Similar Compounds

The composition and purity of various materials were checked by Raman spectroscopy in the course of this work. The vibrational spectra of P_4S_3 have been extensively studied[121,130-133] but there are some questions regarding certain weak peaks and some assignments. The room temperature Raman spectrum of P_4Se_3 has also been recorded.[121,134]

The expected fifteen modes for a seven atom molecule of C_{3v} symmetry transform as $4A_1+A_2+5E$ with the A_1 and E modes being both Raman and IR active.[135] The A_2 mode is totally inactive. The splittings recorded here in a low temperature (-196°C) Raman spectrum for P_4S_3 (Figure III-20) can be explained by factor group analysis.[136] With a space group Pnmb, site symmetry C_s and eight molecules per unit cell each A_1 band could split into four

TABLE III-6 Bond Lengths and Bond Angles of P_4S_3,[a] Disordered $P_2As_2S_3$ and βAs_4S_3.[b]

Bond Lengths

	P_4S_3	$P_2As_2S_3$	% P in bond	βAs_4S_3
M_AS_1	2.080(10)	2.117(2)	89	2.234(16)
M_AS_2	2.091(10)	2.124(2)	89	2.230(8)
M_BS_1	2.094(10)	2.193(2)	41	2.221(12)
M_CS_2	2.092(10)	2.194(2)	34	2.218(10)
M_BM_C	2.236(10)	2.390(1)	38	2.460(7)
M_CM_C	2.334(10)	2.426(1)	34	2.480(7)

Bond Angles

	P_4S_3	$P_2As_2S_3$	βAs_4S_3
$S_2M_AS_2$	99.1(5)	99.73(9)	98.3(5)
$S_2M_AS_1$	99.6(5)	100.11(7)	98.8(4)
$M_AS_1M_B$	102.8(5)	104.92(9)	105.4(5)
$M_AS_2M_C$	103.0(5)	104.90(9)	105.0(4)
$S_1M_BM_C$	103.0(5)	101.48(5)	102.8(3)
$S_2M_CM_C$	103.1(5)	100.80(5)	101.6(2)
$S_2M_CM_B$	103.2(5)	101.48(6)	101.4(4)
$M_CM_BM_C$	60.0(5)	61.01(4)	60.5(2)
$M_BM_CM_C$	60.0(5)	59.50(3)	59.7(1)

[a] Reference 81 [b] Reference 84

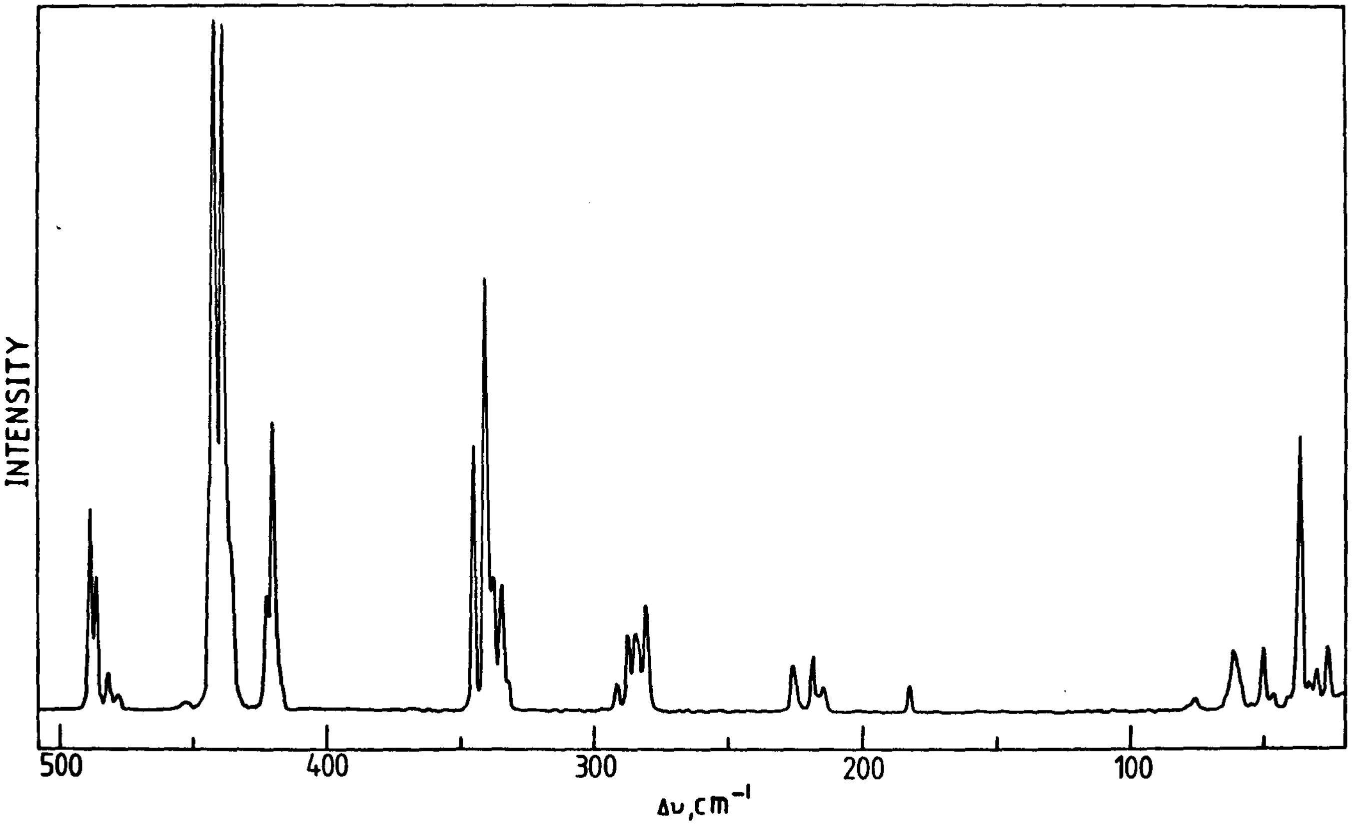


FIGURE III-20. Raman Spectrum of P_4S_3 Recorded at -196°C.

Raman-active bands and four IR-active bands. The E mode bands can give six IR-active and eight Raman-active bands. The A_2 mode, if split, could give four Raman-active and four bands in the IR. Even if the A_2 bands are assumed to be too weak to be observed nine band envelopes are expected but only eight are found for P_4S_3 and six for P_4Se_3.

The number of splittings of several band envelopes in the Raman spectrum of P_4S_3 is consistent with but does not necessarily confirm the assignment of the band envelopes at 487, 442 and 420 cm^{-1} to A_1 modes and those at 340, 283 and 223 cm^{-1} to E modes. A weak band at 187 cm^{-1} and a new weak band found in the Raman spectrum at 450 cm^{-1} cannot be resolved into separate bands. The weak band reported at 145 cm^{-1} was not found even using high receiver gain and high laser power. There has been some question as to whether the band envelope at 487 cm^{-1} also contains another mode. The solution polarization measurements show some residual intensity for this peak, which considering its initial weak intensity, might indicate the presence of another mode. This is certainly not definite.

There are sixteen molecules in the unit cell of P_4Se_3 so little can be said regarding the splittings seen in the solid state Raman spectrum. Comparison with the Raman spectrum of P_4S_3 suggests that the band envelope centered at 360 cm^{-1} probably is due to two A_1 stretching modes. Depolarization measurements for a CS_2 solution of P_4Se_3 allow the bands at 487, 384 and 217 cm^{-1} to all be assigned as A_1 vibrations. Note the band shift from 360 to 384 cm^{-1} on dissolution. The other bands seen in the Raman spectrum of the solid were not detected in the solution Raman spectrum. The spectrum of the solid at -196°C is illustrated in Figure III-21.

The large number of noncoincidences in the Raman and infrared spectra for the compound now known to be αPAs_3S_3 rather than $\alpha P_2As_2S_3$ can be attributed to the weakness of A_1 and E modes in the infrared and Raman spectra, respectively. A molecule of C_s symmetry ($\alpha P_2As_2S_3$) has A' and A" modes which should be active in both types of spectra and few noncoincidences should be expected. The Raman spectra for what are probably different crystal forms of αPAs_3S_3 are listed in Table III-7. Note that the strong band at 276 cm^{-1} differs little in position from the strong band in the Raman spectrum of αAs_4S_3 (272 cm^{-1}) that is assigned to the symmetric stretch involving the As_3 triangle. If the molecule had been $\alpha P_2As_2S_3$ a greater difference would have been expected in probably both the number and position of the normal modes involving stretching of the basal triangle. A Raman spectrum of a crystal known to contain several members of the P/As/S series has several bands in this region.

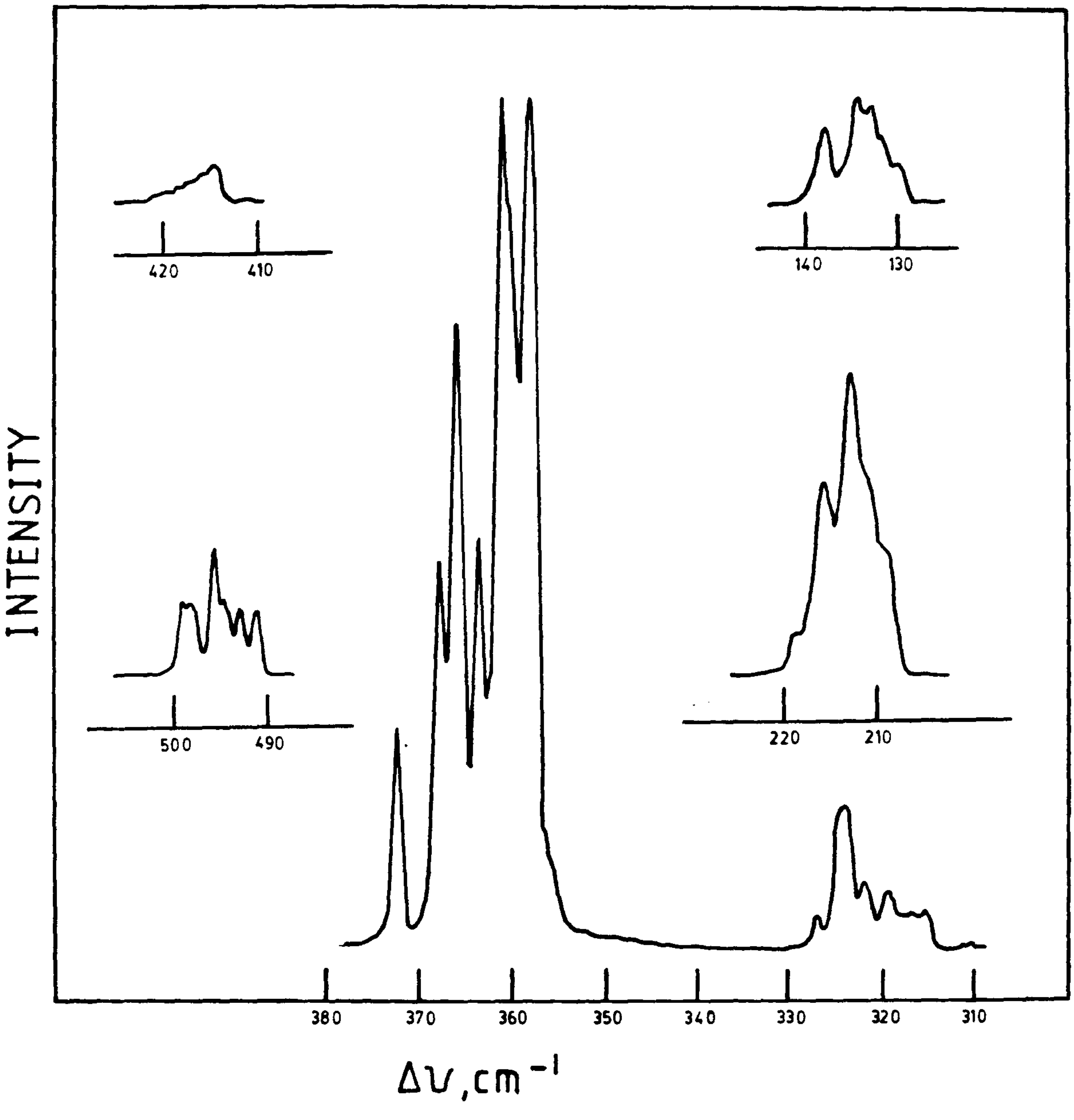


FIGURE III-21. Raman Spectrum of P_4Se_3 Recorded at -196°C.

TABLE III-7 Raman and IR Spectral Data of P_4S_3, P_4Se_3 and αPAs_3S_3

P_4S_3	Assignments	P_4Se_3	Assignments	PAs_3S_3	
		11(sh)[a]			
		14(sh)			
		22(10)			
26(9)[a]		25(sh)		24(3)[b]	[c]
30(6)		28(18)			30(sh)
33(5)		35(11)			33(sh)
36(31)		37(11)			
41(2)		40(10)		43(3)	42(sh)
		44(3)			
46(2)		49(3)			
50(9)		52(3)			
62(9)		59(2)		57(4)	63(sh)
76(2)					
183(3)	A_1?	130(sh)	E	171(3)	173(sh)
		132(sh)		177(18)	180(36)
		133(11)		189(3)	197(sh)
215(3)	E	135(11)		202(100)	201(35)
217(2)		138(8)			206(65)
219(8)		139(sh)		217(11)	219(15)
226(7)					
280(15)	E	209(sh)	A_1		
283(sh)		211(sh)		275(74)	275(100)
284(10)		213(36)			
287(10)		216(22)			
291(3)		219(sh)			298(99)
333(sh)	E	316(5)	E	307(58)	308(25)
335(18)		317(5)		313(sh)	
338(19)		320(8)			
341(13)		322(8)			
345(39)		325(16)			
		327(5)			
418(sh)	$2xA_1$	356(sh)	$2xA_1$	350(86)	347(56)
420(41)		358(96)			353(sh)
422(17)		360(sh)			
436(sh)		361(100)			
439(100)		363(38)			
443(100)		366(63)		366(3)	365(sh)
		368(41)			
		372(22)		373(1)	371(7)
453(1)	E?	415(2)	E?	423(10)	422(22)
479(2)	A_1	481(11)	A_1	460(1)	462(2)
482(6)		483(11)			
487(19)		484(13)			
489(30)		485(22)			
		488(13)			
		489(13)			

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[a] Both recorded at -196°C. [b] From sublimation.

[c] From CS_2 solution.

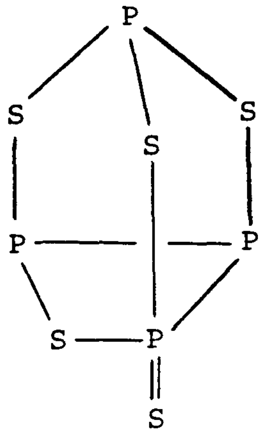
Raman spectra of the mixed crystals of the P/S/Se system are quite complex. An examination of relative intensities for extracts of the melts 4:2:1 and 4:1:2 (P:S:Se) reveals that the peak at 378 cm^{-1} is due to P_4Se_2S and one at 392 cm^{-1} is due to P_4S_2Se. For the other peaks intensity differences did not vary enough to allow assignment to P_4S_2Se or P_4SSe_2. The rather intense band at 485 cm^{-1} is the result of the superposition of all the peaks due to the P_3 stretching modes of all the molecules of the series. This clearly illustrates how little the mode is coupled to others in the molecules. No attempt was made to separate the individual compounds.

III-8 ^{31}P NMR Spectroscopy of αP_4S_5 and Other Phosphorus Sulfides

The compound αP_4S_5 is prepared by the reaction:

$$P_4S_3 + \frac{1}{4} S_8 \xrightarrow[CS_2,\ catalytic\ I_2]{diffuse\ sunlight,\ 3\ days} \alpha P_4S_5 + other$$

products. It has been reported that a CS_2 solution of αP_4S_5 gives an ABCX ^{31}P NMR spectrum[79] but the ^{31}P solid state NMR spectrum[137] only has three signals with chemical shifts of 200, 20 and -120 ppm. In light of this the solution spectrum was investigated.



αP_4S_5

A thoroughly washed solid sample of αP_4S_5 gave a Raman spectrum in good agreement with published data.[132] A saturated solution in CS_2 gave an AMNX ^{31}P NMR spectrum with chemical shifts of 233.3, 126.4, 123.6 and 91.8 ppm (see also Table III-8). The central portion of the spectrum contains two overlapping doublets of doublets of doublets which exhibit some second order effects in peak intensities (Figure III-22).

The coupling constants (Table III-8) readily reveal that the low frequency envelope is due to the basal phosphorus atom that is directly bonded to two other magnetically nonequivalent phosphorus atoms. A high field position is expected considering the small basal bond angle of 66°[138] subtended by two other phosphorus atoms. The other two basal atoms have their signals (126.4, 123.6 ppm) rather close together although one has an exocyclic sulfur attached to it. This has also been observed in P_4S_9[139] where the tricoordinated and

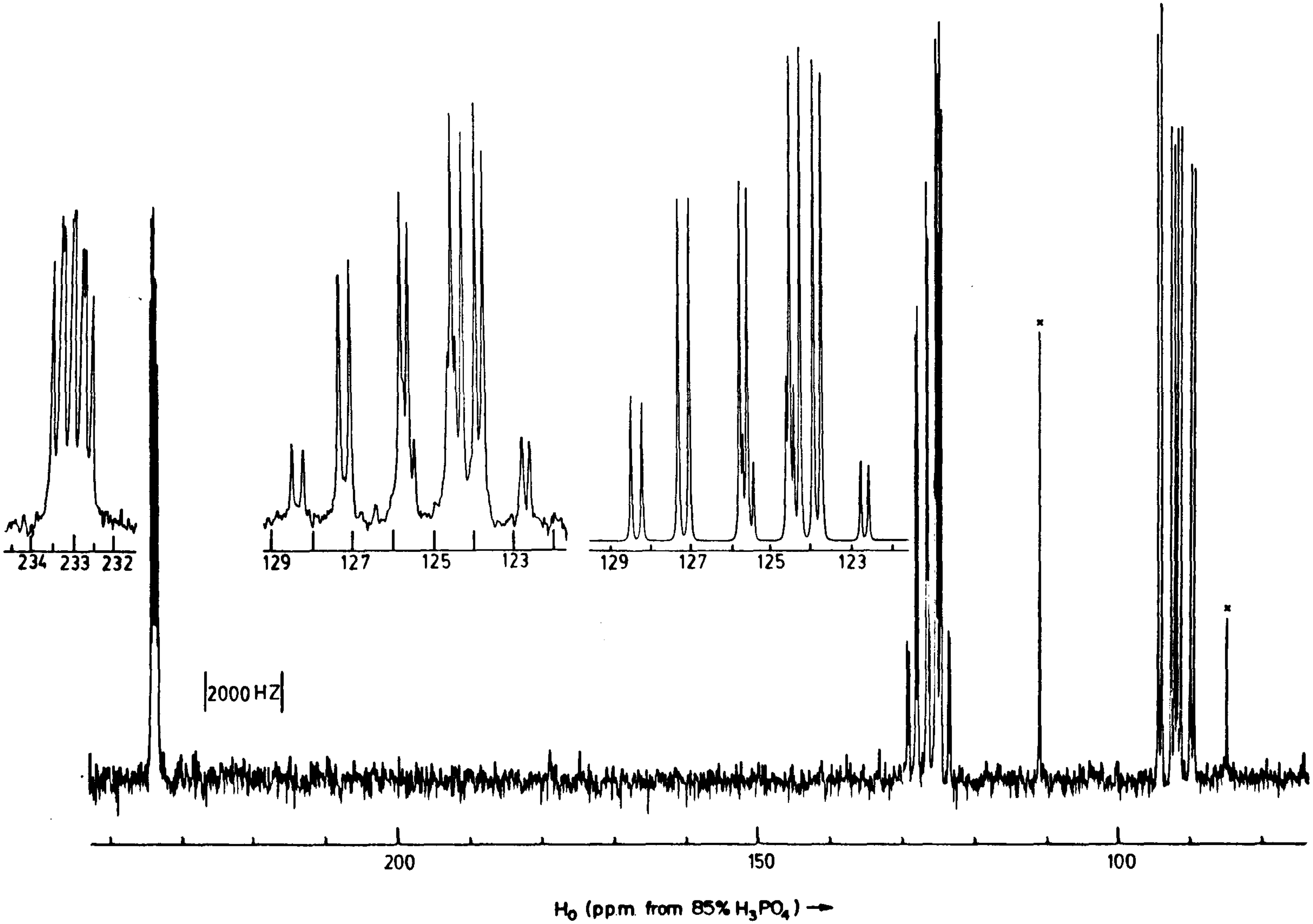


FIGURE III-22. ^{31}P NMR Spectrum of P_4S_5 (X = impurity).

TABLE III-8. Chemical Shifts and Coupling Constants of the Phosphorus Sulfides

Compound	Spin System	Chemical Shifts,[a] ppm				Coupling Constant, Hz					
		1	2	3	4	1-2	1-4	1-3	2-3	2-4	3-4
P_4S_3[b]	AX_3	67.5	-120.6	-120.6	-120.6	71	71	71	0	0	0
αP_4S_4[c]	A_4	202.4	202.4	202.4	202.4	0	0	0	0	0	0
βP_4S_4[c]	A_2MX	207.97	207.97	175.09	86.04	0	18.2	168.4	18.2	168.4	50.4
αP_4S_5[d]	AMNX	233.3	123.6	126.4	91.8	18.6	27.8	53.5	118.4	188.2	282.2
βP_4S_5[d]	A_2X_2	130.0	130.0	80.0	80.0	0	44.1	44.1	44.1	44.1	0
P_4S_6[d]	AM_2X	199.0	178.3	178.3	56.3	45.8	45.8	111.9	0	10.2	10.2
P_4S_9[e]	AB_3	57.3	62.9	62.9	62.9	96	96	96	0	0	0
P_4S_{10}[e]	A_4	56.3	56.3	56.3	56.3	0	0	0	0	0	0

[a] Relative to ext. 85% H_3PO_4. [b] Reference[120] . [c] Reference[71] . [d] This work.
[e] Reference[139] .

tetracoordinated atoms have similar environments and have chemical shifts of 57.3 and 62.9 ppm, respectively. Usually phosphines are to high frequency from the related thiophosphoranes.[123] In the case of the two phosphorus atoms of αP_4S_5 in question it is not possible to positively distinguish which one is to high frequency of the other. Examination of the coupling constants of molecules like αP_4S_5 and P_4S_9 would tend to indicate that coupling constants between a tricoordinated atom and a tetracoordinated atom are larger than those between two tricoordinated atoms. If this is generally true then the peaks centered at 126.4 ppm may be assigned to the tetracoordinated atom.

The signal due to the apical phosphorus is found at 233.3 ppm and is identified by the lack of any large couplings due to directly bonded phosphorus. This is the most deshielded phosphorus yet found for phosphorus sulfides.

The singlets at 110.8 and 84.4 ppm have been assigned to αP_4S_7.[140] However, as the authors state, the absence of the expected splitting of the peaks is unusual. In addition, the ^{31}P NMR spectra of CS_2 solutions of melts of different P:S ratios (2:1, 1:1, 4:5, 4:7) all show these singlets. Their peak intensity ratios vary as well although the peak at 110.8 ppm is always the larger. These singlets are also of significant intensity in the spectrum recorded for the products of the reaction of αP_4S_7 with two moles of triphenyl phosphine. This would indicate, but does not prove, that the compound(s) probably does not have exocyclic sulfur atoms. If the singlets arise from two separate compound one may be due to the isomer of P_4S_6 that is isostructural with P_4O_6.

The CS_2 mother liquor initially removed from the sample gave a very complex ^{31}P NMR spectrum (Figure III-23). Except for the high field doublet due to unreacted P_4S_3 all other peaks are in the vicinity of the P_4S_3 quartet or are to low field of it. It is not unreasonable to expect to find intermediate(s) formed in the production of αP_4S_5. None of the signals can be assigned to $\beta P_4S_3I_2$, αP_4S_4 or βP_4S_4. The former compound could be expected to be present if the initial step was oxidation by iodine. However, only a catalytic amount of iodine was added to a large volume of solvent of which only a small portion was put into the NMR tube. The latter mentioned compound could be expected if the next step in the production of αP_4S_5 was the replacement of the iodine atoms by a sulfur insertion.

The other reasonable alternative is that the first step in the production of αP_4S_5 is the addition of an exocyclic sulfur. An AX_3 pattern would be expected

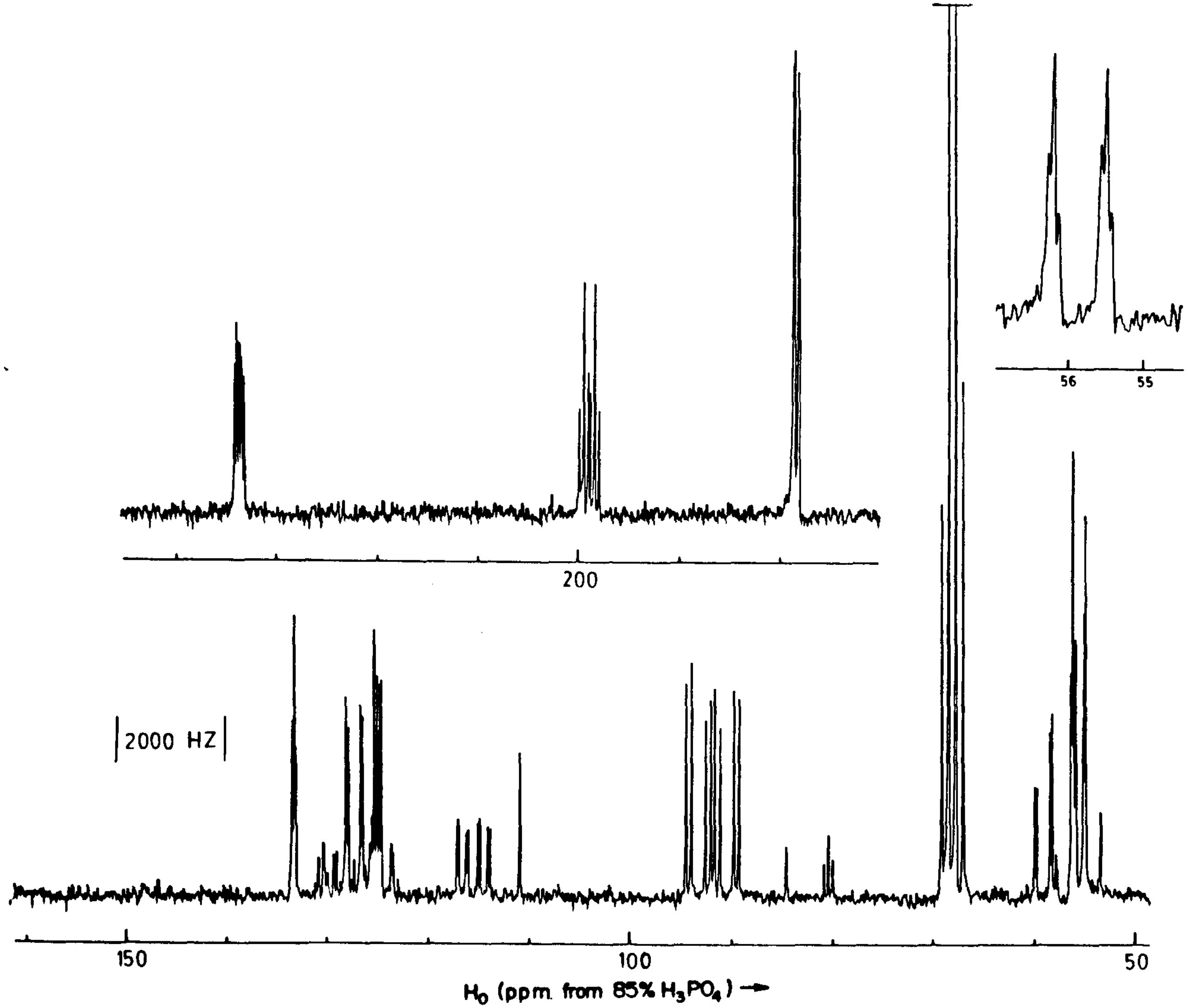


FIGURE III-23. ^{31}P NMR Spectrum of the Mother Liquor from an αP_4S_5 Preparation Insert from P_4S_3 + 2PØ$_3$ Reaction.

if the sulfur atom was added to the apical phosphorus whereas an AM_2X pattern would be seen if sulfur added to a basal phosphorus atom. The latter structure corresponds to that reported for P_4S_4II.[141] It has been produced from 1:1 P:S melts[141] and by slowly heating a 1:1 P_4S_3:αP_4S_5 mixture.[17]

Large band envelopes at 198.7 and 178.3 ppm display the splittings consistent with the A and M parts of an AM_2X spectrum. Peaks due to the X portion of the spectrum can be discerned in the complex part of the spectrum to low frequency of the P_4S_3 quartet. This doublet of triplets is not obscured by other peaks in the ^{31}P NMR spectrum recorded for the reaction of αP_4S_7 with two moles of triphenyl phosphine ($P\phi_3$) or for a fresh CS_2 extraction of a 2:1 P:S melt.

The coupling constants for this new compound are 112, 46 and 10 Hz. Therefore, it is likely that there is at most only one $^1J_{PP}$. If so it is small compared to most directly bonded P-P couplings.[125] Models of all the phosphorus-sulfur cages based on the P_4 tetrahedron containing no dithio linkages show that there are 39 possible molecules in the compositional range P_4S_2 to P_4S_8 for which an AM_2X pattern is possible. Excluding βP_4S_4 only 14 of these have one $^1J_{PP}$ while only two molecules have no direct P-P couplings.

The six molecules having three exocyclic sulfurs are excluded from consideration as this same AM_2X pattern is also seen for CS_2 solutions of a phosphorus-rich sample (2:1 P:S) and for the reaction of αP_4S_7 with two moles of $P\phi_3$. In fact, those with even two exocyclic sulfur atoms (Figure III-24, a-d) are not likely candidates. Structures c-e can also be excluded from consideration because one would expect these to have ^{31}P NMR spectral peaks for the basal tricoordinated phosphorus atoms upfield of at least -40 ppm.[124] As already stated, no unassigned peaks above 53.3 ppm were observed for the mother liquor of the αP_4S_5 reaction. Structures a-g also require that $^1J_{PP}$ be either 10 or 46 Hz but these are usually above 120 Hz.[125] This leaves structures h-j as the most likely possibilities Considering that the largest coupling constant is only 110 Hz and that the compound is present in the $\alpha P_4S_7/P\phi_3$ reaction as a major product structure j seems the most likely although no certain conclusion can be reached on the basis of present evidence. Note that this is the same product as that produced by reacting P_4S_7 with one mole of triphenyl phosphine and is the same isomer of P_4S_6 present in the structure of βP_4S_7. This is really a mixed crystal containing P_4S_7 molecules and the P_4S_6 isomer believed to be formed in the αP_4S_5 preparation.[142,143]

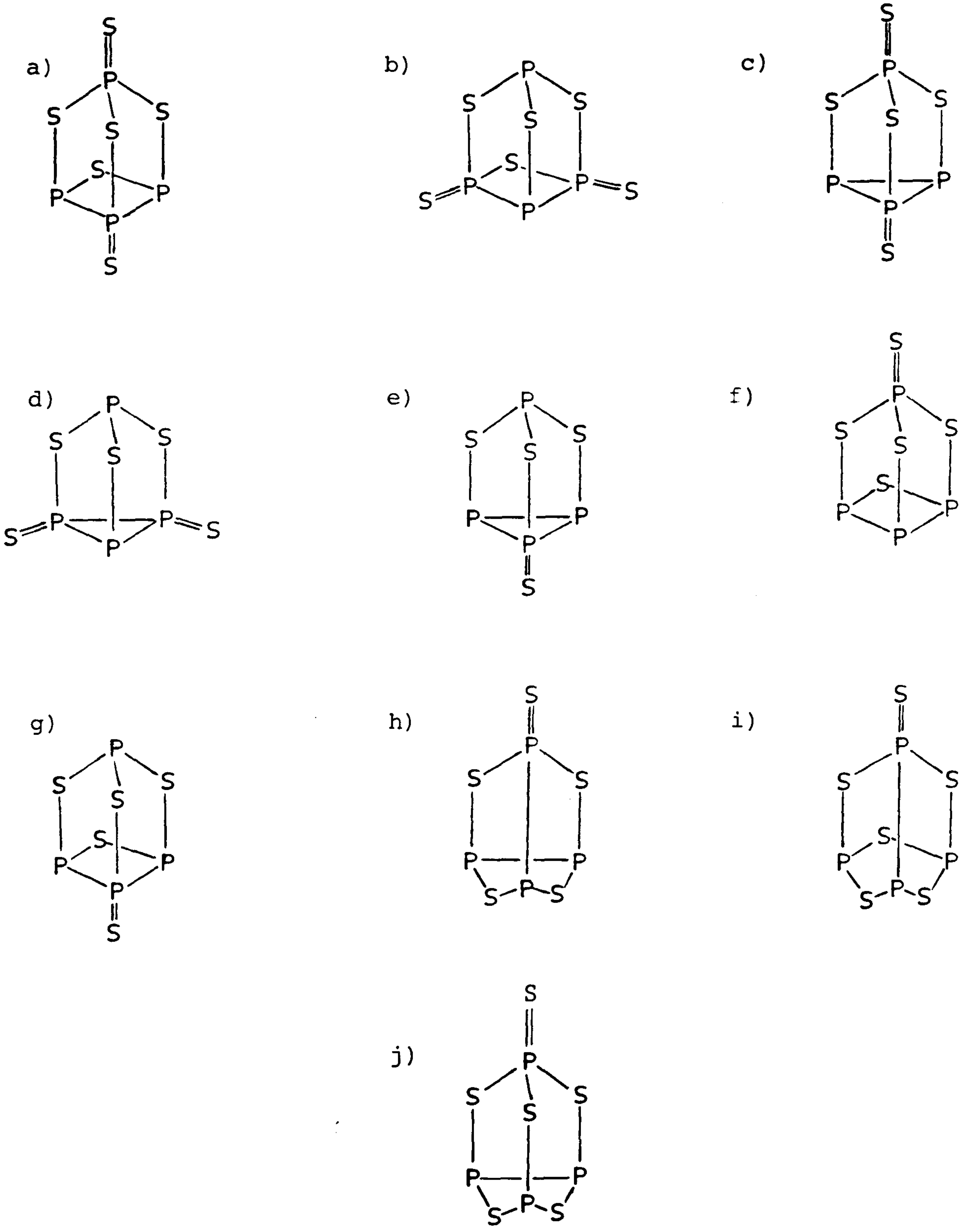


FIGURE III-24. Possible Structures for the Unidentified compound Formed in αP_4S_5 Preparation.

The small triplets observed at 130.0 and 80.0 ppm in the ^{31}P NMR spectrum for the αP_4S_5 preparation are present as major signals along with that for triphenylphosphinesulfide in the ^{31}P NMR spectrum of the above mentioned $\alpha P_4S_7/P\phi_3$ reaction. The crystal structure[79] of this product has shown the compound to be βP_4S_5. The triplet at 133.1 ppm, the doublet of doublets of doublets at 91.7 ppm and the complex series of peaks around 55 ppm are left unassigned at this time.

All the chemical shifts and coupling constants for the phosphorus chalconides are listed in Table III-9. No clearly discernible trends in chemical shifts can be identified. The coupling constants for directly bonded phosphorus atoms are of the expected magnitude. The indirect couplings involving a tetracoordinated phosphorus atom are generally greater than 50 Hz while those involving only tricoordinated phosphorus show a wider range (10-72 Hz).

CHAPTER IV

REACTIONS OF GROUP VB CHALCONIDES WITH HALOGENATING AGENTS

IV-1 Introduction

In general the reactions of VB/VIB compounds with halogens are poorly understood. For example, although $S_3N_3Cl_3$ was first prepared from S_4N_4 and chlorine in chloroform in 1835[144] only recently has the intermediate $S_4N_4Cl_2$[43] been characterized. Both of these compounds are monocyclic with exocyclic chlorine atoms bonded to sulfur. The crystal structure of $S_3N_3Cl_3$ has been determined[145] while the structure of $S_4N_4Cl_2$ has been deduced from the production of N_6S_5 from the reaction of $S_4N_4Cl_2$ with $(CH_3)_3SiNSNSi(CH_3)_3$.[146] Reactions of S_4N_4 with solutions or vapours of the heavier halogens and interhalogens have generally produced sulfur-nitrogen-halogen polymers.[44] The heavier group VB (M) chalogen (E) halides (X), MEX, are also polymeric compounds, often existing as glasses. They are usually produced by fusing the appropriate chalconide and a halide of a group VB element.[147] Reactions of S_4N_4 with $SbCl_5$ gave the adducts $S_4N_4 \cdot SbCl_5$[148] and $S_4N_4 \cdot 2SbCl_5$[149] while three or more moles of $SbCl_5$ gave $(S_4N_4)(SbCl_6)_2$.[150] No comparable reactions had been carried out with As_4S_4.

IV-2 Reactions of As_4S_4 with Cl_2, Br_2 and I_2

In view of the above it was appropriate to study the halogen oxidations of As_4S_4 under mild conditions in an attempt to produce halogenated rings rather than polymeric species. The Raman spectra of the solid material and solutions produced from the reaction of As_4S_4 with two moles of chlorine, bromine or iodine in SO_2 were recorded. From the reactions with chlorine or bromine the solutions were found to contain the liquids AsX_3 and S_2X_2 (X=chlorine or bromine) while the only solid present was unreacted As_4S_4. As arsenic is much easier to oxidize than nitrogen this type of degradation of As_4S_4 is not totally unexpected.

Iodine and As_4S_4 in SO_2 produced a yellow powder indistinguishable in colour from As_4S_4 itself. There were no soluble products. The X-ray powder pattern of the solid was identical to that of AsSI.[151] The solid, stable in air for several months, gave a Raman spectrum which confirmed that no previously known arsenic sulfide or arsenic iodide or sulfur or iodine were present. Clearly defined peaks were present at 354(18), 303(8), 203(100), 179(8), 169(50), 134(14), 131(14), 85(20), 74(15), 63(4), 50(24), 44(4) and 29(4) cm^{-1}. The lack of any peaks between 450 and 550 cm^{-1} indicates that no arsenic-sulfur double bonds are present. The peaks between 300 and 360 cm^{-1} are characteristic of arsenic-sulfur single bonds while the strong band at 203 cm^{-1} is most likely due to an arsenic-iodine stretch. The two most intense vibrations of AsI_3 are at 208 and 187 cm^{-1}.[152]

Attempts to repeat the reaction in dry methylene chloride led to the production of large amounts of AsI_3. The role of the solvent is not understood at this time. No further work was done on the system but it should be noted that the preparation of AsSI in SO_2 is the first room temperature preparation of this compound, albeit in a micro-crystalline state. Its structure is probably similar to that of the antimony analogue.[153]

IV-3 Preparation and Characterization of $\alpha P_4Se_3I_2$

A number of phosphorus-sulfur halides have been reported: SPX_3 (X = F, Cl, Br, I),[3,154] $\alpha P_4S_3X_2$ (X = Cl, Br, I),[48,51] $\beta P_4S_3I_2$,[50] $P_2S_2I_4$,[53] P_2SI_4,[49] $P_2S_5Br_4$ and $P_2S_6Br_2$.[55] The few selenium analogues reported are $SePX_3$ (X = F, Cl, Br, I)[3,54] $P_4Se_2I_2$,[52] $P_2Se_2I_4$ and P_2SeI_4.[54] Generally the selenium compounds appear to be more unstable and are not as well characterized. They are, however, interesting because of the presence of the additional nucleus of spin 1/2 and as a source of more phosphorus-phosphorus coupling constant data.

For $\alpha P_4S_3I_2$ originally only a broad single line at -127 ppm was reported for its ^{31}P NMR spectrum[120] but with the advent of better instrumentation the spectrum was identified as that due to an AA'BB' system with a very small chemical shift difference of only 3.68 ppm.[155] The chemical shift difference for $P_4S_3X_2$ (X = Cl, Br) halides are not reported but it is stated[51] that their ^{31}P NMR spectra are more typical of AA'BB' peak patterns. The similarity of the coupling constants for P_4S_3 and P_4Se_3 leads to the question of whether the spectrum of $\alpha P_4Se_3I_2$ would be like that of $\alpha P_4S_3I_2$ or whether it would be a more typical AA'BB' pattern. Both $\beta P_4S_3I_2$ and $\beta P_4Se_3I_2$ were prepared by the slow addition of iodine to cold solutions of the phosphorus sesquichalconide. Since $\alpha P_4S_3I_2$ can be prepared from the appropriate elemental melt, it seemed reasonable to try to prepare $\alpha P_4Se_3I_2$ from the appropriate melt. Figure IV-1, which illustrates the observed and calculated spectra for $\alpha P_4Se_3I_2$ prepared by this method, shows a recognizable AA'BB' pattern. The chemical shift and coupling constants calculated for $\alpha P_4S_3I_2$ and $\alpha P_4Se_3I_2$ using NUMARIT[116] are listed in Table IV-1. The magnitude of the $^1J_{PP}$ coupling is larger than

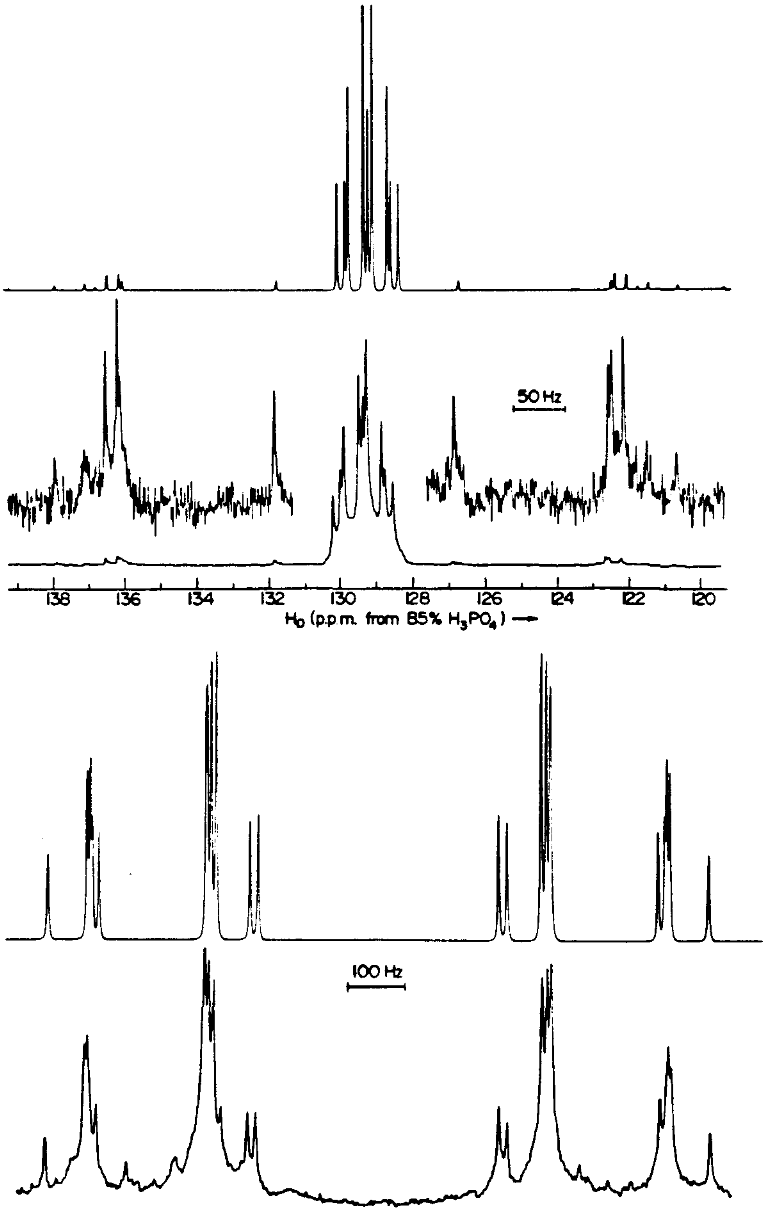
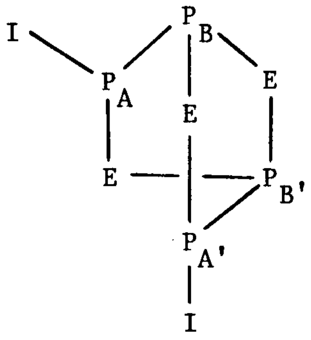


FIGURE IV-1. Calculated and Observed ^{31}P NMR Spectra of $\alpha P_4S_3I_2$ (top) and $\alpha P_4Se_3I_2$ (bottom).

TABLE IV-1 Chemical Shifts (ppm) and Coupling Constants (Hz) of $\alpha P_4S_3I_2$ and $\alpha P_4Se_3I_2$

	δ	$\nu_o\delta$(Hz)	J_{AA}	J_{AB}	$J_{AB'}$	$J_{BB'}$
$P_4S_3I_2$[a]	127.1	134.3	± 8.8	∓ 243.8	± 21.7	± 75.1
$P_4Se_3I_2$	115.7	758.5	± 5.7	∓ 239.7	± 21.5	± 86.7



E=S ,Se

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[a] First calculated in reference 155. Values listed here were independently calculated for this work. Agreement is 0.5 Hz or better.

those seen in the birdcage molecules or βP_4S_4 and more like J_{34} of αP_4S_5 (refer to Table III-22). This may again be due to the effect of an exocyclic moderately electronegative atom on a P-P single bond. It may also be related to the opening up of the structure. It is quite probable that the absolute sign of the direct coupling constant is negative,[125] and the others are positive. The phosphorus atoms attached to the iodine atoms are probably those whose signals are to low field.

The identity of $\alpha P_4Se_3I_2$ is further supported by the fact that the Raman spectrum of $\alpha P_4Se_3I_2$ shows that the stretching and bending modes involving mainly the P-I bond have similar frequencies to those of $\alpha P_4S_3I_2$ (Table IV-2, Figure IV-2).

IV-4 The As_4S_4/$SbCl_5$ and 1:1 As:Se/$SbCl_5$ Systems and Related Reactions

When As_4S_4 or powder from a 1:1 As:Se melt were mixed with excess $SbCl_5$ at low temperature or at room temperature no reaction took place. However, on addition of SO_2 an immediate reaction occurred giving a transitory red solution and then a clear solution from which an easily sublimable white material could be isolated. The red colouration was probably due to ECl_2 or E_2Cl_2 (E = S, Se).

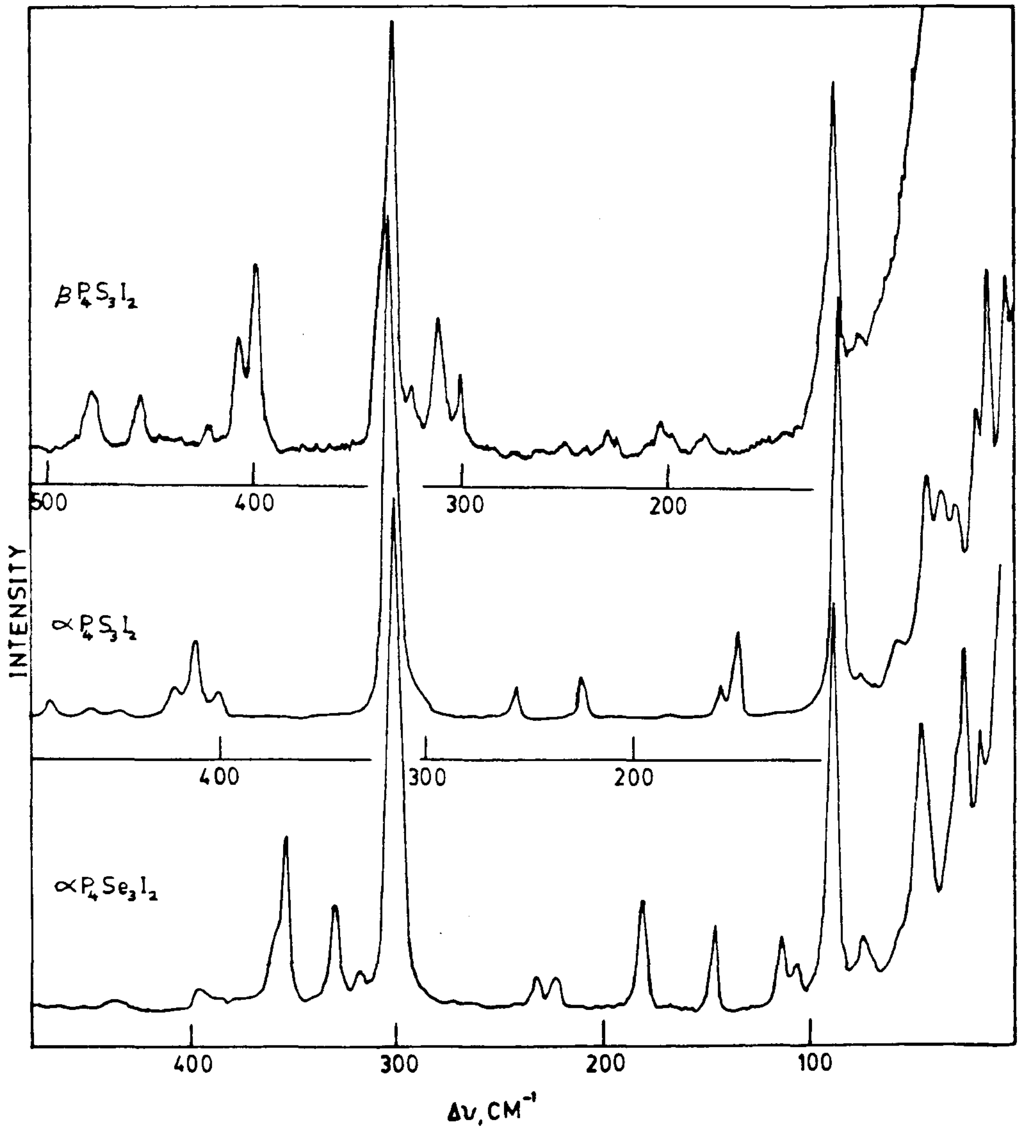


FIGURE IV-2. Raman Spectra of $\beta P_4S_3I_2$, $\alpha P_4S_3I_2$, $\alpha P_4Se_3I_2$

TABLE IV-2 Raman Spectra of $\alpha P_4Se_3I_2$, $\alpha P_4S_3I_2$, $\beta P_4S_3I_2$

$\alpha P_4Se_3I_2$	$\alpha P_4S_3I_2$[a]	$\beta P_4S_3I_2$[a]
9(12)	8(17)	
26.(37)	18(40)	
29 sh[b]	33(24)	
	43(36)	
46(39)		
	50(24)	
55 sh	57(30)	
73(9)	71(7)	
	89(7)	109(4)
89(75)	100(76)	120(73)
107(8)		
114(14)		124 sh
147(16)	150(16)	
181(21)	157(6)	183(6)
		198(6)
		204(8)
223(6)	225(7)	226(4)
233(6)	257(6)	230(6)
	306 sh	300(18)
		312(31)
		325(15)
303(100)	319(100)	335(100)
		339 sh
318(8)	402(5)	400(32)
330(21)	413(15)	408(19)
354(34)	423(6)	425(4)
359 sh	449(2)	
395(4)	464(2)	456(9)
438(2)	484(3)	480(10)

[a] Spectra first reported in ref 50. Values from present work.

[b] sh = shoulder. Recorded in cm^{-1}.

Identification of $AsCl_3$ and excess $SbCl_5$ in the reaction solutions of both the sulfur and selenium systems was made by Raman spectroscopy. Raman spectra of the soluble white products from both reactions showed the presence of $SbCl_3$ and an $SbCl_6^-$ salt. The remaining bands in the Raman spectra were due to either SCl_3^+ or $SeCl_3^+$ which have been previously identified as products of the reactions of SCl_4 and $SeCl_4$ with $SbCl_5$.[156]

Reaction of As_4S_4 with two moles of bromine and excess $SbCl_5$ in liquid SO_2 gave a red solution which quickly went to a light yellow coloured solution with no insoluble products. Slow removal of the solvent left light yellow crystals. A Raman spectrum of the bulk sample showed peaks due to $SbCl_6^-$ and others that could be attributed to SBr_3^+. There were also small peaks due to SCl_3^+ but none attributable to mixed ions such as $SBrCl_2^+$.

IV-5 Crystal Structure of $SCl_3(SbCl_6)$ and Cell Data for $SeCl_3(SbCl_6)$ and $SBr_{1.2}Cl_{1.8}(SbCl_6)$

Although $SCl_3(SbCl_6)$ and $SeCl_3(SbCl_6)$ are not new compounds, X-ray crystallographic data was collected because of recent interest[157] in secondary bonding in MX_3^+ salts. Block-like, light yellow single crystals of $SCl_3(SbCl_6)$ were mounted as described in Chapter II.

Preliminary precession photographs were then made to check crystal quality. Further work was done using the diffractometer described previously. The unit cell dimensions (Table IV-3) were obtained from a least-squares refinement of 2θ, ω and α for 15 high angle ($29° < 2\theta < 32°$) reflections. Data were collected using θ-2θ scans over a scan range ($K\alpha_1$ -0.85°) to ($K\alpha_2$ + 0.85°) with variable scan rates of 2-29.3°/min depending on the intensity of a preliminary 2 second count. Stationary background counts were recorded at each end of the scan, each for one quarter of the scan time. The intensities of the three standard reflections that were monitored after every 67 reflections showed no significant changes over the period of the data collection. A total of 2313 reflections (including standards) in the quadrants h, k, ±ℓ with $2\theta < 55°$ and h,-k, ±ℓ with $2\theta < 35°$ were measured. Lorentz and polarization corrections were applied to all data.

Systematic absences revealed C centering but no glide planes. This and unit cell data indicated that C2, Cm or C2/m was the proper space group. The structure was successfully solved in C2/m. Two independent antimony atoms and two chlorine atoms were located from the Patterson map using SHELX.[118] In subsequent Fourier maps the other atoms were located. With all atoms anisotropic R converged

TABLE IV-3. Unit Cell Data for MX_3 $(SbCl_6)$ (M = S, Se; X = Cl, Br)

Compound	$SCl_3(SbCl_6)$	$SeCl_3(SbCl_6)$	$SBr_{1.2}Cl_{1.8}$-$(SbCl_6)$
System	monoclinic	trigonal	trigonal
Space Group	C2/m	R_3m	R_3m
a(Å)	12.385(2)	10.750(8)	10.691(2)
b(Å)	7.774(1)	10.750(8)	10.691(2)
c(Å)	13.959(3)	18.885(8)	19.114(4)
α(°)	90	90	90
β(°)	108.06(1)	90	90
γ(°)	90	120	120
U($Å^3$)	1277.8(4)	1890(2)	1892.1(7)
D_c(gcm^{-3})	2.46	2.74	2.77
Z	4	6	6
Number of Reflections used in cell determination	15	15	15

to 0.0331 for $F/\sigma F > 6$. No absorption correction was made. The linear absorption coefficient was 38.82 cm^{-1}. After removing systematically absent and zero structure amplitude reflections, an average data set of 1493 reflections was obtained. Of these 1400 were considered observed for $F/\sigma F > 2$. Using the X-ray system with the weighting scheme $w = 1.0/(1.7\ \sigma F_o^2 + 7.0 \times 10^{-4} \times F_o^2)$ two further cycles of least-squares converged to final agreement indices $R_1 = 0.038$ and $R_2 = 0.044$ (62 parameters refined). In the final cycle of least-squares no parameters shifted by more than 9% of its standard error. A final difference Fourier map showed some residual electron density ($<3.2\ e/\mathring{A}^3$) at the antimony positions. Neutral atom scattering curves were used throughout. The minimum trough in the map was $-0.88\ e/\mathring{A}^3$.

Final atomic coordinates are given in Table IV-4 while the unit cell diagram of $SCl_3(SbCl_6)$ is shown in Figure IV-3. The basic shape of both constituent ions is as expected on the basis of VSEPR theory.[158] Bond lengths and bond angles are given in Table IV-5. Final structure factors are listed in Appendix II.

A comparison of the data in Table IV-5 for $SCl_3(ICl_4)$[159] and $SCl_3(SbCl_6)$ show that there is a significant decrease in the S-Cl bond length on going from the ICl_4^-

TABLE IV-4. Final Atomic Positional Parameters (x 10^4) of $SCl_3(SbCl_6)$ with Standard Deviations (x 10^4) in Parentheses.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sb(1)	0(0)	0(0)	0(0)	395(4)	259(4)	387(4)	0	63(3)	0
Sb(2)	0(0)	5000(0)	5000(0)	309(4)	355(4)	365(4)	0	108(3)	0
S(1)	8448(2)	0(0)	2801(2)	416(11)	422(11)	383(11)	0	89(9)	0
Cl(1)	7910(2)	0(0)	3977(2)	652(15)	853(20)	680(16)	0	400(14)	0
Cl(2)	7680(2)	1949(3)	2001(1)	982(15)	575(12)	651(11)	75(9)	-96(10)	239(11)
Cl(3)	0(0)	2979(3)	0(0)	862(20)	262(12)	1514(32)	0	-245(20)	0
Cl(4)	389(2)	0(0)	1767(2)	561(15)	1368(29)	421(13)	0	121(11)	0
Cl(5)	1972(2)	0(0)	274(2)	421(12)	770(17)	572(14)	0	121(10)	0
Cl(6)	330(1)	2851(2)	3928(1)	497(8)	555(9)	622(9)	-208(8)	228(7)	-38(8)
Cl(7)	3052(2)	0(0)	4101(2)	335(10)	601(14)	509(12)	0	76(9)	0

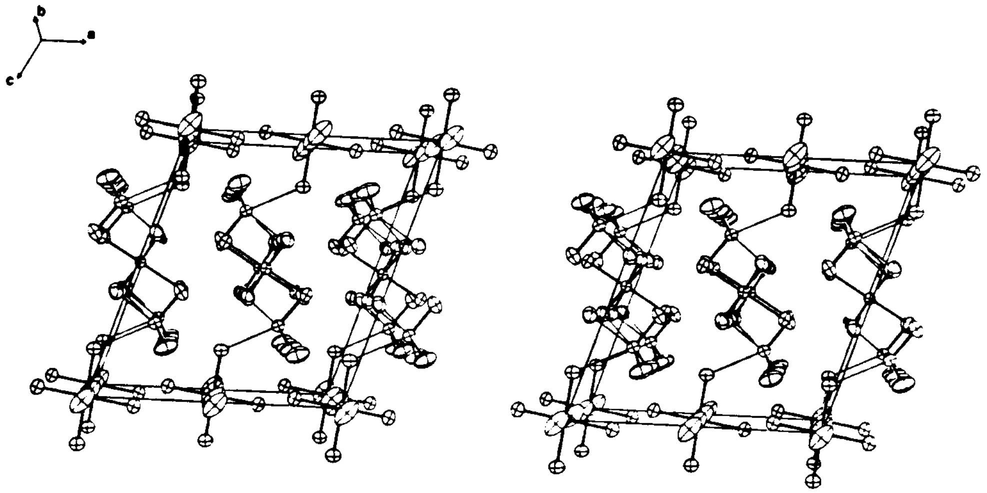


FIGURE IV-3. Stereoscopic View of the Unit Cell of $SCl_3(SbCl_6)$.

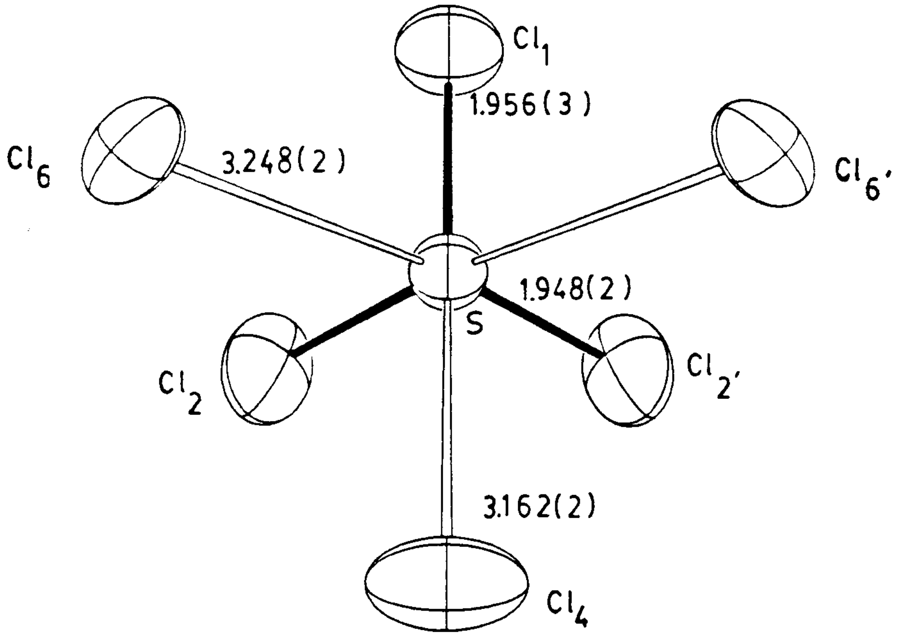


FIGURE IV-4. Intermolecular Contacts to SCl_3^+.

TABLE IV-5. Bond Lengths (Å) and Bond Angles (°) for $SCl_3(SbCl_6)$ and $SCl_3(ICl_4)$ (I)[a]

Bond Lengths (Å)	$SbCl_6^-$ salt	ICl_4^- salt	Bond Angles (°)	$SbCl_6^-$ salt	ICl_4^- salt
S(1) - Cl(1)	1.956(3)	2.002(3)	Cl(1)-S(1) -Cl(2)	104.4(1)	101.9(1)
S(1) - Cl(2)	1.948(2)	1.981(2)ave.	Cl(2)-S(1) -Cl(2)	102.2(1)	100.7(1)
Sb(1)- Cl(3)	2.313(2)		Cl(3)-Sb(1)-Cl(4)	90.0(0)	
Sb(1)- Cl(4)	2.363(2)		Cl(3)-Sb(1)-Cl(5)	90.0(0)	
Sb(1)- Cl(5)	2.355(2)		Cl(4)-Sb(1)-Cl(5)	87.99(8)	
Sb(2)- Cl(6)	2.363(2)				
Sb(2)- Cl(7)	2.352(2)				
S(1) - Cl(4)	3.162(3)	3.097(3)	Cl(4)-S(1) -Cl(1)	152.62(9)	154.9(1)
S(1) - Cl(6)	3.249(2)	3.129(3)	Cl(6)-S(1) -Cl(2)	163.4(1)	156.4(1)
S(1) - Cl(6)'	3.249(2)	3.119(3)	Cl(6)-S(1) -Cl(2)	163.4(1)	167.2(1)

[a] Reference 159 .

salt (1.986(3) Å ave) to the $SbCl_6^-$ salt (1.951(3) Å ave) with a corresponding lengthening of the secondary SCl contacts; from 3.115(3) Å ave to 3.220(4) Å ave for the respective salts. The S-Cl and P-Cl distances in S_2Cl_2 and PCl_3 are 2.07 Å and 2.04 Å, respectively.[160,161]

The structure determination shows that $SCl_3(SbCl_6)$ is definitely ionic and in relation to SCl_3^+ the anion $SbCl_6^-$ is a weaker Lewis base than ICl_4^-. This is consistent with the formation of $ICl_2(SbCl_6)$[162] from ICl_3 and $SbCl_5$ which shows that $SbCl_5$ is a weaker base than ICl_3 and thus one would probably expect $SbCl_6^-$ to be a weaker base than ICl_4^-, as is shown here.

Donation of electron density into antibonding orbitals on the sulfur atoms would lengthen the intramolecular S-Cl bonds in $SCl_3(SbCl_6)$ compared to those in $SCl_3(ICl_4)$ if an existing antibonding interaction decreased. One might expect chlorine atoms of $SbCl_6^-$ and the S-Cl bonds to be colinear for proper orbital overlap. Figure IV-4 shows that the sulfur atoms are surrounded by a distorted octahedron of chlorines. The observed Cl---S——Cl angles are between 150 and 165°. A decrease in the interionic bonding mentioned above should increase the intramolecular Cl—S—Cl angles.

An increase from 100-102° to 102-105° is observed on comparing these intramolecular angles in $SCl_3(ICl_4)$ and $SCl_3(SbCl_6)$, respectively.

Colourless single crystals of $SeCl_3(SbCl_6)$ were mounted and the data collected and analysed by Dr. F. Sawyer. The unit cell parameters are given in Table IV-3 An attempt to solve the structure showed the compound to be ionic and consist of $SeCl_3^+$ and $SbCl_6^-$ ions. However, the cations were found to be disordered and the structural analysis was therefore not completed. This was also found to be the case for the crystals containing SBr_3^+.

IV-6 Raman Spectra of the $MX_3(SbCl_6)$ Salts (M = S, Se, Te) and $SBr_{1.2}Cl_{1.8}(SbCl_6)$

The Raman spectral data for $SCl_3(SbCl_6)$ are given in Figure IV-5, Tables IV-6,8. The Raman spectrum of SCl_3-$(SbCl)_6$ shows from the number of bands that the ions must be distorted from the free ion symmetries of C_{3v} and O_h for the cation and anion, respectively. The site symmetries of SCl_3^+ and $SbCl_6^-$ in the crystal are C_s and C_i, respectively. Figure IV-6 gives the appropriate correlation diagrams. A complete factor group analysis is not necessary here. Using the correlation diagram and polarization and

TABLE IV-6 . Raman Spectra of $ECl_3(SbCl_6)$ (E = S, Se, Te) and $SBr_{1.2}Cl_{1.8}(SbCl_6)$

$SCl_3(SbCl_6)$[a]	assignments	$SeCl_3(SbCl_6)$[a]	assignments	$TeCl_3(SbCl_6)$[b]	assignments	$SBr_{1.2}Cl_{1.8}$- $(SbCl_6)$[c]	assignments
535(63)	$SCl_3^+,\nu_3(E)$	396(sh)	$SeCl_3^+,\nu_3(E)$	381(47)	$TeCl_3^+,\nu_3(E)$	411(21)	$SBr_3^+,\nu_3(E)$
521(48)						389(31)	
500(99)	$SCl_3^+,\nu_1(A)$	407(100)	$SeCl_3^+,\nu_1(A)$	395(100)	$TeCl_3^+,\nu_1(A)$	371(33)	$SBr_3^+,\nu_1(A)$
336(79)	$SbCl_6^-,\nu_1(A_{1g})$	353(20)		355(28)			
328(100)		318(43)	$SbCl_6^-,\nu_1(A_{1g})$	309(84)	$SbCl_6^-,\nu_1(A_{1g})$	333(100)	$SbCl_6^-,\nu_1(A_{1g})$
294(21)	$SbCl_6^-,\nu_2(E_g)$	277(16)	$SbCl_6^-,\nu_2(E_g)$	254(25)	$SbCl_6^-,\nu_2(E_g)$	286(28)	$SbCl_6^-,\nu_2(E_g)$
286(33)							
275(27)	$SCl_3^+,\nu_2(A)$	198(21)	$SeCl_3^+,\nu_2(A)$			242(10)	?
266(5)	?			186(18)	$TeCl_3^+,\nu_2(A)$ and $TeCl_3^+,\nu_4(E)$ and $SbCl_6^-,\nu_5(T_{2g})$	209(30)	?
216(11)	$SCl_3^+,\nu_4(E)$	184(36)	$SeCl_3^+,\nu_4(E)$ and $SbCl_6^-,\nu_5(T_{2g})$	176(28)		182(54)	$SBr_3^+,\nu_2(E)$ and $SbCl_6^-,\nu_5(T_{2g})$
208(23)		169(17)		169(39)		176(75)	
175(72)	$SbCl_6^-,\nu_5(T_{2g})$	162(26)		163(37)		163(23)	
166(9)		130(16)		146(25)		133(23)	$SBr_3^+,\nu_4(E)$
						123(41)	

a) This work. b) Unpublished work of M. Collins. c) SCl_3^+ peaks not listed.

TABLE IV-7 . Vibrational Frequencies of Isoelectronic Group VB Halides[a]

PCl_3	$AsCl_3$	$SbCl_3$	PBr_3	Assignments for MX_3
507	412	377	392	$\nu_1(A_1)$
260	194	164	161	$\nu_2(A_1)$
494	387	356	392	$\nu_3(E)$
187	155	128	116	$\nu_4(E)$

a) Reference 152.

TABLE IV-8. Raman Bands of the Cations EX_3^+ (E = S, Se; X = Cl, Br) and $TeCl_3^+$

SCl_3^+

	AsF_6^- [a]	SO_3Cl^- [b]	$AlCl_4^-$ [b,c]		$NbCl_6^-$ [d]	$TaCl_6^-$ [d]	$SbCl_6^-$ [e,b,f]			ICl_4^- [g]		$SnCl_6^{-2}$ [b]
$\nu_1(A_1)$	519[h]	509	494	498	496	497	500	501	500	485[i]	482[j]	484
$\nu_2(A_1)$	284	284	271	276	275	265	~280[k]	280	274	279	282	269
$\nu_3(E)$	543	526	530	533	519	532	532	535	535	512	510	
		519	516	521	516	518	521	524	522	498	496	
$\nu_4(E)$	214	228	206	215	215	215		210	216	212	205	207
		221		208	210				208			

$SeCl_3^+$

	AsF_6^- [a]	SO_3Cl^- [b]	$AlCl_4^-$ [b]	$GaCl_4^-$ [b]	$NbCl_6^-$ [d]	$TaCl_6^-$ [d]	$SbCl_6^-$ [e,b,f]		
$\nu_1(A_1)$	437	416	416	418	405	405	412	406	407
$\nu_2(A_1)$	200	207	-	204	195	198		197	198
$\nu_3(E)$	390	392	395	394	-	391	395[k]		396
$\nu_4(E)$	168	181	186	169	160	159		184	184-130[ℓ]

continued...

TABLE IV-8 (continued)

$TeCl_3^+$	AsF_6^- [e,a]		SO_3Cl^- [b]	$AlCl_4^-$ [b]	$NbCl_6^-$ [d]	$TaCl_6^-$ [d]	$SbCl_6^-$ [e,b,m]		
$\nu_1(A_1)$		412	391	392	408	406	395	394	395
$\nu_2(A_1)$	187	170			177-144[ℓ]	189-145[ℓ]		184	186-163[ℓ]
$\nu_3(E)$	385	385	371	367	390-356[ℓ]	390-358[ℓ]	384	381	381
$\nu_4(E)$	166	150			177-144[ℓ]	189-145[ℓ]	166	169	163-145[ℓ]

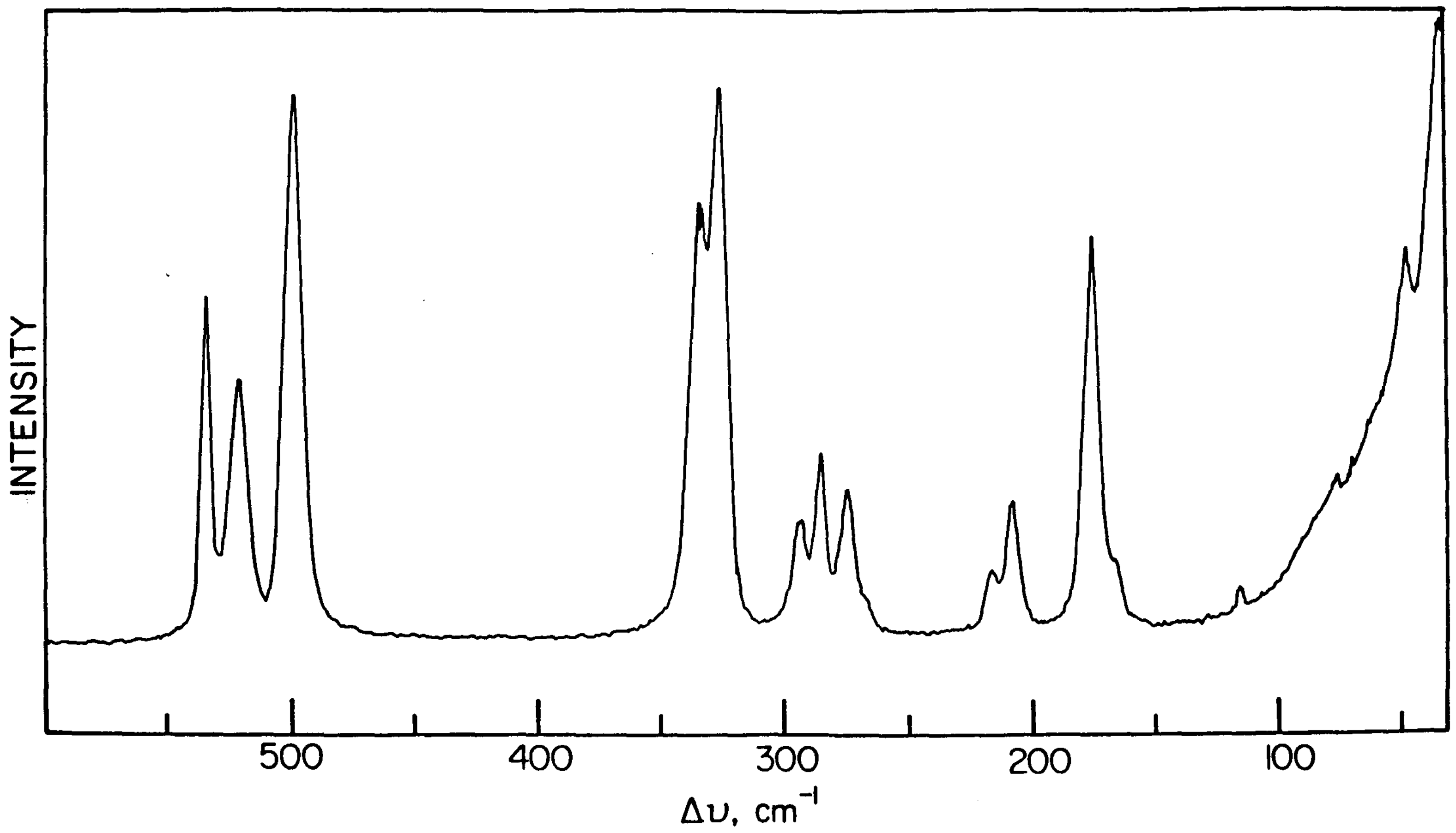
SBr_3^+	AsF_6^- [n]	SbF_6^- [n]	$SbCl_6^-$ [f]
$\nu_1(A_1)$	375	379	371
$\nu_2(A_1)$	175	175	182-163[ℓ]
$\nu_3(E)$	429 414	421 410.5	411 388
$\nu_4(E)$	128	127.5	133 123

[a] Reference 163. [b] Reference 156. [c] Reference 164. [d] Reference 165 For the Se and Te compounds these are not definite assignments, see text.

[e] Reference 166. [f] This work. [g] Reference 167.

[h] All in cm^{-1}. [i] Form I. [j] Form II. [k] IR data. [ℓ] Not readily assignable.

[m] Unpublished work of M. Collins. [n] Reference 168.



<u>FIGURE IV-5</u>. Raman Spectrum of $SCl_3(SbCl_6)$.

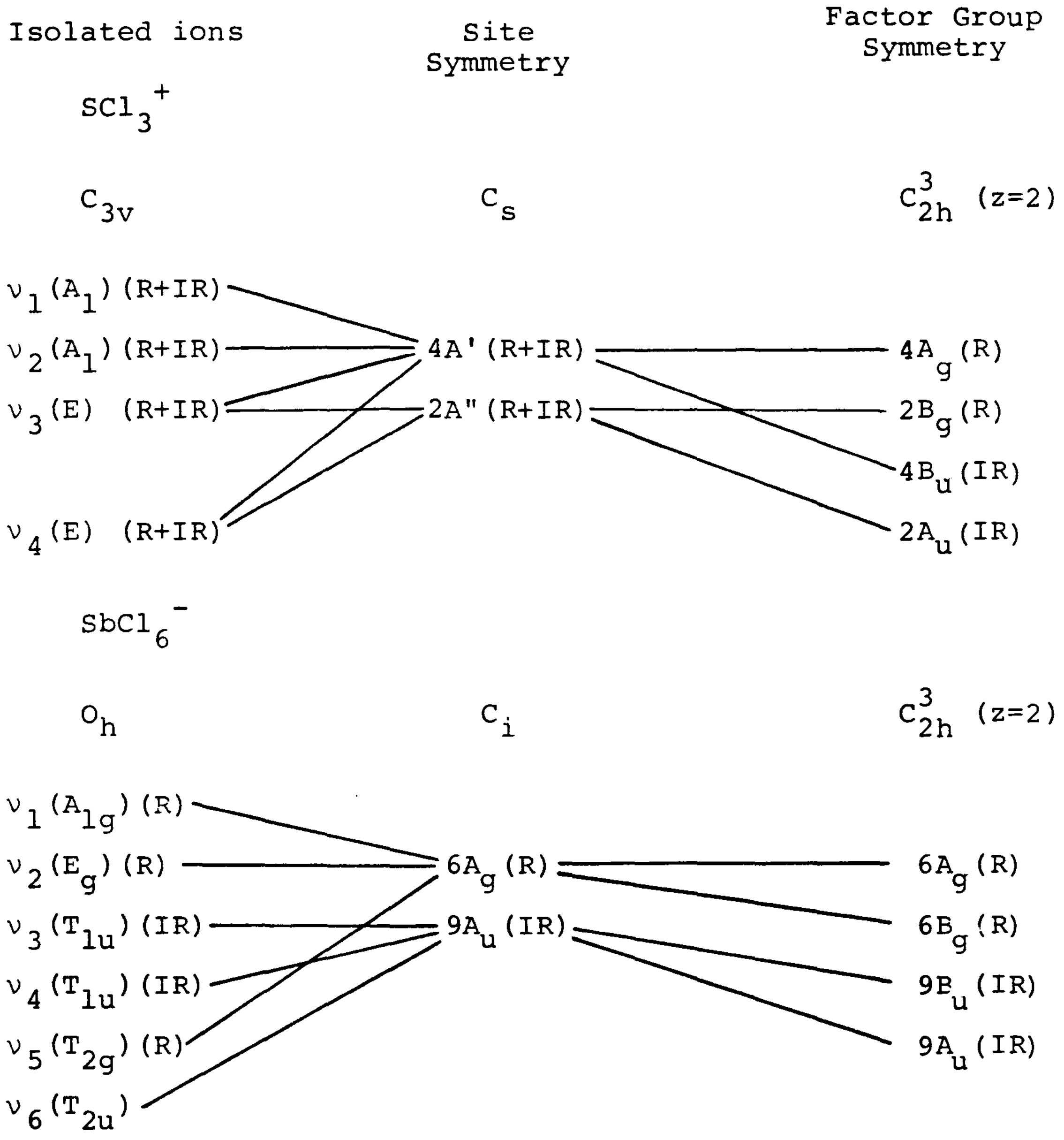


FIGURE IV-6. Correlation Diagram for $SCl_3(SbCl_6)$.

assignment data for $SCl_3(AlCl_4)$[164] the bands at 500 and 275 cm^{-1} were respectively assigned to the nondegenerate symmetric stretch and bend of SCl_3^+. The third and fourth Raman active modes of a C_{3v} MX_3^+ ion are degenerate E vibrations split here into A' and A" components, both Raman active. The pair of peaks at 535, 521 cm^{-1} are assigned to the asymmetric stretch while the peaks at 216 and 208 cm^{-1} are assigned to the asymmetric bend.

Comparing the data here to that in Table IV-8 the intense band at 328 cm^{-1} is assigned to the totally symmetric breathing mode of the $SbCl_6^-$ ion. The ν_2 vibration, doubly degenerate in O_h symmetry, is here split into two A_g components appearing at 294 and 286 cm^{-1}. A third vibration normally seen in the Raman spectrum of octahedral species is the triply degenerate in-plane bend. Two of the three A_g components are seen at 175 and 169 cm^{-1}. The very weak shoulder at 266 cm^{-1} is unassigned.

The last unassigned peak in the Raman spectrum of $SCl_3(SbCl_6)$ is the strong band at 336 cm^{-1}, in the region of an Sb-Cl stretch. This peak cannot be assigned to $\nu_3(T_{1u})$ which only appears in infrared spectra.[169] Splitting of the degeneracy of ν_3 by C_i site symmetry or even using the factor group symmetry of the crystal results in components which are only infrared allowed.

A peak in the same region of the Raman spectrum of[165] $SCl_3(NbCl_6)$ is also evident. For $SCl_3(SbCl_6)$ and $SCl_3(NbCl_6)$ the difference between the peak in question and ν_1 is 8 and 6 cm^{-1}, respectively. It seems reasonable to attribute them to factor group splitting.

The assignments for $SeCl_3(SbCl_6)$, $TeCl_3(SbCl_3)$ and $SBr_3(SbCl_6)$ were made with reference to the above, the information listed in Table IV-8, and the assignments for the isoelectronic group V halides (Table IV-7). The Raman spectra of $SeCl_3(SbCl_6)$ (Figure IV-7) and $TeCl_3(SbCl_6)$ each show a peak just above 350 cm^{-1} which can tentatively be assigned to ν_1 of $SbCl_5$. Generally, where assignments are known, the corresponding vibrations appear at higher wavenumber for the salts than for the neutral group VB halides with the exception of ν_1 in $SCl_3(SbCl_6)$, $SBr_3(SbCl_6)$ and $SeCl_3(SbCl_6)$. In the first two ν_1 is weaker than ν_3. Other notable exceptions are NCl_3, PI_3, ClO_3^-, XeO_3 and group VB hydrides.[152] An examination of the data in Table IV-6 shows that ν_1 and ν_2 of the MX_3^+ ions usually decrease with an increase in the Lewis basicity of the anion. A decrease in ν_1 and ν_2 of $SbCl_6^-$ is shown by the series SCl_3^+, $SeCl_3^+$ and $TeCl_3^+$.

It has been suggested that there are no "free" $SeCl_3^+$ ions in $SeCl_3(NbCl_6)$ and $SeCl_3(TaCl_6)$ because the

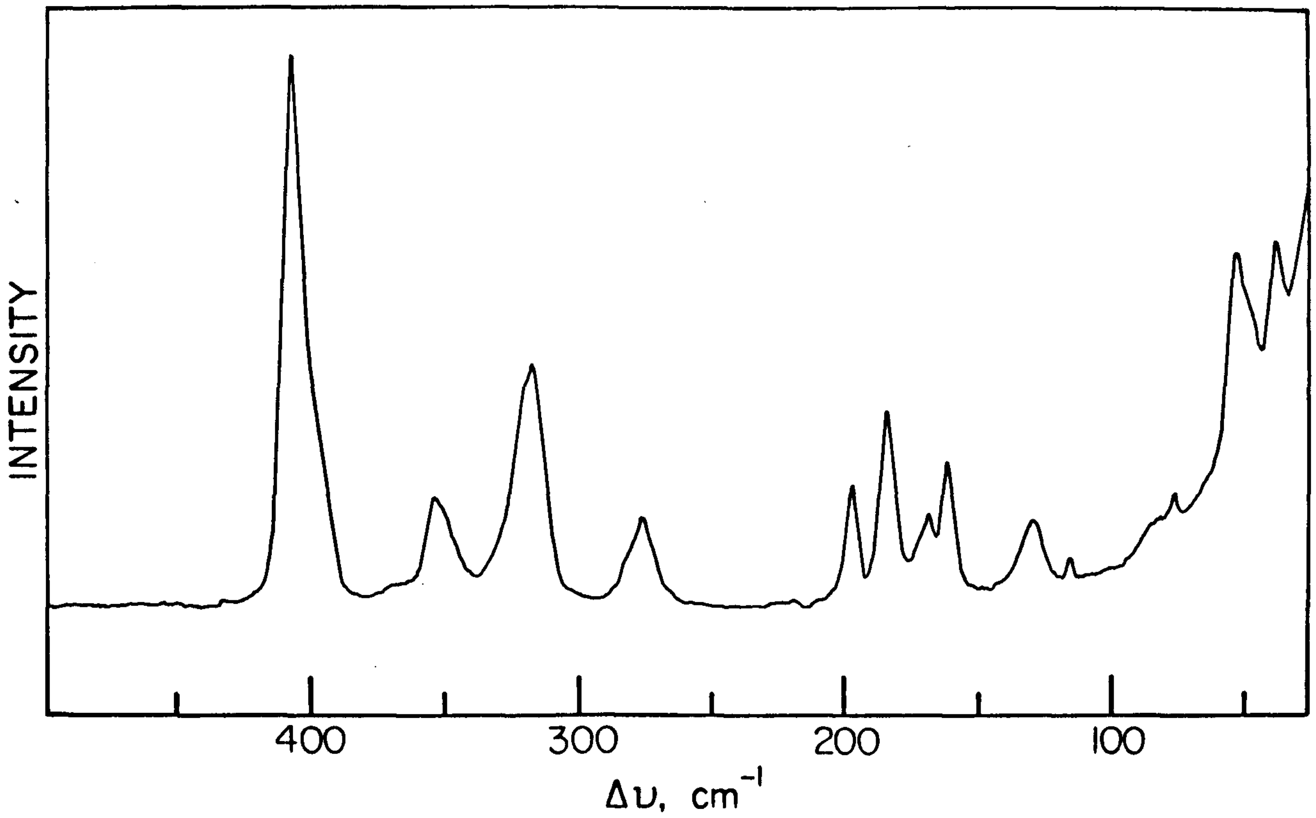


FIGURE IV-7. Raman Spectrum of $SeCl_3(SbCl_6)$.

Se-Cl stretch occurs at 405 cm^{-1} which is considered to be too low.[165] A $Tl_2Cl_9^{-2}$ type structure or an edge-bridging model ($Cl_3SbCl_2MCl_4$, M = Nb, Ta) were favoured. The $Tl_2Cl_9^{-2}$ ion has three parallel triangles of chlorine atoms, each pair of triangles being separated by a thallium atom.[170] However, the X-ray crystallographic data for $SeCl_3(SbCl_6)$ definitely shows the presence of $SeCl_3^+$ ions, although there appear to be significant cation-anion interactions. In this compound ν_1 is found in the Raman spectrum at 407 cm^{-1}. In addition, the similar sizes of the elements niobium, tantalum and antimony in the +5 oxidation state (effective ionic radii: 0.65 Å, 0.65 Å, 0.61 Å, respectively),[106] and the existence of the dimer $SbNbCl_{10}$[171] rather than a salt like $NbCl_4(SbCl_6)$ all suggest a similar basicity for the three hexachloro anions. One would therefore expect $SeCl_3(NbCl_6)$ and $SeCl_3(TaCl_6)$ to contain the $SeCl_3^+$ ion. There may however be slightly stronger interionic interactions in the latter compounds.

IV-7 Experimental Section

IV-7(i) Preparation of $SCl_3(SbCl_6)$ from As_4S_4 and $SbCl_5$.

Powdered, dried As_4S_4 (0.2719 gm, 0.6353 mmole) was put into a dry double arm ampoule vessel in the dry box. Antimony pentachloride (~1.50 cc, ⩾11.4 mmoles) was syringed into the other arm of the vessel. The arm containing the As_4S_4 was cooled in liquid nitrogen and the $SbCl_5$ poured through the first. No reaction on contact of the $SbCl_5$ with the As_4S_4 at low temperature or room temperature was observed. On addition of SO_2 the mixture heated up and a deep red color formed which quickly disappeared on stirring to give a solution with a light yellow color. The next day the SO_2 was pumped out and the $SbCl_3$ and $SCl_3(SbCl_6)$ separated by vacuum sublimation.

IV-7(ii) Preparation of $SeCl_3(SbCl_6)$ from a fused 1:1 As:Se melt and $SbCl_5$.

Dried powder from a 1:1 As:Se melt (0.3637 gm, 0.5909 mmoles, assuming As_4Se_4) was put into a pre-dried double arm ampoule vessel in the dry box. Antimony pentachloride (~1.40 cc, ⩾10.6 mmoles) was syringed into the other arm of the vessel. Pouring the $SbCl_5$ through the frit onto the As/Se powder cooled to -196°C produced no immediate reaction. After some warming the mixture suddenly heated up to about 60°C and went blood-red in color. This quickly disappeared and was replaced by a light green-yellow color. The next day anhydrous SO_2 was added and all the $SbCl_3$ was washed into the other arm of the ampoule leaving behind $SeCl_3(SbCl_6)$.

IV-7(iii) Preparation of $SeCl_3(SbCl_6)$ from $SeCl_4$ and $SbCl_5$.

Crystals of $SeCl_4$ (0.1093 gm, 0.4951 mmoles) were added in the dry box to a double arm ampoule vessel equipped with teflon valves. The vessel had been rigorously dried on the vacuum line prior to use. Antimony pentachloride (~0.06 cc, ~0.5 mmoles) was syringed into the vessel onto the $SeCl_4$. No apparent reaction took place over the next hour. Sulfur dioxide was then distilled into the vessel and stirred overnight by means of a magnetic stir-bar in the vessel. The next day the clear solution was poured through the frit and then the sulfur dioxide was slowly removed by cooling the other arm of the vessel leaving crystals of $SeCl_3(SbCl_6)$.

IV-7(iv) Preparation of $(SBr_3)_{0.6}(SCl_3)_{0.4}SbCl_6$ - Attempted Preparation of $SBr_3(SbCl_6)$.

Dry sulfur (0.2056 gm, 6.412 mmoles) was put into one arm of a pre-dried double arm ampoule vessel and $SbCl_5$ (~0.80 cc, ~6.4 mmoles) was syringed into the other arm of the vessel. The vessel, equipped with teflon valves, was then removed from the dry box and Br_2 (62.4 mm Hg, 12.83 mmoles) was distilled onto the sulfur at -196°C. The vessel was then allowed to warm and the bromine reacted with the sulfur and then the $SbCl_5$ was poured through the frit onto the mixture resulting in a reddish solution. The reaction was left stirring overnight. Any excess $SbCl_5$, Br_2 and the $SbCl_3$ produced were removed by washing with small portions of SO_2. Yellow, translucent crystals of what was later shown to be $(SBr_3)_{0.4}(SCl_3)_{0.6}SbCl_6$ were left behind.

CHAPTER V

REACTIONS OF As_4S_4, ARSENIC-SELENIUM MELTS AND OTHER GROUP VB CHALCONIDES WITH LEWIS ACIDS

V-1 Introduction

The reactions of compounds such as As_4S_4 with oxidizing agents and Lewis acids have not previously been studied although the reactions of S_4N_4 with oxidizing agents have been observed to give a number of new compounds. In fact the only ionic derivative of As_4S_4 that has been definitely characterised is the $As_4S_6^{2-}$ anion which has been studied as a piperidinium salt.[172]

V-2 Investigation of the Solubility and Adduct Formation of As_4S_4

In an attempt to obtain solution spectra for As_4S_4 to aid in the vibrational assignments for As_4S_4 and any subsequent complexes produced, many solvents were tried. It was found that As_4S_4 is insoluble at room temperature in H_2O, dilute HCl, dilute HNO_3, 98% H_2SO_4, methanol, acetone, dioxane, formaldehyde, petroleum ether, acetonitrile, DMSO, nitrobenzene, pyridine, N,N-dimethylformamide, CCl_4, CH_2Cl_2, PCl_3, $OPCl_3$, $SOCl_2$, SO_2, AsF_3, HSO_3F and anhydrous HF. It decomposes in aqua regia giving copious amounts of sulfur initially while in 30% oleum there is immediate reaction to produce what appears to be S_8^{+2}. The decompositions were not investigated further. Extremely small amounts of As_4S_4 can be recrystallized from hot carbon disulfide or benzene but the solution concentration are such that solution Raman spectra could not be obtained for polarization measurements.

The intermolecular forces in realgar, As_4S_4, are greater than those in S_4N_4 as indicated by[173] its higher melting point 307°C (vs. 178.2°C for S_4N_4). A comparison of intermolecular contacts show all three forms of As_4S_4 have arsenic-sulfur contacts that are relatively shorter than the sum of the van der Waals radii than the corresponding contacts in S_4N_4. The three arsenic compounds also have intermolecular arsenic-arsenic contacts (e.g., in αAs_4S_4, As····As 3.51—3.62, Σ van de Waals radii = 4.00) while S_4N_4 has no significant contacts other than the sulfur-nitrogen contacts already mentioned.

As mentioned earlier the number of adducts of S_4N_4 is quite large and covers a wide range of acceptor strengths.[39] The As_4S_4 molecule has lone pairs on both arsenic and sulfur atoms and one might expect that it would be possible to form adducts with Lewis acids. To this end the reactions of As_4S_4 with TaF_5, NbF_5, BCl_3, PF_5, SO_3, WF_6 and PCl_5 were investigated. For S_4N_4 1:1 adducts have been prepared with the first five of these Lewis acids while PCl_5 oxidizes S_4N_4 to give a complex mixture that may include $P_3N_3Cl_3$ and SCl_2.[173]

Raman spectra of the solutions resulting from stirring methylene chloride suspensions of βAs_4S_4 with methylene chloride solutions of TaF_5, NbF_5, WF_6, or PCl_5 or mixtures of βAs_4S_4 with BCl_3 or SO_3 in SO_2 showed no new species. The Raman spectra of the solids could also be assigned to the reactants. The reaction of PF_5 with βAs_4S_4 over a period of days gave only αAs_4S_4 which suggests that a very weak donor-acceptor complex may have formed which was an intermediate in the rearrangement of the As_4S_4 molecules. It would appear that the strength of intermolecular forces in As_4S_4 mentioned above is such that adduct formation is not competitive.

V-3 The $As_4S_4/AsF_5(SbF_5)$ and Arsenic-Selenium Melt $AsF_5(SbF_5)$ Systems

Reactions of S_4N_4 with AsF_5 and SbF_5 have led to the production of the interesting salts $S_3N_2(AsF_6)$,[28] $S_6N_4(AsF_6)_2$, $S_4N_4(SbF_6)_2$ and $S_4N_4(Sb_3F_{14})(SbF_6)$.[8,31,174]

The adduct $S_4N_4 \cdot AsF_5$ has also been prepared in this laboratory and characterized by X-ray crystallography.[175] It would apppear that the formation of this adduct is the first step in the oxidation of S_4N_4 to produce the cations mentioned above.

In every case, independent of the stoichiometry used, the As_4S_4/AsF_5 and As_4S_4/SbF_5 reactions in SO_2 initially gave a transient bright yellow solution. The color may be due to the formation of an intermediate adduct or ion. However, this could not be identified as a Raman spectrum of the solid obtained after the rapid removal of the SO_2 showed that only $As_3S_4(AsF_6)$ (described below), As_4S_4 and sulfur were present. The UV spectrum of a 1:3 As_4S_4/AsF_5 mixture in SO_2 recorded immediately after warming to room temperature showed only the characteristic absorption curve of the $As_3S_4^+$ cation above the SO_2 absorption cut-off. Low temperature ^{19}F NMR spectra were recorded for 1:3 $As_4S_4:AsF_5$ reactions in SO_2 (-74°C), SO_2ClF (-78°C) and SO_2/SO_2ClF (-78°C) but only a signal due to AsF_3 was observed.

For $As_4S_4:AsF_5(SbF_5)$ ratios of up to 1:3, the bright yellow solutions fade to a very light yellow from which a light yellow powder precipitates. Raman spectroscopy indicated that the powder contained varying amounts of sulfur and an AsF_6^- (SbF_6^-) salt. Elemental analysis (pp. 209-210) and X-ray crystallography proved that salts of the ions $As_3S_4^+$ and $As_3Se_4^+$ were produced. Formation of these compounds is consistent with the stoichiometry

$$As_4S_4 + 3MF_5 \ (M = As,\ Sb) \xrightarrow{SO_2} As_3S_4(MF_6) + 2MF_3$$

However, the presence of some unreacted As_4S_4 and varying amounts of sulfur indicate that the overall reaction is not as simple as the above equation suggests. It seems that there is a competing reaction involving degradation of the As_4S_4 molecule to AsF_3 and sulfur. The Raman spectrum of the unreacted βAs_4S_4 from a 1:3 As_3S_4:AsF_5 reaction shows an additional band at 232 cm^{-1} and a few other weaker bands. The peak at 232 cm^{-1} has been seen before by some workers[176,177] in the Raman spectrum of αAs_4S_4 and could possibly be due to some As_4S_4(II) formed by rearrangement during the reaction.

Sulfur dioxide suspensions of the 1:1 As:Se powdered melt (probably consisting mainly, if not entirely, of As_4Se_4) were reacted with AsF_5 or SbF_5 in 1:3 mole ratios. Quickly warming the frozen solutions to room temperature produces an orange solution from which an orange powder readily precipitates. Infrared data[178,179] indicated that hexafluoroarsenate or hexafluoroantimonate salts were formed and Raman spectra showed the cations of both salts to be the same. X-ray crystallography and elemental analysis proved that the hexafluoroantimonate salt was $As_3Se_4(SbF_6)$.

The insoluble solid remaining after complete removal of the soluble SbF_6^- salt was yellow with flecks of black in it. The latter was probably starting material. The arsenic-selenium melt itself is black. The compounds SbF_3, $SbF_5 \cdot SO_2$ and $Sb_6F_{13}(SbF_6)_5$ are all white. A Raman spectrum of the yellow solid gave the peaks listed in Table V-5. No peaks were observed in the region of Sb-F stretches, however a Mössbauer spectrum kindly recorded by Dr. T. Birchall and Mr. R. Myers showed absorptions at -14.5 ± 0.2 and 2.2 ± 0.1 mms^{-1} which may be assigned, respectively, to SbF_3[180] and a compound containing antimony (V) bonded to fluorine. The latter is probably a compound containing $Sb_xF_{5x+1}^-$ (x = 1,2,3). The similarity of the Raman spectrum with those of the $As_3Se_4^+$ salts and its insolubility suggests that it is a salt of $As_3Se_4^+$ with a polymeric antimony-fluorine anion. Attempts to sublime the material led to decomposition. The insoluble material was not analyzed as it was intimately mixed with SbF_3 and a small amount of what appeared to be starting material.

V-4 Structures of the Birdcage Cations $As_3S_4^+$ and $As_3Se_4^+$ in $As_3S_4(AsF_6)$, $As_3S_4(SbF_6)$ and $As_3Se_4(SbF_6)$

V-4(i) Crystal Data

The X-ray crystallography was performed by Dr. J. F. Sawyer of this department. Crystals of (As_3S_4)-(SbF_6) were obtained as clear yellow platelets while those of the isomorphous $(As_3S_4)(AsF_6)$ were darker yellow in appearance and were irregular prisms and rhombs. The major crystal form found for $(As_3Se_4)(SbF_6)$ was orange diamond-shaped plates. These were mostly too small for the X-ray studies, but a few larger, slightly more irregular crystals were also present and the structure was eventually solved using one of these larger crystals. All crystals used in the structure determinations were sealed in Lindemann capillaries under a dry-air atmosphere. Crystals of $(As_3Se_4)(SbF_6)$ sealed in capillaries tended to darken in color from orange to dark red. This appears to be a surface effect as the diffraction patterns are unaffected by these color changes, and is presumably due to traces of moisture/oxygen in the atmosphere of the dry-box in which the crystals were sealed. Crystals that are left in the reaction vessel do not exhibit any color changes. Similar marked changes of color of salts of S-N cations have also been observed.[30,31]

$(As_3S_4^+)(SbF_6^-)$ is orthorhombic with $\underline{a}$ = 20.453 (4), $\underline{b}$ = 5.990 (1), $\underline{c}$ = 9.609(2) Å, $\underline{U}$ = 1177.3(4) $Å^3$, Z = 4, D_c = 3.32 g/cm^3, fw = 588.8, F(000) = 1072. MoK$\bar{\alpha}$ radiation (λ = 0.71069 Å, μ(MoK$\bar{\alpha}$) = 120.5 cm^{-1}. Systematic absences, $\underline{h}0\underline{\ell}$, $\underline{h}$ = 2n and $0\underline{k}\underline{\ell}$, $\underline{\ell}$ = 2n indicated space groups $\underline{Pcam}$ (a non-standard setting [ba$\bar{c}$] of No. 57 $\underline{Pbcm}$) or $\underline{Pca2_1}$ (No. 29). The distribution of the normalised structure factors and the satisfactory structure solution showed that the correct space group is $\underline{Pcam}$.

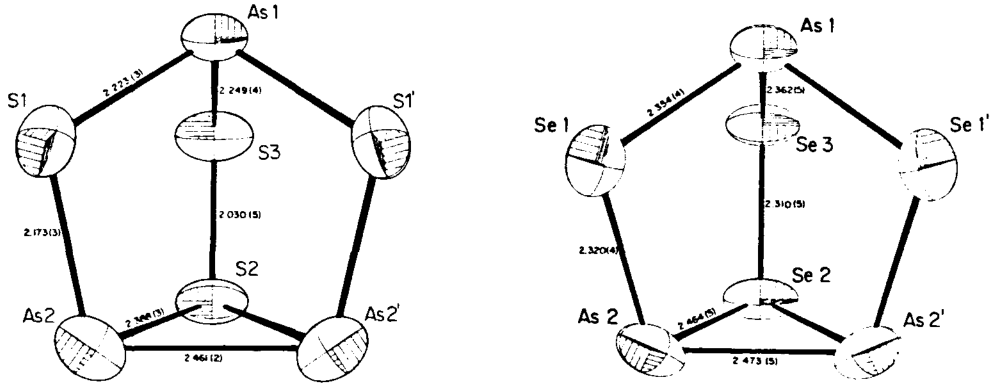
The isomorphous $(As_3S_4^+)(AsF_6^-)$ is orthorhombic with $\underline{a}$ = 19.962(4), $\underline{b}$ = 5.930(1), $\underline{c}$ = 9.441(3) Å, $\underline{U}$ = 1115.8(5) $Å^3$, Z = 4, D_c = 3.22 g/cm^3, fw = 541.9, F(000) = 1000. MoK$\bar{\alpha}$ radiation (λ = 0.71069 Å), μ(MoK$\bar{\alpha}$) = 132.6 cm^{-1}. Space group $\underline{Pcam}$.

$(As_3Se_4^+)(SbF_6^-)$ is monoclinic with $\underline{a}$ = 6.224(3), $\underline{b}$ = 9.564(5), $\underline{c}$ = 10.643(5) Å, β = 92.65(4)°, $\underline{U}$ = 632.9(5) $Å^3$, Z = 2, D_c = 4.07 g/cm^3, fw = 776.4, F(000) = 680. MoK$\bar{\alpha}$ radiation (λ = 0.71069 Å), μ(MoK$\bar{\alpha}$) = 226.8 cm^{-1}. The systematic absence, $0\underline{k}0$, $\underline{k}$ = 2n, indicated space groups $\underline{P}2_1/\underline{m}$ or $\underline{P}2_1$. The distribution of the normalised structure factors and the satisfactory structure solution showed that the space group is $\underline{P}2_1/\underline{m}$.

V-4(ii) Discussion of the Crystal Structures of $As_3S_4(AsF_6)$, $As_3S_4(SbF_6)$, and $As_3Se_4(SbF_6)$

V-4(iia) The Cations $As_3S_4^+$ and $As_3Se_4^+$

The structure determinations show that $As_3S_4(AsF_6)$ and $As_3S_4(SbF_6)$ consist of $As_3S_4^+$ cations and hexafluoroantimonate (arsenate) anions while the $As_3Se_4(SbF_6)$ contains the isostructural $As_3Se_4^+$ cation along with hexafluoroantiomonate anions. The $As_3S_4^+$ and $As_3Se_4^+$ cations both have crystallographic mirror symmetry and overall symmetry C_s. The bond distances and angles of the $As_3S_4^+$ ion in the AsF_6^- and SbF_6^- salts show only very small differences. The structure of this cation can be considered to be derived from a tetrahedron of three arsenic and one sulfur (formally S^+) atoms with the three edges to a common arsenic bridged by sulfur atoms. Similarly, the $As_3Se_4^+$ cation consists of a tetrahedron of three arsenic and one selenium (as Se^+) atoms with three edges to a common arsenic bridged by selenium atoms (Figure V-1). This structural type is found for a number of other cage compounds of the non-metals. Some examples of this are the two forms of As_4S_3,[83,84] and As_4Se_3,[85] those of P_4S_3[81] and P_4Se_3,[82] the ions Sb_7^{-3},[64] As_7^{-3},[63], P_7^{-3} [62] and in the



<u>FIGURE V-1</u>. The Cations $As_3S_4^+$ and $As_3Se_4^+$.

organocyclo triarsane, 4-methyl-1,2,6-triarsatricyclo-[2,2,1,$0^{2,6}$]heptane[88] and in the compounds discussed in Chapter III. However, this is the first time that the triangular base of this structural type has been found containing a group VIB atom.

The arsenic-arsenic bond length in this base is 2.461(2) Å for the $As_3S_4^+$ cation and 2.473(5) Å for the $As_3Se_4^+$ cation. This is comparable to the arsenic-arsenic bond lengths in the base of the As_7^{3-} [63] and α and β As_4S_3 structures[83,84] (Table V-1). Table V-2 gives final atomic positions and thermal parameters. Complete bond distance and bond angle listings for the salts are given in Table V-3. In the organo cyclotriarsane structure the As-As bonds in the base are noticeably shorter at 2.41-2.42 Å and it has been suggested that these bonds have some multiple bond character.[88] It should also be noted in this context that this compound has been found to form a complex with $Cr(CO)_5$ in which one of the basal arsenic atoms is coordinated to the chromium with As-As distances in this structure of 2.406(2), 2.408(2) and 2.462(2) Å. It is interesting to note that the longest distance is between the two As atoms not coordinated to the chromium.[181] The As-As distances in the structures of As_4S_4, As_4S_5 and the anion $As_4S_6^{2-}$, which have structures based on the cuneane polyhedron, are however significantly longer at

TABLE V-1 Arsenic-Arsenic, Arsenic-Sulfur and Arsenic-Selenium Bond Lengths in Various Cluster Compounds

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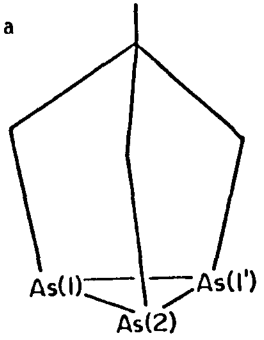
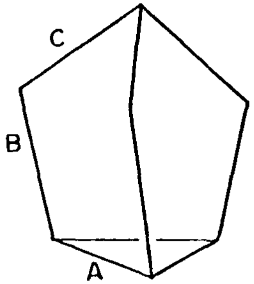
$CH_3C(CH_2As)_3$ [a]



As(1) - As(2) 2.405(5)
As(1) - As(1') 2.422(5)

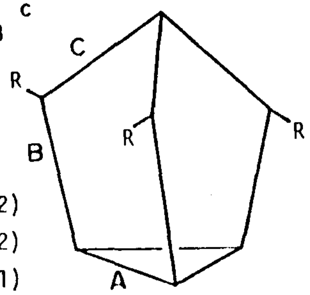
As_7^{3-} [b]

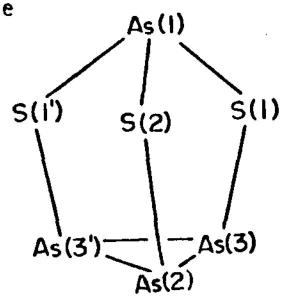
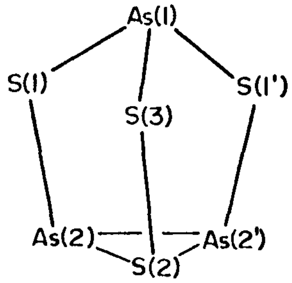
A: 2.498
B: 2.399
C: 2.432



$As_7(SiMe_3)_3$ [c]

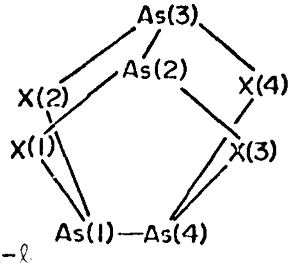
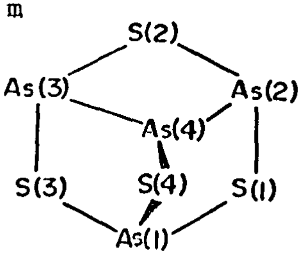
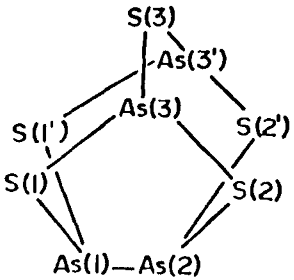
A: 2.444(2)
B: 2.427(2)
C: 2.407(1)



		As-As		As-S(Se)	
αAs_4S_3 [d,e]		As(2) - As(3)	2.445(6)	As(1) - S(1)	2.220(9)
		As(3) - As(3')	2.450(10)	As(1) - S(2)	2.216(11)
				As(2) - S(2)	2.213(12)
				As(3) - S(1)	2.200(3)
βAs_4S_3		As(2) - As(3)	2.460(7)	As(1) - S(1)	2.230(8)
		As(3) - As(3')	2.480(7)	As(1) - S(2)	2.234(16)
				As(2) - S(2)	2.221(12)
				As(3) - S(1)	2.218(10)
$As_3S_4^+$ [f]		As(2) - As(2')	2.459(2)	As(1) - S(1)	2.223(3)
				As(1) - S(3)	2.249(4)
				As(2) - S(1)	2.173(3)
				As(2) - S(2)	2.388(3)

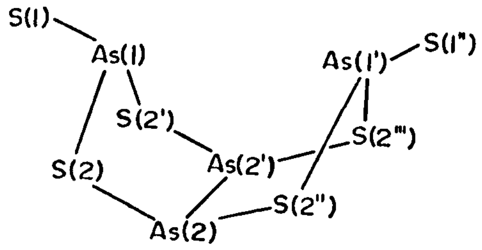
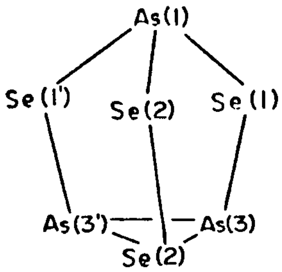
(continued...)

TABLE V-1 (continued)

$\alpha(As_4S_4)^g$		As(1) - As(4) (≡ As(2) - As(3))	2.593(6)	As(1) - S(1) As(1) - S(3)	2.252(9) 2.241(9)	As(2) - S(2) As(2')- S(3')	2.241(9) 2.238(9)
$\beta(As_4S_4)^h$		As(1) - As(4) As(2) - As(3)	2.571(1) 2.566(1)	As(1) - S(1) As(1) - S(2) As(2) - S(1) As(2) - S(3)	2.242(2) 2.232(2) 2.243(2) 2.238(2)	As(3) - S(2) As(3) - S(4) As(4) - S(3) As(4) - S(4)	2.247(2) 2.238(2) 2.231(2) 2.228(2)
As_4Se_4 $^{i-\ell}$		As(1) - As(4) As(2) - As(3)	2.571(3) 2.560(3)	As(1) - Se(1) As(1) - Se(2) As(2) - Se(1) As(2) - Se(3)	2.393(3) 2.381(3) 2.385(3) 2.384(3)	As(3) - Se(2) As(3) - Se(4) As(4) - Se(3) As(4) - Se(4)	2.387(3) 2.386(3) 2.376(3) 2.378(3)
$As_4S_4(II)^m$		As(2) - As(4) As(3) - As(4)	2.519(3) 2.550(3)	As(1) - S(1) As(1) - S(3) As(1) - S(4) As(2) - S(1)	2.263(4) 2.235(4) 2.260(4) 2.226(4)	As(2) - S(2) As(3) - S(2) As(3) - S(3) As(4) - S(4)	2.257(4) 2.269(4) 2.240(4) 2.199(4)
$As_4S_5^n$		As(1) - As(2)	2.546(11)	As(1) - S(1) As(2) - S(2) As(3) - S(1)	2.229(10) 2.254(10) 2.230(11)	As(3) - S(2) As(3) - S(3)	2.241(11) 2.268(8)

(continued...)

TABLE V-1 (continued)

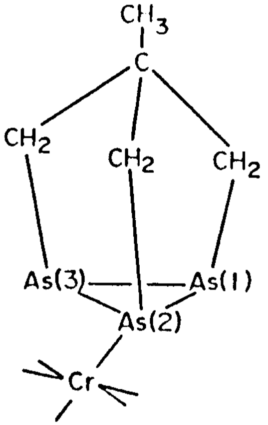
	As-As		As-S(Se)			
As_2S_3 o (orpiment)			As(1) - S(1)	2.292(5)	As(2) - S(1)	2.243(5)
			As(1) - S(2)	2.270(5)	As(2) - S(2)	2.293(5)
			As(1) - S(3)	2.289(5)	As(2) - S(3')	2.308(5)
$As_4S_6^{2-}$ p  	As(2) - As(2')	2.579(9)	As(1) - S(1)	2.302(11)		
			As(1) - S(2)	2.183(10)		
			As(2) - S(2)	2.231(8)		
As_2Se_3 q			As(1) - Se(1)	2.37	As(2) - Se(1)	2.32
			As(1) - Se(2)	2.44	As(2) - Se(2)	2.37
			As(1) - Se(3)	2.56	As(2) - Se(3)	2.36
$As_3Se_4^{+}$, r  	As(2) - As(2')	2.473(5)	As(1) - Se(1)	2.354(4)		
			As(1) - Se(3)	2.362(5)		
			As(2) - Se(1)	2.320(4)		
			As(2) - Se(2)	2.464(5)		

contd.....

(continued...)

TABLE V-1 (continued)

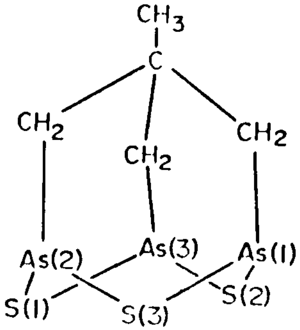
$MeC(CH_2As)_3Cr(CO)_5$ [s]



As-As

As(1)	- As(2)	2.406(2)
	- As(3)	2.462(2)
As(2)	- As(3)	2.408(2)

$MeC(CH_2AsS)_3$ [t]



As(1)	- S(2)	2.237(3)
	- S(3)	2.242(3)
As(2)	- S(3)	2.250(3)
	- S(1)	2.243(3)
As(3)	- S(1)	2.242(3)
	- S(2)	2.239(3)

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[a] Ref. 88. [b] Ref. 63. [c] Ref. 87. [d] Ref. 83. [e] Ref. 84. [f] Ref. this work. [g] Ref. 69. [h] Ref. 70. [i] Ref. 72. [j] Ref. 73. [k] Ref. 74. [ℓ] Ref. 75. [m] Ref. 77. [n] Ref. 19. [o] Ref. 69. [p] Ref. 172. [q] Ref. 95. [r] Ref. this work. [s] Ref. 181. [t] Ref. 88.

TABLE V-2. Final Atomic Positional (x 10^4) and Thermal Parameters (x 10^3)* with Standard Derivations in Parentheses.

Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
(a) $[As_3S_4][MF_6^-]$, M = Sb, As.									
Sb	3357.0(4)	5119(2)	2500(0)	30.2(5)	41.2(5)	45.6(6)	1.7(4)	0	0
As	3354.4(9)	5154(3)	2500(0)	32.1(10)	39.5(11)	46.0(11)	4.6(11)	0	0
As(1)	98.6(6)	543(2)	2500(0)	32.7(7)	37.8(8)	55.3(9)	5.6(6)	0	0
	85.5(9)	519(3)	2500(0)	29.7(10)	33.1(10)	50.0(11)	6.4(8)	0	0
As(2)	1700.0(5)	55(2)	1219(1)	43.3(6)	54.7(7)	54.4(7)	-1.5(4)	12.8(5)	-2.4(6)
	1728.7(7)	9(3)	1197(2)	41.0(8)	54.3(10)	58.0(10)	-3.3(6)	12.5(7)	-3.3(8)
S(1)	750(1)	1486(5)	743(3)	58(1)	50(1)	38(1)	2(1)	-4(1)	6(1)
	758(2)	1473(6)	713(4)	54(2)	47(2)	36(2)	-1(2)	-2(2)	5(2)
S(2)	1353(2)	-3150(7)	2500(0)	30(2)	28(2)	79(3)	4(1)	0	0
	1377(2)	-3255(7)	2500(0)	17(3)	25(2)	74(3)	2(2)	0	0
S(3)	361(2)	-3103(6)	2500(0)	40(2)	34(2)	101(3)	-3(2)	0	0
	350(2)	-3149(8)	2500(0)	35(2)	27(2)	102(5)	-3(2)	0	0
F(1)	3858(6)	6482(16)	1142(10)	152(8)	90(6)	87(6)	-13(6)	46(6)	22(5)
	3850(5)	6285(18)	1235(11)	93(6)	81(7)	71(6)	-13(6)	19(6)	20(6)
F(2)	2880(7)	3722(20)	1143(15)	186(11)	107(8)	193(12)	-13(8)	-135(10)	-25(9)
	2875(7)	4015(23)	1235(16)	129(10)	103(9)	131(11)	-16(8)	-71(9)	-8(9)
F(3)	3915(6)	2695(19)	2500(0)	99(8)	64(7)	104(9)	41(6)	0	0
	3833(7)	2778(22)	2500(0)	82(9)	52(8)	87(10)	22(7)	0	0
F(4)	2791(7)	7517(23)	2500(0)	85(8)	73(8)	215(18)	43(7)	0	0
	2879(8)	7517(24)	2500(0)	80(10)	45(8)	218(22)	39(7)	0	0

(continued....)

TABLE V-2. (continued)

(b) $[As_3Se_4^+][SbF_6^-]$.

Sb(1)	4978(4)	2500	8324(2)	53(2)	63(2)	34(1)	0	1(1)	0
Se(1)	-3495(6)	2500	2228(4)	44(2)	102(4)	31(2)	0	-3(2)	0
Se(2)	1461(4)	647(3)	3484(3)	55(2)	44(2)	63(2)	8(1)	3(1)	4(1)
Se(3)	-3195(6)	2500	4399(3)	37(2)	99(3)	30(2)	0	5(1)	0
As(1)	564(6)	2500	4819(4)	45(2)	59(3)	36(2)	0	-9(2)	0
As(2)	-305(5)	1207(4)	1583(3)	68(2)	65(2)	40(1)	-2(2)	7(1)	-15(1)

Atom	X	Y	Z	U	Atom	X	Y	Z	U
F(1)	3645(4)	3863(27)	7352(23)	115(8)	F(3)	-3612(47)	1203(32)	9261(27)	143(10)
F(2)	7283(49)	2500	7233(29)	92(9)	F(4)	2849(70)	2500	9513(42)	149(15)

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*Anisotropic temperature factors U_{ij} are expressed in the form exp $[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2k\ b^*c^*U_{23})]$.

TABLE V-3. Bond Distances (Å) and Bond Angles (°) with Standard Deviations in Parentheses[a]

	Cations			
	$[As_3S_4^+]$			$[As_3Se_4^+]$
Bond lengths (Å)	$[SbF_6^-]$	$[AsF_6^-]$		
As(1) - S(1)	2.223(3)	2.230(4)	As(1) - Se(1)	2.354(4)
As(1) - S(3)	2.249(4)	2.239(5)	As(1) - Se(3)	2.362(5)
As(2) - As(2')	2.461(2)	2.461(2)	As(2) - As(2')	2.473(5)
As(2) - S(1)	2.173(3)	2.172(4)	As(2) - Se(1)	2.320(4)
As(2) - S(2)	2.388(3)	2.398(4)	As(2) - Se(2)	2.464(5)
S(2) - S(3)	2.030(5)	2.052(6)	Se(2) - Se(3)	2.310(5)
Bond Angles (°)				
S(1) - As(1) - S(1')	98.83(11)	98.39(14)	Se(1) - As(1) - Se(1')	97.65(17)
S(1) - As(1) - S(3)	95.96(10)	96.00(13)	Se(1) - As(1) - Se(3)	98.41(14)
S(1) - As(2) - As(2')	102.17(8)	102.16(11)	Se(1) - As(2) - As(2')	103.35(15)
S(1) - As(2) - S(2)	99.20(11)	99.80(14)	Se(1) - As(2) - Se(2)	103.19(15)
S(2) - As(2) - As(2')	58.99(6)	59.12(7)	Se(2) - As(2) - As(2')	59.87(11)
As(1) - S(1) - As(2)	106.00(12)	106.03(16)	As(1) - Se(1) - As(2)	103.68(16)
As(2) - S(2) - As(2')	62.02(9)	61.75(12)	As(2) - Se(2) - As(2')	60.26(14)
As(2) - S(2) - S(3)	106.60(15)	105.52(19)	As(2) - Se(2) - Se(3)	104.47(17)
As(1) - S(3) - S(2)	104.60(19)	105.40(24)	As(1) - Se(3) - Se(2)	102.86(20)

(continued...)

TABLE V-3. (continued)

			Anions	
Bond lengths (Å)				
M - F(1)	1.849(10)	1.689(11)	Sb - F(1)	1.84(3)
- F(2)	1.831(14)	1.673(14)	- F(2)	1.89(3)
- F(3)	1.847(12)	1.702(14)	- F(3)	1.80(3)
- F(4)	1.845(14)	1.693(15)	- F(4)	1.87(5)
Bond angles (°)				
F(1) - M - F(2)	89.7(5)	89.5(6)	F(1) - Sb - F(2)	89(1)
- F(3)	90.3(4)	90.0(5)	- F(3)	178(1)
- F(4)	90.3(4)	90.0(5)	- F(4)	94(1)
- F(1')	89.7(5)	90.0(5)	- F(1')	90(1)
- F(2')	178.5(5)	179.1(6)	- F(3')	91(1)
F(2) - M - F(3)	88.3(5)	89.3(6)	F(2) - Sb - F(3)	89(1)
- F(4)	91.2(5)	90.8(6)	- F(4)	175(2)
- F(2')	90.8(6)	91.1(7)	F(3) - Sb - F(4)	88(1)
F(3) - M - F(4)	179.3(6)	180.0(7)	- F(3')	87(1)

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[a] Primed atoms are related to the corresponding unprimed atoms by reflection through the mirror plane.

2.55-2.59 Å.

In addition to the compounds in Table V-1, several other examples of arsenic-arsenic bonds have been characterised crystallographically. Of particular note is the very short As-As bond of 2.343(7) Å in the complex $(CO)_4Mo(Me_2P\text{-}As(Me)\text{-}As(Me)\text{-}PMe_2)$.[183] Comparable short As-As bonds of 2.372, 2.273 have been observed in the[184] complexes $As_3Co(CO)_3$ and $As_2Co_2(CO)_6$, respectively. However, these structures are based on tetrahedra of arsenic and cobalt atoms so that the actual bonds in these structures are expected to be 'bent' and therfore shorter than a normal single bond. Finally, the arsenic-arsenic bond lengths in pentameric arsenomethane, arsenobenzene $(PhAs)_6$, tetrameric $(AsCF_3)_4$ and the complex cyclohexa-1-4-(tetracarbonylchromium)2,3,5,6(dimethylarsenic) are 2.428, 2.456, 2.454 and 2.442 Å, respectively.[185,186] All these distances are shorter than the As-As distances of 2.51 Å in metallic arsenic.[187] It appears therefore, that the As-As bond in the triangular base of the $As_3S_4^+$ and $As_3Se_4^+$ cations is somewhat longer than most As-As bonds. This is somewhat surprising in view of the fact that these bonds are usually regarded as 'bent' bonds.

There are three independent arsenic-sulfur bonds in the $As_3S_4^+$ cation (Figure V-1). The As-S bond in the base of the cation is longest at 2.388(3) Å in the hexafluoroantimonate salt and 2.398(4) Å in the hexafluoroarsenate salt. Intermediate in length are the two As-S bonds to As(1) which have an average length of 2.235 Å although it may be noted that in the hexafluoroantimonate salt the two bonds As(1)-S(1) [2.223(3) Å] and As(1)-S(3) [2.249(4) Å] have significantly different lengths. Finally the distance As(2)-S(1) is the shortest at 2.173(3) Å. The ordering of the arsenic sulfur distances in the $As_3S_4^+$ cation is the same as that found for the distances in the homopolyatomic analogues P_7^{3-}, As_7^{3-} and Sb_7^{3-}. A good compilation of arsenic-sulfur bond lengths in a variety of compounds has been given by Draeger.[188] For three-coordinate arsenic, As-S distances range from 2.18 - 2.35 Å so that the distances As(2)-S(1) and As(2)-S(2) in the $As_3S_4^+$ cation are significantly shorter and longer respectively than most As-S distances. In α and β As_4S_4 and its isomeric form II the As-S bonds have essentially "normal" lengths in the range 2.199-2.269 Å.[69,70,77]

The lengths of the arsenic-sulfur bonds can be accounted for if it is assumed that there is a tendency for the positive charge on the basal S atom in I of Figure V-2 to be delocalised onto the other non-adjacent S atoms. This can be represented by the inclusion of the two resonance structures II which would cause a lengthening of the As-S bonds in the triangular base and a shortening of the type b As-S bonds. Delocalisation of charge onto the adjacent S atom can only occur as in III with the generation of a 4-valent S atom and it is not unreasonable to assume that this structure is not of great importance. This is consistent with the average S-S bond length of 2.041(1) Å, that is very similar to the bond lengths of 2.048 Å and 2.04 Å in S_8 and S_8^{2+},[189,190] respectively. The bonds in these latter molecules are always regarded as "normal" single bonds although it should be emphasised that there is no conclusive evidence that this is the case. For comparison the bond length in S_4^{2+}, which nominally has a bond order of 1.25, is 2.014(3) Å.[191] Indeed the relationships between bond length and bond order for bonds between heavy atoms such as sulfur and arsenic are very uncertain. Even in the neutral molecule, As_4S_3, the As-As bonds in the triangular base are longer than "normal" and no satisfactory explanation for this has been given. It would seem that a given bond, e.g., an As-As single bond, can vary considerably in length with the nature and arrangement of the attached atoms.

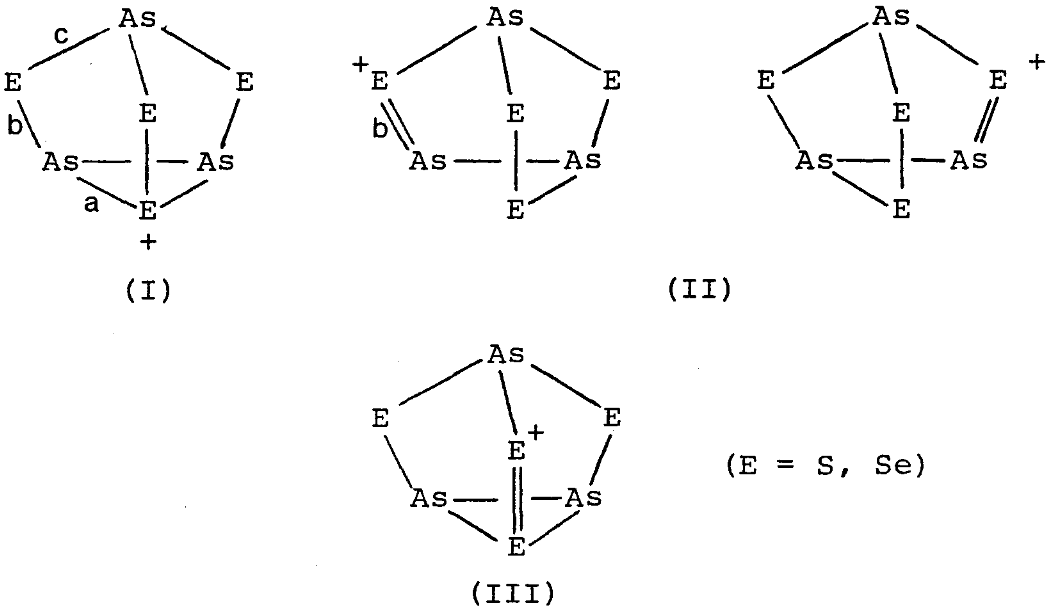

FIGURE V-2. Resonance Structures of $As_3E_4^+$ Ions, E=S,Se.

Similarly, in the $As_3Se_4^+$ cation there are again three different arsenic-selenium bond lengths; that in the base is longest at 2.464(5) Å, the two bonds to As(1) are intermediate in length (2.358(5) Å, ave.) and finally As(2)-Se(1) is shortest at 2.320(4) Å. The ordering of the lengths of these bonds in terms of position in the structure is the same as in the $As_3S_4^+$ cation, although the differences between the three As-Se bond lengths in $As_3Se_4^+$ is less than those between the analogous As-S bond lengths in the $As_3S_4^+$ cation.

The lengths of these As-Se bonds may be compared to the sum of the covalent radii for As and Se of 2.38 Å and the average As-Se distances of 2.384(5) in

As_4Se_4[72-75] and As-Se distances of 2.32-2.56 Å calculated for polycrystalline As_2Se_3 by a Monte Carlo fitting technique.[72] Apart from these values the few other As-Se distances that have been reported in the literature are for compounds containing $AsSe_3^{3-}$ and related ions; for example, the As-Se distance in Ag_3AsSe_3 is 2.411 Å.[192]

The unique Se-Se bond in the $As_3Se_4^+$ cation, of length 2.310(5) Å, is slightly shorter than the Se-Se bonds in several forms of cyclooctaselenium (2.335 Å)[193] and the bonds in dimorpholinodiselane (2.346(1) Å) and dimorpholinotriselane (2.352(1) Å)[194] which may be regarded as "normal" single bonds. However, this bond length is still considerably larger than the Se-Se bonds of 2.283(4) and 2.236(8) Å observed for the Se_4^{+2} cation which, on the basis of simple valence bond and MO treatments, have bond orders of 1.25.[195,196] Furthermore, it has been noted elsewhere[197] that, in compounds containing chains of sulfur and selenium atoms, adjacent bonds can interact to produce alternations in bond lengths along the chain. This effect is more pronounced when one of the S or Se atoms is positively charged as in the Se_{10}^{2+} cation.[197] The bond adjacent to the positive charge is always observed to be long, and then the bonds are alternately short and long, the effect diminishing with increasing distance from the positive charge. A similar effect is noted in the $As_3S_4^+$ and $As_3Se_4^+$ cations.

The $As_3Se_4^+$ ion has a more regular structure than that of $As_3S_4^+$. The angles in the triangular base are all equal to 60° in $As_3Se_4^+$ whereas in $As_3S_4^+$ there are two angles of 59° and one of 62°. All the other bond angles are slightly smaller than 109.5° and those at S are slightly larger than those at Se. That the $As_3S_4^+$ cation is more distorted than the $As_3Se_4^+$ cation can be readily seen by comparing some internal contact distances. Thus, in $As_3Se_4^+$ the contacts As(1)...As(2) and As(1)...Se(2) are very similar at 3.676(5) and 3.653(5) Å, respectively, while in the two $As_3S_4^+$ cations the As(1)...As(2) and As(1)...S(2) contacts are respectively 3.511(2) and 3.389(3) Å for the hexafluoroantimonate salt and 3.517(2) and 3.415(4) Å for the hexafluoroarsenate salt. The significant difference in the two As(1)...S(2) contacts in these two salts may be related to the different strengths of several short interionic contacts which are significantly less than the neutral atom van der Waals distances (As...F < 3.335 Å, S...F < 3.20 Å).

V-4(iib) Interionic Contacts and the Anions

There are three contacts of note (Figure V-3, Table V-4) in the structures of $(As_3S_4)(AsF_6)$ and $(As_3S_4)(SbF_6)$.

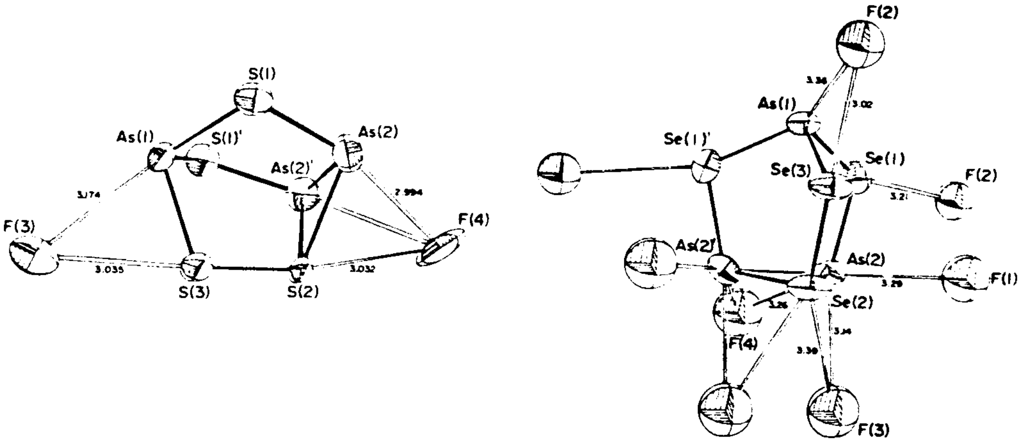

FIGURE V-3. Interionic Contacts in $As_3S_4(AsF_6)$ and $As_3Se_4(SbF_6)$.

TABLE V-4. Selected Intra- and Inter-ionic Contacts (Å) and Some Related Angles (°)

		$As_3S_4^+$			
		Intra-ionic			
	SbF_6	AsF_6		SbF_6	AsF_6
As(1)...As(2)	3.511(2)	3.517(2)	S(1)...S(1')	3.817(4)	3.745(5)
As(1)...S(2)	3.389(3)	3.415(4)	S(1)...S(3)	3.320(4)	3.321(5)
As(2)...S(3)	3.550(4)	3.549(5)	S(1)...S(2)	3.475(4)	3.498(5)
As(2)...S(1')	3.610(3)	3.609(4)			
		Inter-ionic (As...F < 3.35, S...F < 3.20 Å)			
As(1)...F(3^{I})	3.107(12)	3.174(14)	S(1) - As(1)...F(3^{I})	128.7(1)°	129.1(1)°
			S(3) - As(1)...F(3^{I})	65.0(2)°	65.6(3)°
S(3)...F(3^{I})	2.968(13)	3.036(15)	As(1) - S(3)...F(3^{I})	71.6(2)°	72.7(3)°
			S(2) - S(3)...F(3^{I})	176.1(3)°	177.6(4)°
			As(1)...F(3^{I})...S(3)	43.4(2)°	42.2(2)°
As(2)...F(4^{II})	2.970(12)	2.994(14)	S(1) - As(2)...F(4^{II})	164.1(2)°	165.4(2)°
			As(2') - As(2)...F(4^{II})	65.5(1)°	65.7(1)°
			As(2)...F(4^{II})...As(2')	48.9(2)°	48.5(2)°

(continued...)

TABLE V-4 (continued)

S(2)...F(4^{II})	2.965(13)	3.032(16)	S(3) - S(2)...F(4^{II})	171.6(3)°	169.5(4)°
			As(2) - S(2)...F(4^{II})	66.4(4)°	65.7(2)°
			As(2)...F(4^{II})...S(2)	47.5(2)°	46.9(2)°
[N.B. No contacts to S(1)]					
			As(1)...F(3^{I}) - M^{I}	166.9(6)°	162.2(7)°
			S(3)...F(3^{I}) - M^{I}	123.5(5)°	120.0(6)°
			As(2)...F(4^{II})-M^{II}	150.7(4)°	147.0(5)°
			S(2)...F(4^{II}) - M^{II}	121.4(6)°	115.4(7)°

$(As_3Se_4)(SbF_6)$

Intra-ionic

As(1)...As(2)	3.676(5)	Se(1)...Se(1^{III})	3.544(4)
As(1)...Se(2)	3.653(5)	Se(1)...Se(3)	3.570(4)
As(2)...Se(3)	3.775(5)	Se(1)...Se(2)	3.750(5)
As(2)...Se(1^{III})	3.761(4)		

(continued...)

TABLE V-4 (continued)

As(1)...F(2^{IV})	3.36(3)	Se(1) - As(1)...F(2^{III})	129.2(2)
		Se(3) - As(1)...F(2)	60.8(5)
As(2)...F(3^{V})	3.14(3)	Se(1) - As(2)...F(3)	162.2(6)
		Se(2) - As(2)...F(3)	73.3(6)
		As(2^{III}) - As(2)...F(3)	67.7(3)
As(2)...F(4^{V})	3.26(4)	As(2^{III}) - As(2)...F(4)	67.7(3)
		Se(2) - As(2)...F(4)	121.1(5)
		Se(1) - As(2)...F(4)	113.6(8)
As(2)...F(1^{VI})	3.29(3)	As(2^{III}) - As(2)...F(1)	132.9(5)
		Se(1) - As(2)...F(1)	79.8(4)
		Se(2) - As(2)...F(1)	73.5(5)
Se(1)...F(2^{VII})	3.21(11)	As(1) - Se(1)...F(2)	156.4(6)
		As(2) - Se(1)...F(2)	96.9(6)
Se(2)...F(3^{V})	3.39(3)	Se(3) - Se(2)...F(3)	158.3(5)
		As(2) - Se(2)...F(3)	62.6(5)
Se(3)...F(2^{IV})	3.02(3)	As(1) - Se(3)...F(2)	76.1(6)
		Se(2) - Se(3)...F(2)	179.0(6)
		As(2)...F(1^{VI}) - Sb^{VI}	124.4(11)
		Se(3)...F(2^{IV}) - Sb^{IV}	124.9(13)
		Se(1)...F(2^{VII}) - Sb^{VII}	110.3(5)
		As(2)...F(3^{V}) - Sb^{V}	136.2(14)
		Se(2)...F(3^{V}) - Sb^{V}	104.7(12)
		As(2)...F(4^{V}) - Sb^{V}	157.3(5)

^{I} $-\frac{1}{2}+x,-y,z$ ^{II} $x,-1+y,z$ ^{III} $x,\frac{1}{2}-y,z$ ^{IV} $-1+x,y,z$ ^{V} $x,y,-1+z$
^{VI} $-x,-\frac{1}{2}+y,1-z$ ^{VII} $1-x,-y,1-z$.

The fluorine atom F(4) forms short contacts of approximately the same length to all three atoms in the base of the cation. In the hexafluoroantiomonate structure the contacts, of lengths 2.940(12) [As(2)...F(4') x 2] and 2.965(13) Å [S(2)...F(4')], are 0.41 and 0.23 Å less than van der Waals limits. In the hexafluoroarsenate structure the corresond-ing contacts are of lengths 2.994(14) (x2) and 3.032(16) Å, or 0.36 and 0.17 Å less than van der Waals limits.

The remaining short inter-ionic contacts in the $As_3S_4^+$ structure involve atom F(3) of a second SbF_6^- anion which appears to be bridging the As(1)-S(3) bond of the cation. These contacts in the hexafluoroantiomonate structure are of lengths 3.107(12) [As(1)...F(3")] and 2.968(13) Å [S(3)...F(3")] ca. 0.24 Å less than the respective van der Waals limits. [In the AsF_6^- structure the analogous contacts are of lengths 3.174(14) and 3.036(15) Å].

In $(As_3S_4)(SbF_6)$ the average SbF and AsF bond lengths in the anions are 1.843(13) Å and 1.689(13) Å, respectively, and are close to the distances of 1.844(7) and 1.719(3) Å observed in the crystal structures of $K(SbF_6)$[198] and $K(AsF_6)$[199] respectively. Cis and trans angles in the AsF_6^- and the SbF_6^- anions of the $As_3S_4^+$ structures do not deviate significantly from 90° and 180°. As a result of the interactions of fluorine atoms in the anions with the apex and base of the $As_3S_4^+$ cations the packing of these compounds consists of rows of alternating anions and cations along c (Figure V-4).

In the $As_3Se_4(SbF_6)$ structure the positions of the fluorine atoms in the hexafluoroantimonate anion are not as well defined as those in the anions of the $As_3S_4^+$ salts so that some of the contact distances in the former structure are not as reliable. The atoms in the base of the cation are involved in three unsymmetrical fluorine bridges to the fluorine atoms in two anions related by a cell translation along a. These contacts are weaker than those to the $As_3S_4^+$ cations and are close to the van der Waals limits [As(2)...F(3) = 3.14 Å, Se(2)...F(3) = 3.39 Å, and As(2)...F(4) = 3.26 Å (x2)]. The shortest interionic contact in the $As_3Se_4(SbF_6)$ structure of length 3.02 Å is to the bridging selenium atom Se(3). A similar contact to the other bridging selenium atom Se(1) is poorly defined [Se(1)...F(2) = 3.21(11) Å]. Another feature of the contacts to the $As_3Se_4^+$ cation is absence of any short contacts to the apical arsenic atom As(1).

The short anion-cation contacts observed in the present structures are analogous to those observed in the sulfur-nitrogen cations $S_3N_2^+$, $S_6N_4^{2+}$ and $S_4N_3^+$ (all of which principally involve the S-S bond in each

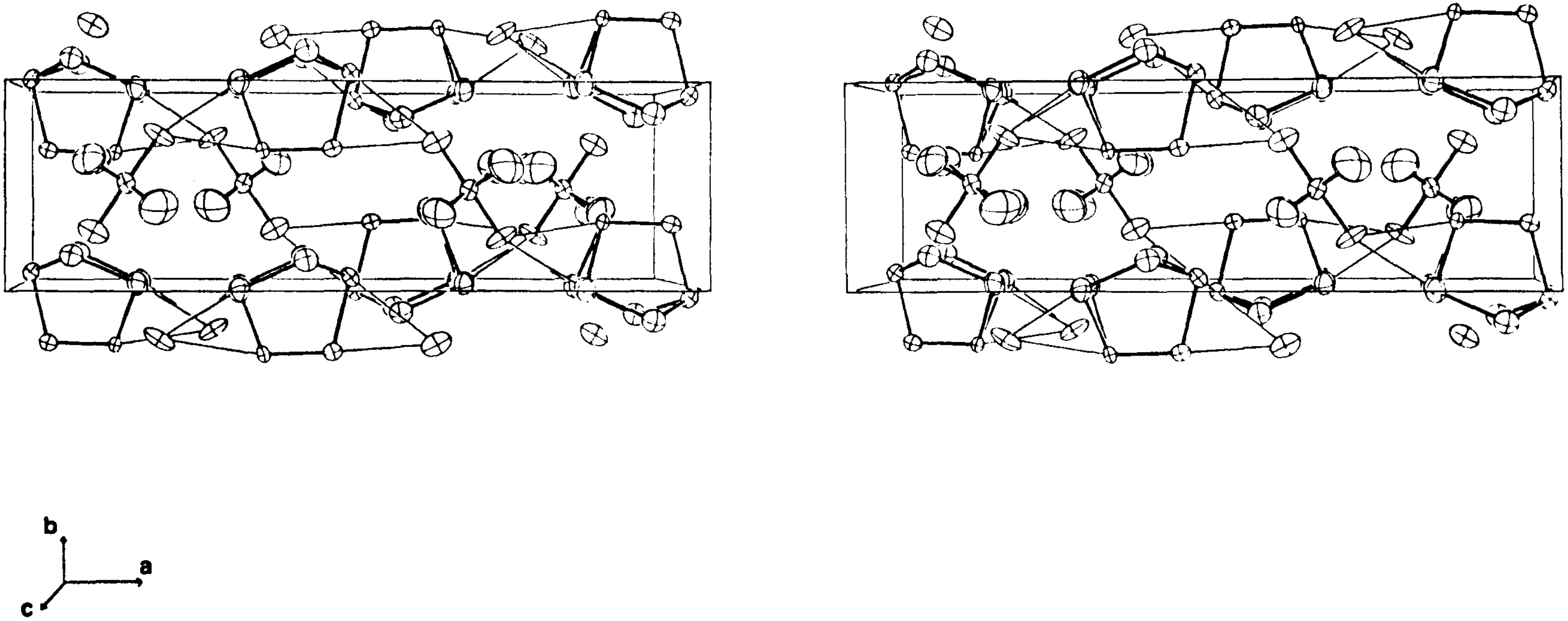

FIGURE V-4. Stereoscopic View of the Unit Cell Diagram of $As_3S_4(SbF_6)$.

ring), the mixed S-Se-N cation $Se_4S_2N_4^{2+}$ (involving the diselenide bond)[200] and the homo- and hetero-polyatomic cations of the Group VI elements.

The average antimony-fluorine bond length in the anion of $(As_3Se_4)(SbF_6)$ is 1.85(4) Å similar to the bond length observed in $K(SbF_6)$.[198] *Cis* and *trans* angles in this anion deviate by up to 5° from 90° and 180°. A view of packing of $(As_3Se_4)(SbF_6)$ is given in Figure V-5.

V-5 Infrared and Raman Spectra of the $As_3S_4^+$ and $As_3Se_4^+$ Salts and Related Compounds

X-ray crystallography has shown that both the $As_3S_4^+$ and $As_3Se_4^+$ cations have C_s symmetry. The representations of the Raman and infrared active normal vibrations for both ions are $\Gamma vib\ (C_s) = 9A' + 6A''$. Both A' and A" vibrations are Raman and infrared active so fifteen bands are expected for each cation in both spectra.

Raman and infrared band frequencies, intensities and assignments for $As_3S_4(AsF_6)$, $As_3S_4(SbF_6)$, $As_3Se_4(AsF_6)$, $As_3Se_4(SbF_6)$, αAs_4S_3, βAs_4S_3, αAs_4S_4 and βAs_4S_4 are listed in Tables V-5 and V-6 and the Raman and infrared spectra for the compounds studied here are reproduced in Figures V6-15 except for the IR spectrum of $As_3S_4(AsF_6)$ which was of poor quality.

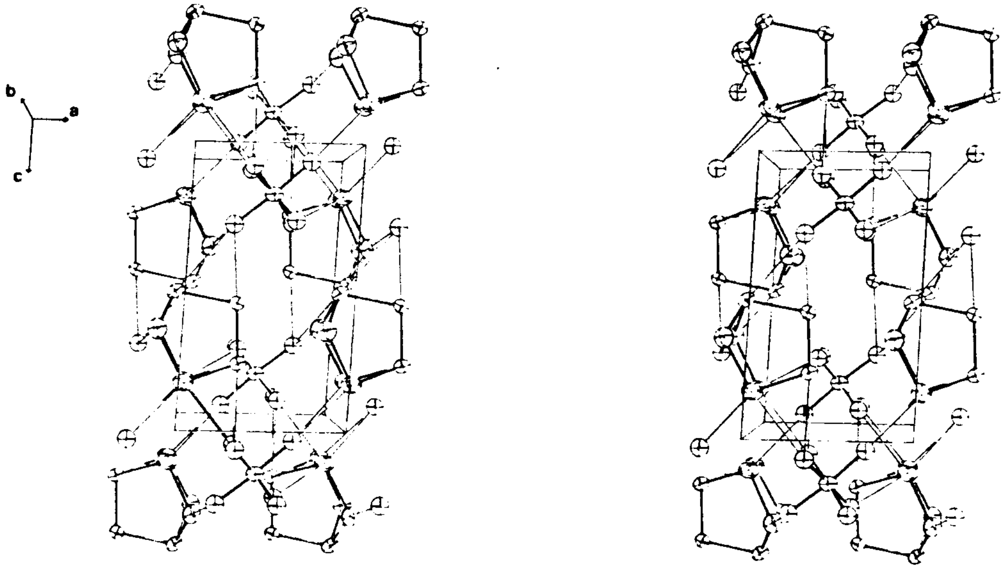

FIGURE V-5. Stereoscopic View of the Unit Cell of $As_3Se_4(SbF_6)$.

As noted earlier, As_4S_4 is insoluble in all solvents studied. Similarly, $As_3S_4(SbF_6)$ was found to be insoluble in CS_2, CH_2Cl_2, SO_2ClF, 98% H_2SO_4, AsF_3, BCl_3 and SbF_5. $As_3Se_4(SbF_6)$ was insoluble in CS_2 and CH_2Cl_2; slightly soluble in HF and was found to decompose in CH_3CN and HSO_3F. Although these salts were soluble in SO_2 their solubility, ca. 10^{-3} M for $As_3Se_4(SbF_6)$, was not sufficient for a solution Raman spectrum. This was also the case for $As_3S_4(AsF_6)$ in AsF_3. Assignments were therefore limited to the anion vibrations.

A comparison of some As-S, As-As, As-Se, Se-Se and S-S stretching frequencies (Table V-7) shows that As-As stretches range from 200-300 cm^{-1}, sulfur-sulfur stretches are usually above 450 cm^{-1} and As-S stretches are generally above 300 cm^{-1}. Hence, the gap from 250 cm^{-1} to about 330 cm^{-1} in the Raman spectra of the $As_3S_4^+$ salts probably separates the arsenic-sulfur stretches from the bends. Any weak bands within this region are due to the SbF_6^- anion. Considering the length of the S-S bond in $As_3S_4^+$ one would have expected an S-S vibration in the usual region above 450 cm^{-1}. However, the bands in the range 388-407 cm^{-1} probably represent the stretching modes involving this bond in $As_3S_4^+$. From

TABLE V-5 Infrared and Raman Spectra of Some Arsenic-Sulfur Compounds

$As_3S_4(AsF_6)$		$As_3S_4(SbF_6)$			αAs_4S_3	βAs_4S_3		αAs_4S_4	
Raman	IR	Raman	IR	Assignments	Raman[a]	IR[201]	Raman[a]	Raman[a]	IR[177]
682(9)	684s	648(20)	653s	ν_1, AsF_6^-, SbF_6^-					
670(7)	671s	637(7)	633s	ν_3, AsF_6^-, SbF_6^-					
		520(2)							
561(2)	561m	561(3)	560w	ν_2, AsF_6^-, SbF_6^-					
		407(6)	407sh						
406(10)									
		402(21)	398vs						
			388sh						
368(26)							375(5)	375(5)	375s
364(27)	372sh	369(54)	370m		368(10)	370vs	367(5)	368(8)	369s
-	351m	-	355s		348(26)		353(18)	355(100)	361m
340(16)	341sh	344(19)	342m		340(8)	340vs	336(7)	344(30)	341s
								340(21)	
329(71)	329m	329(74)	328s					328(4)	329sh

(continued...)

TABLE V-5 (continued)

389(10)	399vs	290(3)	285	ν_4, AsF_6^-, SbF_6^-					
				ν_5, AsF_6^-, SbF_6^-					
	391vs	278(7)							
					271(100)	273m	272(100)		
250(64)	250w	250(59)	250s						
229(65)	231w	231(60)	230s				237(2)		
							231(1)	224(26)	225s
					221(16)	217vw	214(13)	221(55)	
-	214vw	-	214w		211(31)		210(28)	212(3)	212m
207(24)	-	207(26)	205w		203(28)		206(33)	210(1)	210m
						202w	204(19)		
197(100)	-	197(100)	-		197(17)	-	202(14)	193(77)	193m
190sh	186sh	-	186sh		184(14)	185w	182(6)	183(85)	183m
182(40)	182s								
		181(49)	179vs		178(35)	177s	177(14)		
177(14)	178s								

(continued...)

TABLE V-5 (continued)

				174(15)	173s	171(17)	172(5)	169m
						169(18)	166(5)	
						152(7)		
136(17)	-	135(18)	-				143(12)	141vw
131(2)								
				120(1)		121(7)	124(2)	
				70(0.5)				
							66(7)	
						55(6)	60(22)	
				53(5)			55(17)	
				50(3)			50(15)	
						43(48)	56(47)	
				42(4)			40(4)	
				39(3)				
				36(5)		32(15)		
				33(6)		29(14)		
				28(13)		23(5)	27(38)	
				17(3)				

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[a] Previously recorded (ref. 121) but additional splittings reported here.

TABLE V-6 Infrared and Raman Data for the $As_3Se_4^+$ Salts.[a]

$As_3Se_4(AsF_6)$		$As_3Se_4(SbF_6)$		Insoluble[b] $As_3Se_4^+$ Salt	Assignments	
Raman	IR	Raman	IR			
	681s		654s		ν_1	MF_6^-
	670s		639sh		ν_3	MF_6^-
	562m		564vw		ν_2	MF_6^-
	395vs		287vs	285(11)	ν_4,ν_5	MF_6^-
	288m		buried	280(14)		
			278sh			
272(11)	275m	271(6)	275sh			
263(44)	261s	261(45)	260s	264(11)		
247(6)	249sh	247(55)	248sh	247(86)		
244(58)	244m	243(53)	243sh			
238(40)	237sh	240(47)	237m	237(40)		
			230sh			
199(25)	199m	199(30)	199m	221(14)		
				202.5(17)		
183(47)	182m	183(40)				
			176m	186(100)		
171(16)		172(32)		167(21)		
153(39)		152(39)	151w	149(18)		

(continued...)

TABLE V-6 (continued)

148(11)	146vw	144(11)		1405(6)
115(100)	118m	115(100)	117m	115(15)
109(16)	111m	109(32)	110m	106(18)
				100(14)
93(15)	96w	93(13)	92w	91(68)
59(9)		60(60)	63	76(22)
40sh				

[a] All spectra were run at R.T. and the Raman spectra were obtained using a He-Ne laser (6328 Å). The Raman of the SbF_6^- salt is a time average spectrum of 38 scans.

[b] Anion not determined.

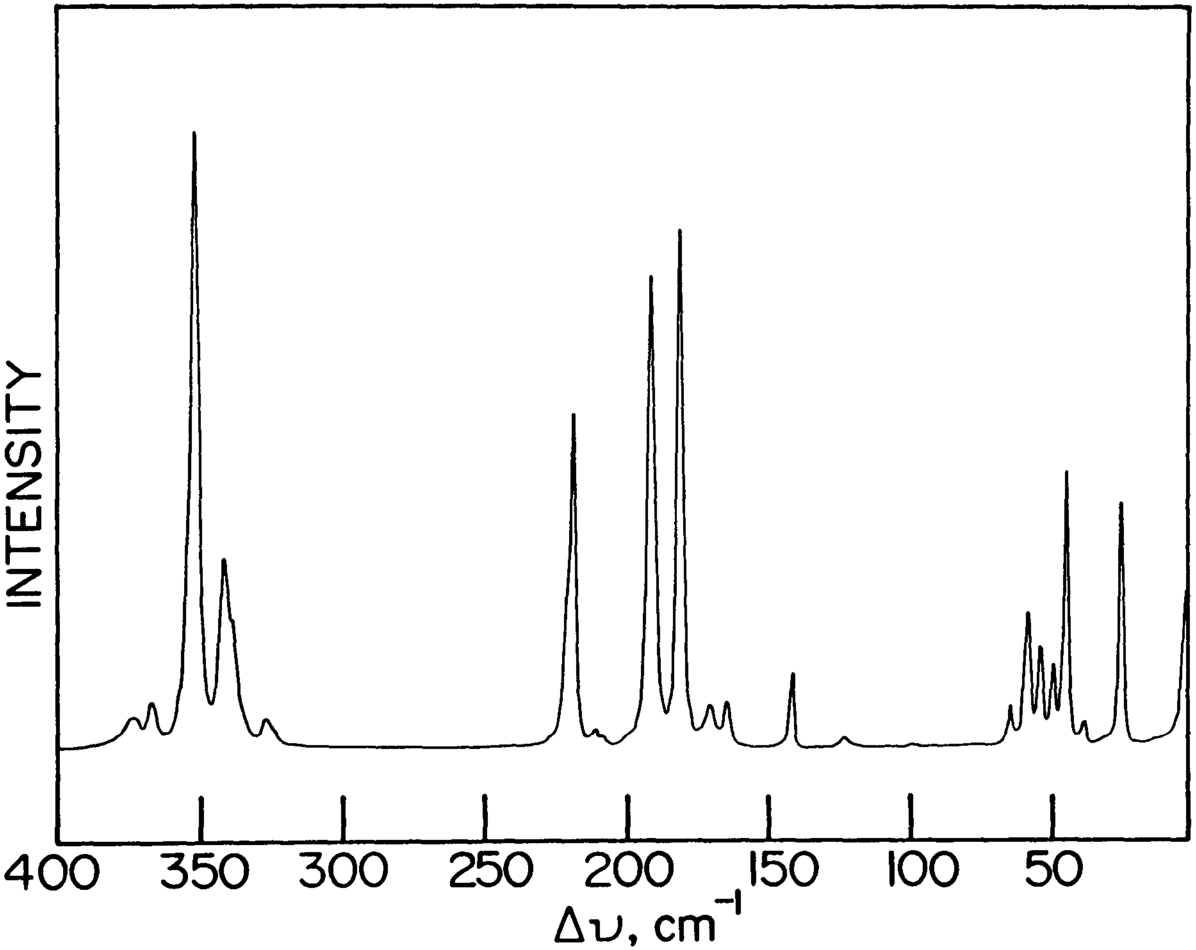


FIGURE V-6. Raman Spectrum of αAs_4S_4.

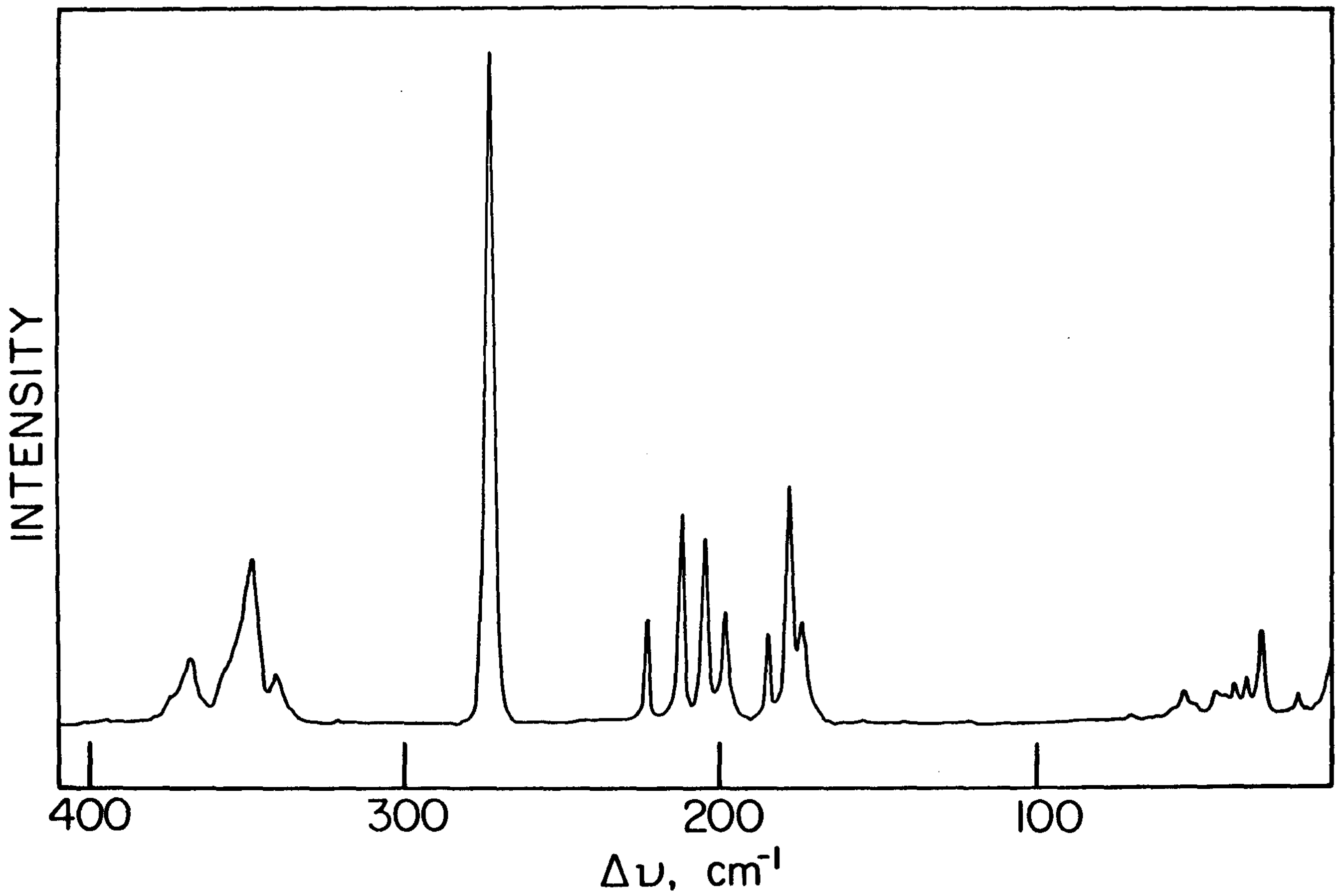


FIGURE V-7. Raman Spectrum of αAs_4S_3.

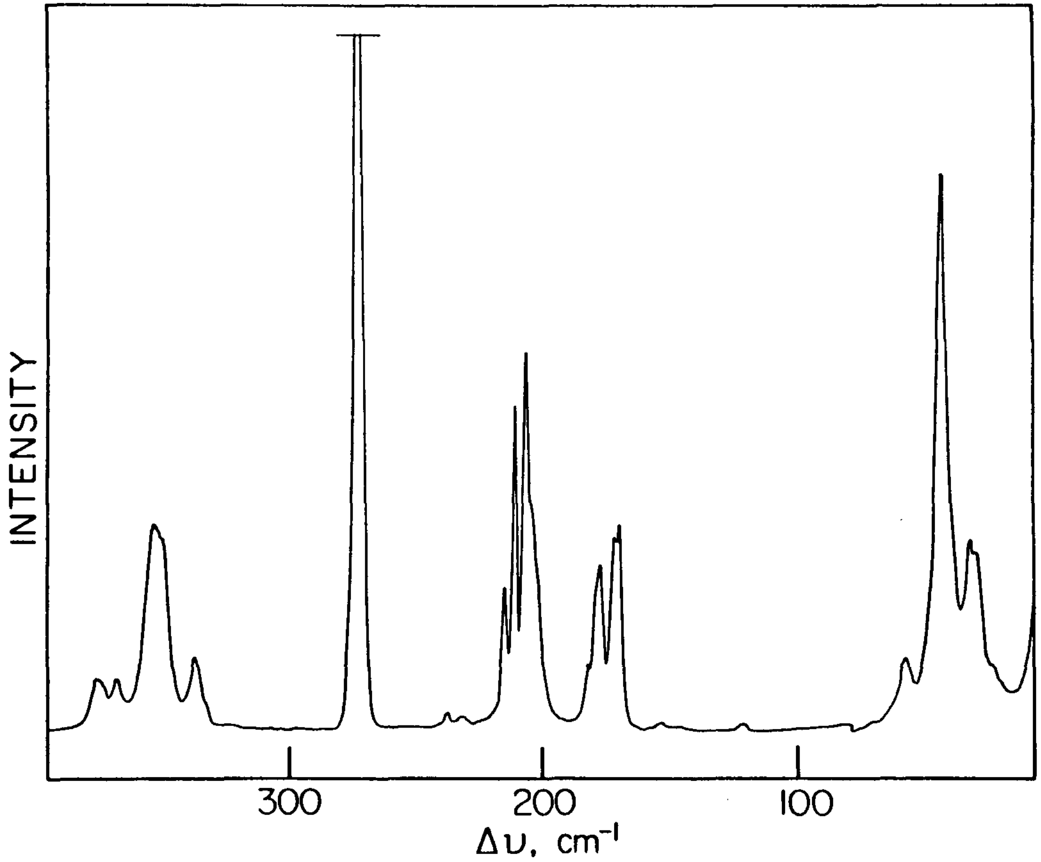


FIGURE V-8. Raman Spectrum of βAs_4S_3.

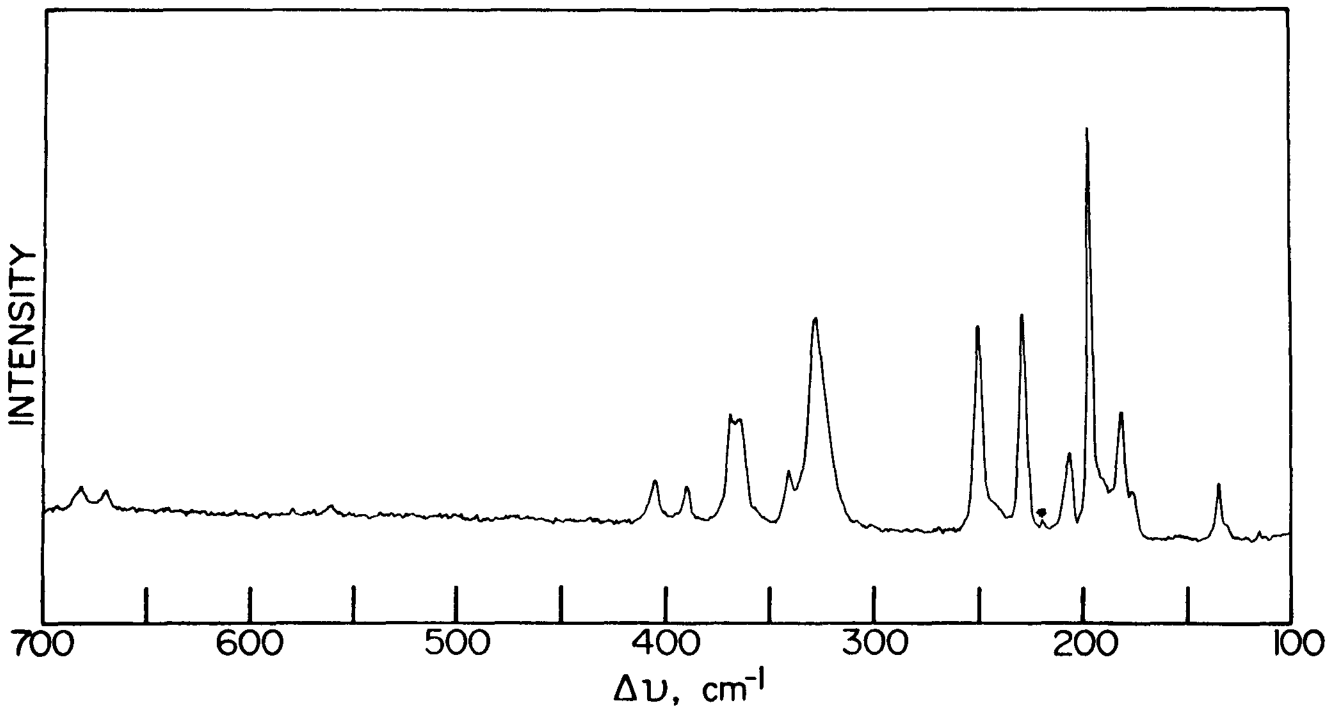


FIGURE V-9. Raman Spectrum of $As_3S_4(AsF_6)$ (* = sulfur).

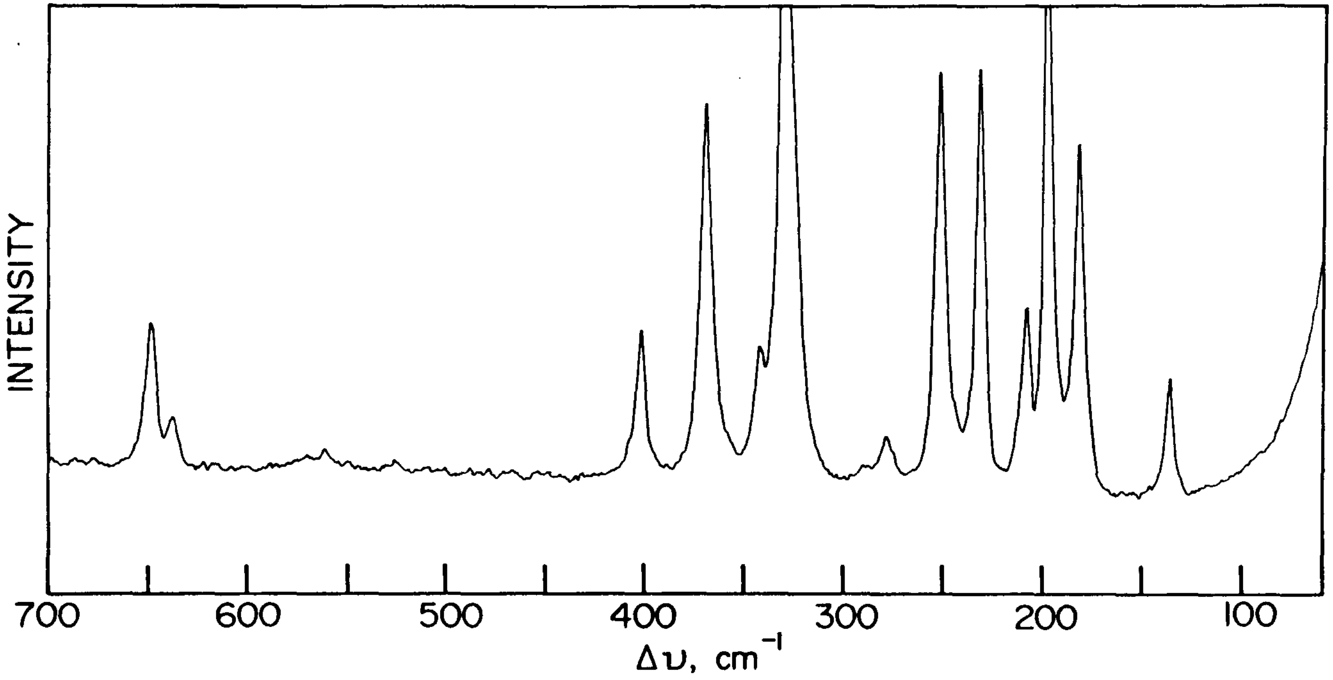


FIGURE V-10. Raman Spectrum of $As_3S_4(SbF_6)$.

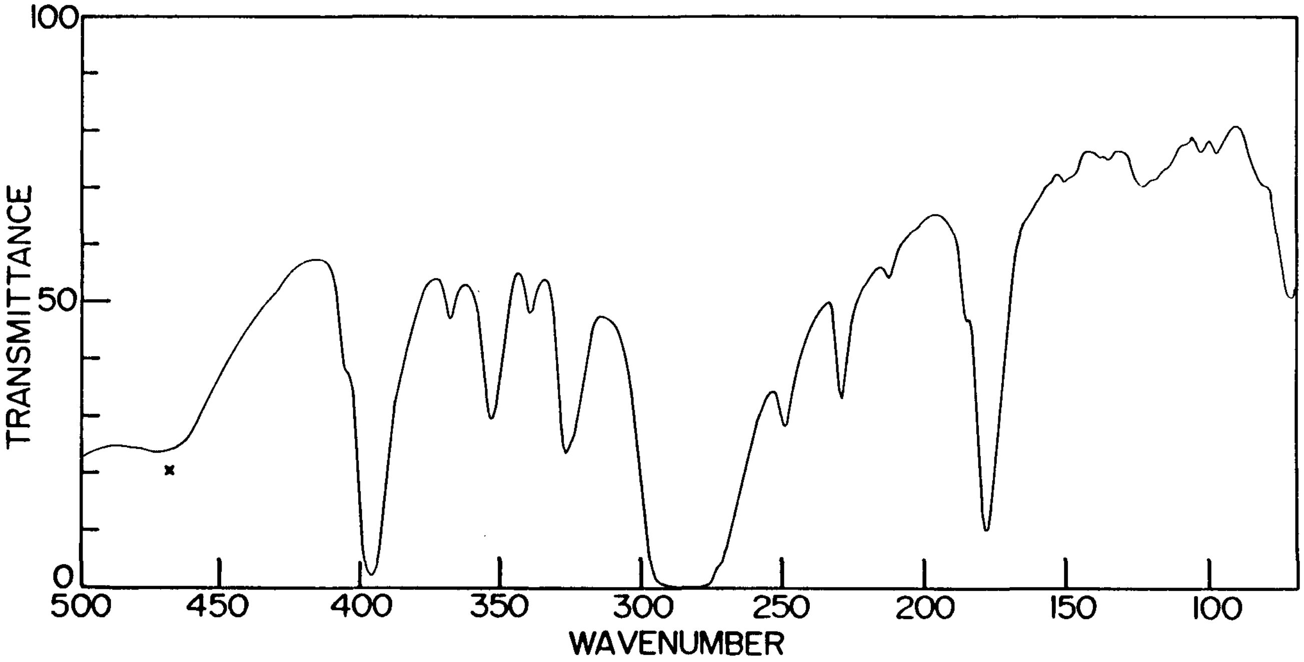


FIGURE V-11. Infrared Spectrum of $As_3S_4(SbF_6)$ (X = polyethylene).

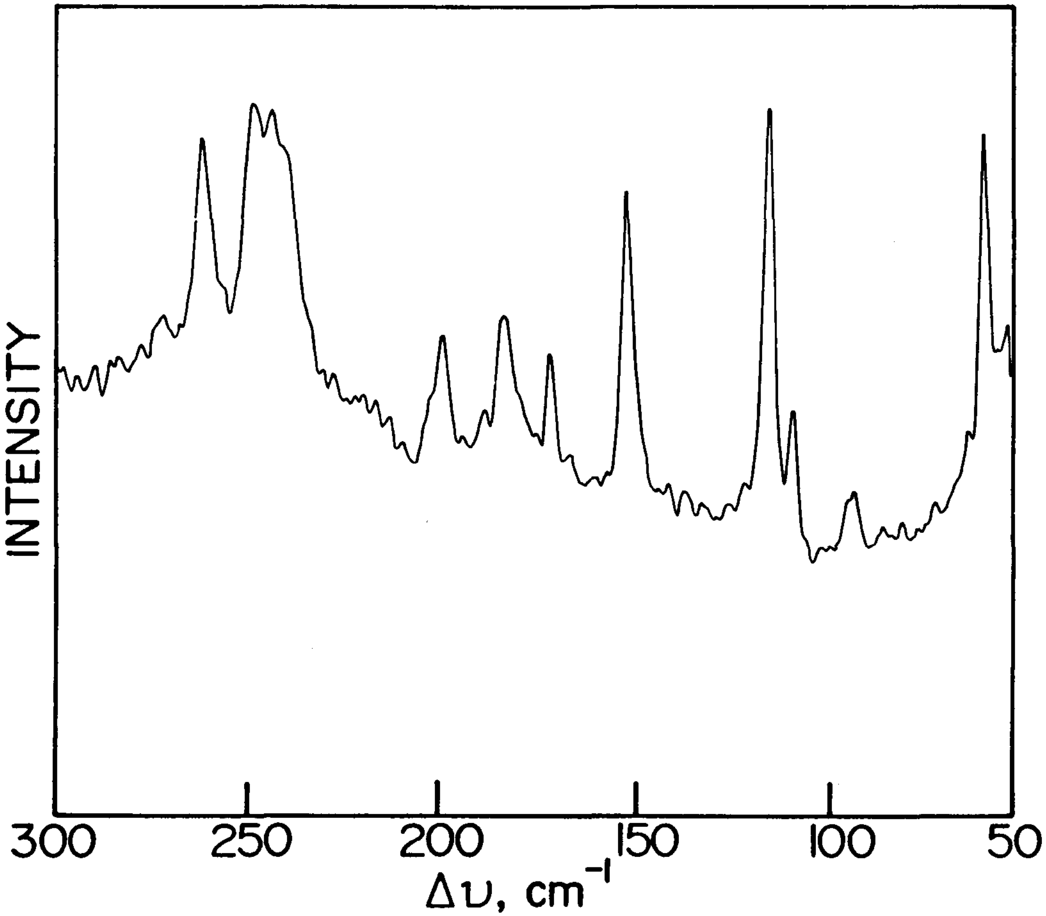


FIGURE V-12. Raman Spectrum of As_3Se_4 (SbF_6).

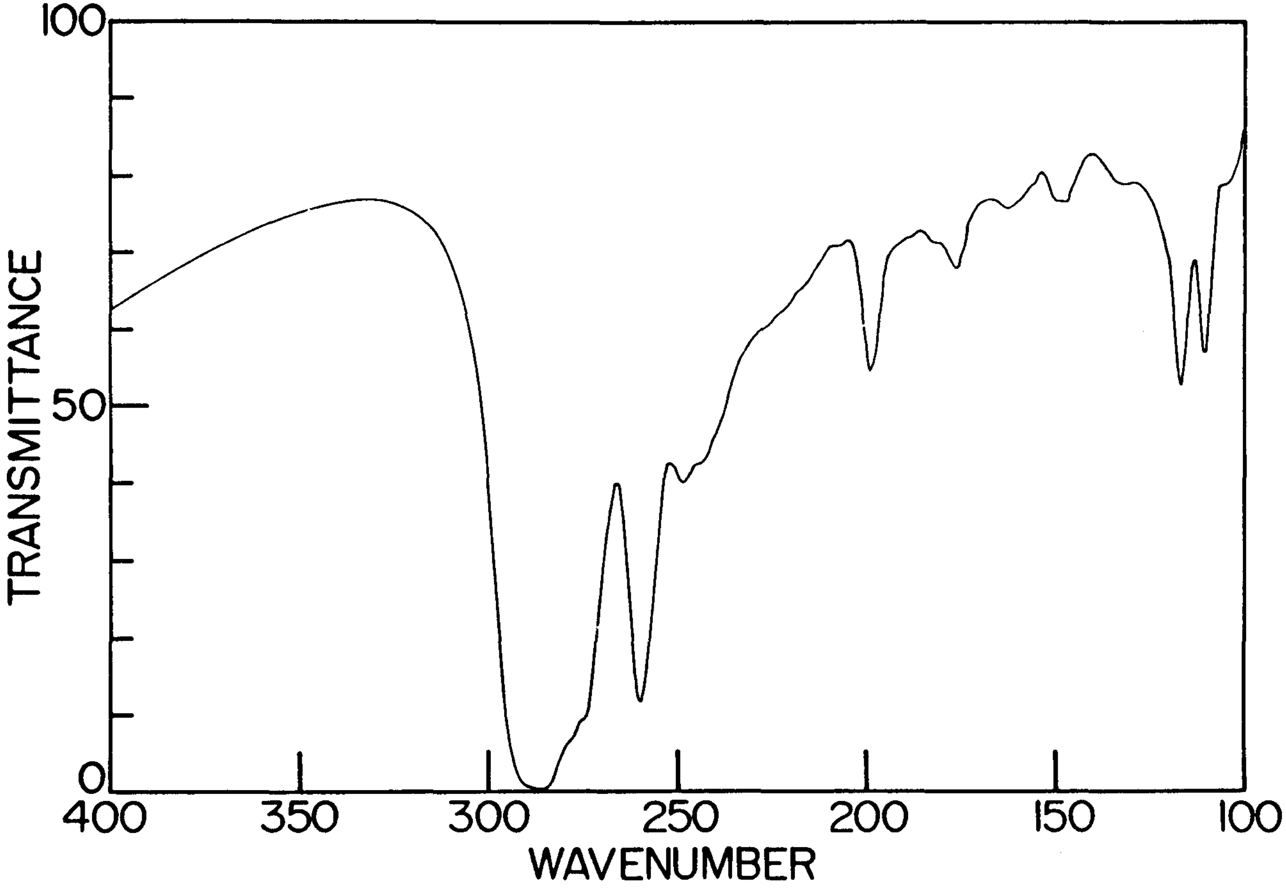


FIGURE V-13. Infrared Spectrum of $As_3Se_4(SbF_6)$.

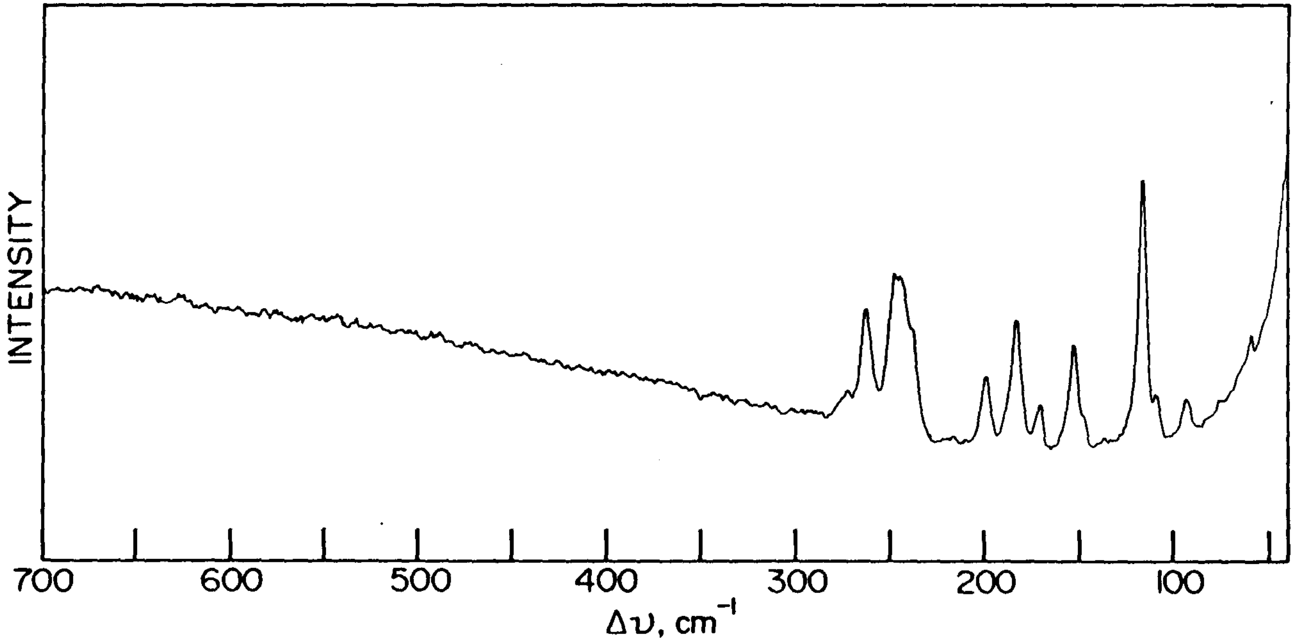


FIGURE V-14. Raman Spectrum of $As_3Se_4(AsF_6)$.

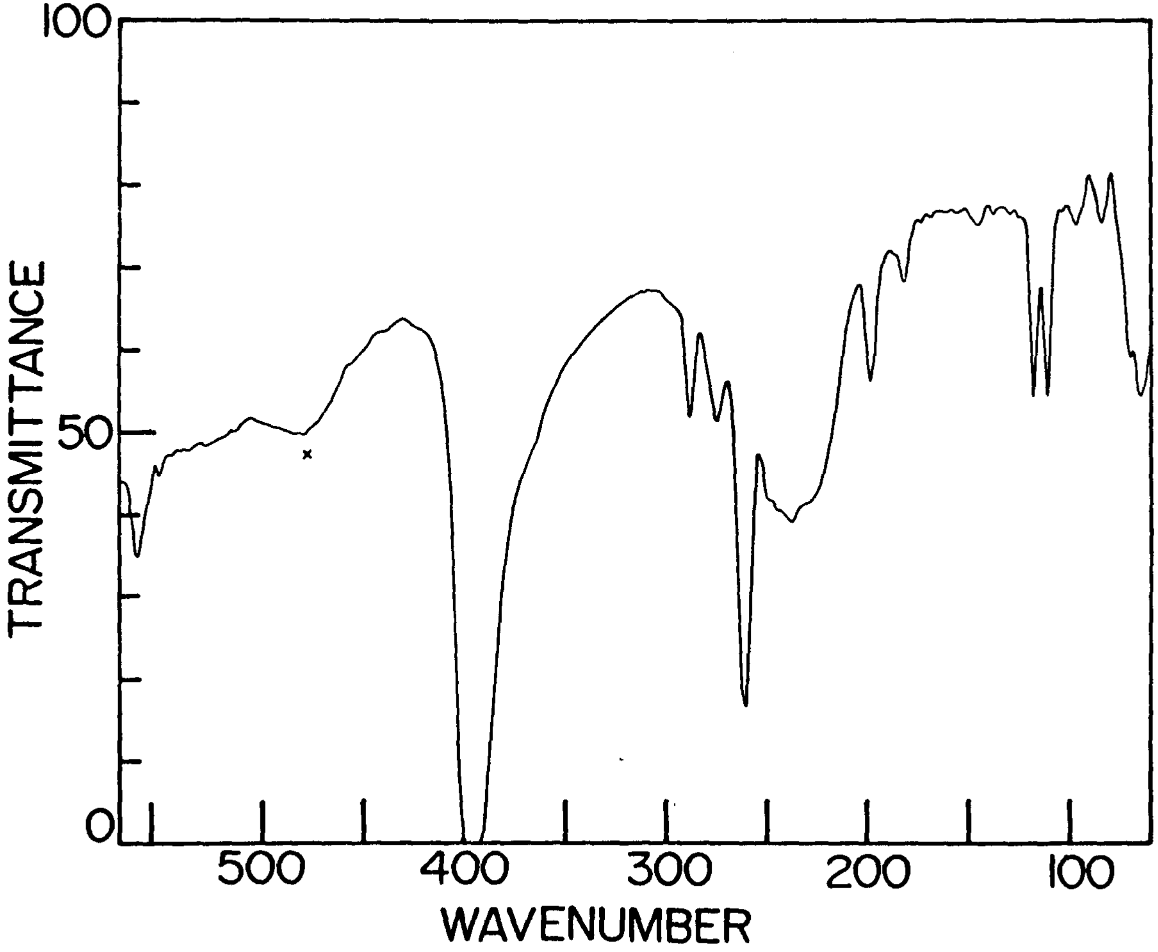
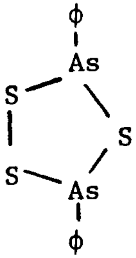
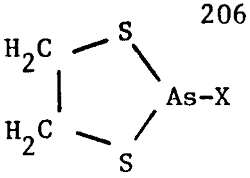
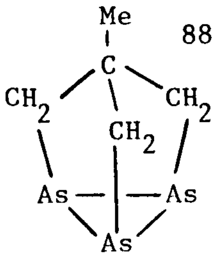


FIGURE V-15. Infrared Spectrum of $As_3Se_4(AsF_6)$ (X = polyethylene).

TABLE V-7 Characteristic Vibrational Data of (i) As-S, (ii) As-As, (iii) As-Se, (iv) Se-Se and (v) S-S Bonds.

(i) As-S	cm^{-1}	(ii) As-As	cm^{-1}
Compound		Compound	
As_2S_3[201-204]	382,368,360,354,326,310 294,290	trans-Me_2As-$AsMe_2$[208]	272
αAs_4S_4[a]	375,368,355,344,340,328	cis-Me_2As-$AsMe_2$[208]	254
βAs_4S_4[70]	381,360,350,341	$(MH_3As)_5$, M=Ge,Si[209]	~270
αAs_4S_3[a]	375,367,353,335.5	trans-$(CF_3)_2As$-$As(CF_3)_2$[210]	202
βAs_4S_3[a]	368,348,340		
		PAs_3(g)[211]	298 ν_2
			313 ν_3
 [205]	373 asym	As_4 (g)[212]	340 ν_1
	345 sym		250 ν_2
 [206] X = Cl, Br	390,360	 [88]	300,252,246

(continued...)

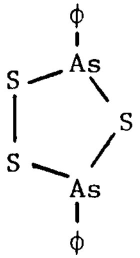
TABLE V-7 (continued)

$As(S_2PFMe)_3$ [207]	360	As_4S_3 (α or β)[121,201,9]	272
$As(S_2PFEt)_3$ [207]	368,350		

(iii) As-Se		(iv) Se-Se	
Compound		Compound	
As_2Se_3 [201]	279,273,254,230,222,206	Se_4^{+2} [215]	327
As_4Se_4 [73]	253-205	$[(Se(C_2F_5))_{4n}]^{2n+}$ [216]	347
$\phi_2AsSeMe$ [213]	301	αSe [217]	254,249,239
$\phi As(SeMe)_2$[213]	295,268	trigonal Se[217]	237,233
$As(SeMe)_3$ [213]	270,256	$CF_3Se\text{-}SeCF_3$ [216]	289
$(AsSeMe)_3$ [214]	300,274,246,225	Se_2Cl_2 [218]	292
		Se_2Br_2 [218]	286

(continued...)

TABLE V-7 (continued)

(v) S-S		(v) S-S (continued)	
Compound		Compound	
S_8 [220]	475,471,437	ϕ_2S_2 [228]	542
S_4^{2+} [221]	584	S_2Cl_2 [219]	540
S_2Br_2 [218]	531		
$S-SO_3^{2-}$ [222]	435		
F_3CSSCF_3 [223]	535	 [206]	490
S_2 [224]	590		
S_3^{2-} [224]	580,548		
H_2S_2 [225,226]	510		
$(CH_3)_2S_2$ [227]	524		

[a] This work.

the values in Table V-7 (ii) and Gordy's Rule[229] it is probable that the bands at 250 cm^{-1} and 230 cm^{-1} are due to As-As stretches. One can also tentatively assign the symmetry of the vibrations at 197 and 136 cm^{-1} as A' and those at 355 and 214 cm^{-1} as A" on the basis of their respective absences in the infrared and Raman spectra.

Spectroscopic data for compounds containing both arsenic and selenium are limited. Table V-7 (iii and iv) show that As-Se and Se-Se stretches usually occur between 220 and 300 cm^{-1}. The number of bands in the Raman spectra of $As_3Se_4(AsF_6)$ and $As_3Se_4(SbF_6)$ at least shows that the cation does not have pseudo C_{3v} symmetry due to the similar masses of arsenic and selenium and similar bond strengths of As-As and Se-Se bonds. The band in the spectra at 260 cm^{-1} may be due to the As-As stretch.

Solid state effects allow ν_1-ν_5 of the anions to be seen in both the infrared and Raman spectra. Also, ν_3 of the AsF_6^- anion appears to come at a lower frequency than ν_1, which is unusual.

The Raman spectra of As_4S_3 agree well with the previously recorded Raman spectra.[121] They are reported here because of additional splittings seen in the spectra. Two previous reports[176,177] of a band at 235 cm^{-1} in the Raman spectrum of αAs_4S_4 have not been confirmed in this work or by some other workers.[70] The bands previously reported at 222 and 345 cm^{-1} were found to be doublets at 221, 224 and 340, 344 cm^{-1}, respectively. Unless crystal field splitting is occuring this requires the reassignment of the latter doublet as an E type stretch with further reassignments for the 328, 368 and 375 cm^{-1} bands from B_1, E and E to some new arrangement of B_1, B_2 and E.

V-6 Electronic Absorption and NMR Studies of the Oxidation of Various Group VB Chalconides

A cursory examination of the oxidation of some VB/VIB compounds and melts in SO_2 was made by means of electronic absorption spectroscopy and ^{31}P NMR spectroscopy. The former cannot lead to any definitive conclusions since any cationic species that might be produced could be 1) insoluble in SO_2; 2) have no absorption in the region studied or 3) have all the spectral bands obscured by those of known species. However, as the group VIB cations, which are probable products of these reactions, have previously been studied by this technique quick identification of their presence was possible. The group VIB cations were considered likely products because of the ease of oxidation by AsF_5 of the group VIB elements compared to the VB elements. Table V-8 presents the experimental results as well as the assignments for the electronic absorption spectra. All absorption peaks were assignable to Group VIB cations. The ultraviolet region could not be studied because of solvent absorption below 330 nm. In all cases, except for As_4S_4 and 1:1 As:Se melts, what appeared to be unreacted material remained in the reaction bulb after the reaction was completed. It should be noted here that significantly larger amounts of AsF_5 were used in the oxidation of As_4S_4 and 1:1 As:Se melts than were used to produce the cations $As_3S_4^+$ and $As_3Se_4^+$. A large excess of AsF_5 with a 1:1 Sb:S melt oxidized all the material present giving $S_8(AsF_6)_2$ and $(Sb_6F_{13})(SbF_6)_5$.[38] The latter was identified by Raman spectroscopy. The reaction As_4S_4 with $S_8(AsF_6)$ in a 1:2 ratio in SO_2 could not be studied using a conventional electronic absorption spectrometer because of the speed of the reaction. However, sulfur (as S_8) and $As_3S_4(AsF_4)$ could be identified by Raman spectroscopy. It was found that reactions of AsF_5 with P_4Se_3 in SO_2 give only PF_5, PF_3 and AsF_3 as soluble products as shown by ^{31}P and ^{19}F NMR spectroscopy. The reaction of P_4Se_3 with 3 moles

TABLE V-8 Electronic Absorption Spectra for Reaction of VB/VIB Compounds with AsF_5 in SO_2

Reaction	Absorption Bands	Assignment
$P_4Se_3 + 3AsF_5$	680,470	Se_8^{+2}
$As_4S_4 + >3AsF_5$	936,714,429;575	$R_2^{a};S_5^{+}$
1:1 As:Se + $>3AsF_5$	680,470	Se_8^{+2}
1:1 As:Te + $3AsF_5$	~510,~410	Te_4^{+2}
$As_2Te_3 + 3AsF_5$	513,428,358	Te_4^{+2} and Te_6^{+4}
1:1 Sb:S + $3AsF_5$	940,710,425;570	$R_2;S_5^{+}$
$Sb_2Se_3 + AsF_5$	680,460	Se_8^{+2} and/or Se_{10}^{+2}
$Sb_2Te_3 + AsF_5$	510,~420(sh)	Te_4^{+2}
$Bi_2Se_3 + AsF_5$	680,460	Se_8^{+2} and/or Se_{10}^{+2}
$Bi_2Te_3 + AsF_5$	530,430,360	Te_4^{+2} and Te_6^{+4}

[a] Unidentified radical. Ref. 231.

of AsF_5 at room temperature only momentarily produces Se_8^{+2} as identified by visible absorption spectroscopy of the SO_2 solutions. Presumably it is consumed as it also acts as an oxidant for P_4Se_3. Reactions left up to three days gave no products soluble in SO_2 while X-ray powder photography and Raman spectroscopy show P_4Se_3 to be the only insoluble product.

The reaction of P_4S_3 with three moles of AsF_5 or SbF_5 in SO_2[230] produces several species of which PF_5 and PF_3 are the main phosphorus-containing compounds as shown by ^{31}P NMR spectroscopy. None of the other products have been characterized as yet. More work is necessary to satisfactorily characterize these reactions.

V-7 Experimental Section

V-7(i) The Reaction of As_4S_4 with AsF_5 in a 1:3 Mole Ratio; The Preparation of $As_3S_4(AsF_6)$

In a typical experiment arsenic pentafluoride (0.699 mmol) was condensed into a vessel containing powdered As_4S_4 (α or β) (0.233 mmol) under about 14 cm^3 of frozen SO_2 at -196°C. As the reaction mixture was warmed to room temperature a bright yellow solution immediately formed which lightened in colour in about five minutes. After 1/2 h the formation of a light yellow precipitate was observed. The reaction was left stirring for at least 12 h. After the precipitate had been allowed to settle the solution was carefully poured through the frit at the same time as the other side was cooled. The SO_2 was then distilled back and the extraction repeated many times because of the low solubility of the product. Varying amounts of sulfur were mixed with the final crystalline product. In addition the reaction with βAs_4S_4 also gave an unidentified insoluble yellow powder mixed with unreacted βAs_4S_4.

V-7(ii) The Reaction of As_4S_4 with $S_8(AsF_6)$ in a 1:2 Mole Ratio

The compound $As_3S_4(AsF_6)$ can also be made using $S_8(AsF_6)_2$ as oxidant. An SO_2 solution of 0.336 mmol of $S_8(AsF_6)_2$ poured onto 0.671 mmol of βAs_4S_4 immediately gave a pale yellow solution and precipitate. The Raman spectrum of the solid showed the presence of the compound $(As_3S_4)(AsF_6)$, a large amount of sulfur and unreacted βAs_4S_4.

V-7(iii) The Reaction of As_4S_4 with SbF_5 in a 1:3 Mole Ratio; The Preparation of $As_3S_4(SbF_6)$

For $As_3S_4(SbF_6)$ 0.3727 mmol of As_4S_4 powder and 1.1181 mmol of SbF_5 were added to different sides of the double ampoule vessel. This was followed by condensation of SO_2 onto the SbF_5, warming and dissolution of the SbF_5. On pouring the solution through the frit the reaction proceeded in the same manner as for the reaction with AsF_5.

Analysis of the soluble solid product gave:

	Found	Calculated for $As_3S_4(SbF_6)$
As	39.94	38.18
S	20.88	21.78
Sb	18.20	20.68
F	18.64	19.36

V-7 (iv) The Reaction of 1:1 and 4:3 As:Se Melts with Three Moles of AsF_5; The Preparation of $As_3Se_4(AsF_6)$

Using similar amounts and conditions as described above, the reaction of a 1:1 or 4:3 As:Se melt and AsF_5 turned to light green-yellow solution that quickly gave a bright yellow-orange solution. After a few minutes a bright orange precipitate formed. This precipitate was extracted with SO_2 and crystals were grown as described above. This air-sensitive solid compound was not very stable, darkening in colour usually in less than two days even when stored in a dry box. A black insoluble unidentified product was also present in the reaction chamber.

V-7 (v) The Reaction of a 1:1 As:Se Melt with Three Moles of SbF_5; The Preparation of $As_3Se_4(SbF_6)$

The reaction was carried out by putting 2.369 mmol of powder from a 1:1 As:Se melt and 7.106 mmol of SbF_5 in separate arms of a double ampoule vessel. Sulfur dioxide was condensed onto the SbF_5 which dissolved on warming to room temperature. This solution was then poured through the frit onto the powder and immediately stirred. As with the preparation of the AsF_6^- salt, a light yellow-green then bright yellow-orange solution was formed with subsequent precipitation of a bright orange precipitate. Multiple extractions removed the soluble product leaving behind a mixture of yellow and black powders.

Analysis of the soluble material yielded the following results:

	Found	Calculated for $As_3Se_4(SbF_6)$
As	27.22	28.95
Se	40.50	40.68
Sb	17.94	15.68
F	13.92	14.68

Crystals of $As_3Se_4(SbF_6)$ were formed by slowly distilling SO_2 from a solution of the compound.

CHAPTER VI

SUMMARY AND CONCLUSIONS

VI-1 Summary and Conclusions

This thesis has dealt mainly with several aspects of the chemistry of the chalconides of phosphorus and arsenic. In almost every case it was found that the sulfides and selenides of phosphorus and arsenic are not converted to cationic species by either oxidizing Lewis acids or by the halogens. This behaviour is in contrast to that of many S-N compounds which give cations such as $S_4N_4^{+2}$ and $S_3N_2Cl^+$.[30,3] The only exceptions to this generalization were found to be the reactions of As_4S_4 and As_4Se_4 with AsF_5 and SbF_5 which gave the new cations $As_3S_4^+$ and $As_3Se_4^+$. A summary of the Lewis acid and oxidation reactions of group V chalconides are given in Table VI-1.

Interest in the structure and oxidation of P-As-S-Se compounds led to the preparation of several new ternary and quaternary compounds containing phosphorus. It is significant that all these compounds have the birdcage structure - a tetrahedron with three edges of a common apex bridged. A number of interesting trends in the ^{31}P chemical shifts and coupling constants were observed.

TABLE VI-1. Summary of Lewis Acid/Oxidation Reactions of the Group VB-Chalconides Studied

Compound	Lewis Acid/Oxidant	Molar Ratio with respect to Chalconide	Product(s) Identified
P_4S_3	AsF_5 [a]	1:3	PF_3,PF_5,AsF_3,other products
	$S_8/(I_2$ catalytic amount)	1:0.25	αP_4S_5,βP_4S_5,P_4S_6, other products
P_4Se_3	AsF_5	1:3	PF_3,PF_5,AsF_3
	I_2	1:1	$\alpha P_4Se_3I_2$
$\alpha(\beta)As_4S_4$	X_2, (X = Cl,Br)	1:2	AsX_3,S_2X_2
	Br_2	1:2	$(SCl_3)_{1.8}(SBr_3)_{1.2}(SbCl_6)$, $SbCl_3$
	$SbCl_5$	1:>10	
	I_2	1:2	AsSI
	TaF_5,NbF_5,BCl_3, SO_3,WF_6,PCl_5	1:3	no reaction
	MF_5 (M=As,Sb)	1:$\leqslant$3(>3)	$As_3S_4(MF_6)$,AsF_3 (sulfur cations)

(continued...)

TABLE VI-1 (continued)

βAs_4S_4	PF_5	1:3	αAs_4S_4
1:1 As:Se	AsF_5	1:⩽3(>3)	$As_3Se_4(AsF_6)$,AsF_3 (sulfur cations)
	SbF_5	1:⩽3(>3)	$As_3Se_4(SbF_6)$,AsF_3,As_3Se_4 (Sb_nF_{5n+1})? (selenium cations)
	$SbCl_3$	1:3	$SeCl_3(SbCl_6)$,$AsCl_3$,$SbCl_3$
4:3 As:Se	AsF_5	1:3	$As_3Se_4(AsF_6)$,AsF_3
1:1 As:Te As_2Te_3 1:1 Sb:S	AsF_5	1:3	Chalcogen cations
Sb_2Se_3 Sb_2Te_3 Bi_2Se_3 Bi_2Te_3	AsF_5	1:1	Chalcogen cations

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[a] Work of G.J. Schrobilgen and J.E. Vekris.

The ^{31}P NMR spectra of αP_4S_5, βP_4S_5 and what is thought to be a form of P_4S_6 have been recorded. The reinvestigation of the ^{31}P NMR spectrum of P_4Se_3 and the recording of its ^{77}Se NMR spectrum have led to the calculation of a new set of coupling constants. The ^{31}P NMR data for the binary phosphorus chalconides do not show any clear trends.

A few reactions of some binary compounds and mixtures of Sb, Bi, Se and Te with AsF_5 were also investigated. Cations such as Bi_9^{+5} and Te_4^{+2} have been studied previously and it therefore seemed reasonable to expect that cations containing two or more of these elements might be produced in oxidizing systems. The structure of such cations would be of considerable interest for comparison with those of the known polyatomic cations. However, for the particular reactions studied (see Table VI-1) no new compounds could be detected by the methods used.

The reactions involving bromine, various chlorinating agents or chlorine as oxidizing agents usually produced the familiar halides of the elements. No neutral or cationic cages were produced but the compounds $SCl_3(SbCl_6)$ and $SeCl_3(SbCl_6)$ were formed. These along with $SCl_{1.8}Br_{1.2}(SbCl_6)$ were examined because of the continuing interest[157] in the secondary bonding in this type of compound. Structural and spectroscopic data were interpreted to show that the products of the reactions of $NbCl_5$ and $TaCl_5$ with $SeCl_4$ are the ionic compounds $SeCl_3(NbCl_6)$ and $SeCl_3(TaCl_6)$, respectively.

Iodine, a much weaker oxidant, has been employed to prepare the new molecular cage compound $\alpha P_4Se_3I_2$. Crystalline AsSI can be obtained, by reaction of iodine and As_4S_4, at room temperature rather than by the usual high temperature method.[147] The compound AsSI is polymeric. No cations have been produced using iodine as an oxidant for the VB/VIB compounds.

One conclusion that can be drawn from the present work is that the M_7 birdcage structure is favoured by the P and As chalconides. This is evidenced by the large number of molecules produced as well as the production of the ions $As_3S_4^+$ and $As_3Se_4^+$. In addition, the attempted oxidative reactions involving compounds already exhibiting this structure (P_4S_3, P_4Se_3, As_4S_3) have generally led to no reactions, polymerization or complete degradation of the molecule rather than formation of other possible cages and clusters such as: a cage ($P_3S_3^+$), a simple ring (AsS_3^+) or a tetrahedron (As_3S^+).

The action of the oxidizing agents Cl_2, Br_2 and $SbCl_5$ on the VB/VIB compounds did not produce any novel compounds. This is probably due to the relative ease of oxidation of phosphorus and arsenic compounds compared to nitrogen in S-N compounds. The lower electronegativities of phosphorus and arsenic compared to nitrogen also results in the chalcogen atoms attached to phosphorus or arsenic being more susceptible to oxidative attack. The production of the molecular compounds $\alpha P_4Se_3I_2$ and AsSI rather than ionic species is also not too surprising considering the polarizability of iodine.

VI-2 Suggestions for Future Work

Much remains to be done in the area of Group VB chalconide chemistry. More specifically, substantial work is necessary to determine: 1) structural parameters for many of the compounds prepared; 2) possible formation of other molecules having the S_4N_4 molecular structure and 3) which structural forms are produced by oxidation.

Separation of the ternary and quaternary Group VB chalconides could be undertaken. This might be achieved by chromatography or by zone refining. Crystal structures could then be determined for individual compounds allowing the NMR data to be more fully evaluated. Complete leaching of the melts should be carried out with examination of the remaining solids. It is quite possible that insoluble compounds with, for example, the S_4N_4 structure have been produced.

Table VI-2 gives the first order ^{31}P NMR spectral types and the number of each for cage compounds of phosphorus and sulfur based on the P_4 tetrahedron, excluding all those with dithio linkages. Some of the geometrical possibilities are probably too highly strained to exist but considering the wide range of known phosphorus sulfides it is not unreasonable to expect that at least one isomer of P_4S_8 might be produced.

TABLE VI-2 ^{31}P NMR Patterns for Possible Phosphorus-Sulfur Cages

Elemental Composition	Number of Exocyclic Sulfurs				
	0	1	2	3	4
	Spectral Patterns and Number of Each ( )				
P_4	A_4(1)				
P_4S	A_2B_2(1)	AB_3[a](1)			
P_4S_2	A_4(1),A_2BC(1)	A_2BC(2)	A_2B_2(1)		
P_4S_3	AB_3(2),AA'BB'(1), A_2BC(1)	A_2BC(3),ABCD(1)	A_2B_2(2),ABCD(1)	AB_3(1)	
P_4S_4	A_4(1),A_2BC(1)	AB_3(2),A_2BC(3), ABCD(3)	A_2B_2(1),AA'BB'(1), A_2BC(2),ABCD(2)	A_2BC(2)	A_4(1)
P_4S_5	A_2B_2(1)	A_2BC(3),ABCD(1)	AA'BB'(2),A_2BC(3) ABCD(3)	A_2BC(3), ABCD(1)	A_2B_2(1)
P_4S_6	A_4(1)	A_2BC(2)	A_2B_2(1),AA'BB'(1) A_2BC(2),ABCD(2)	AB_3(2),A_2BC(3) ABCD(3)	A_4(1),A_2BC(1)
P_4S_7		AB_3(1)	A_2B_2(2),ABCD(1)	A_2BC(3),ABCD(1)	AB_3(2),AA'BB'(1), A_2BC(1)
P_4S_8			A_2B_2(1)	A_2BC(2)	A_4(1),A_2BC(1)
P_4S_9				AB_3(1)	A_2B_2(1)
P_4S_{10}					A_4(1)

[a] Does not necessarily imply second order. Spectrum could also be A_3B.

It should be possible to study the phosphorus-sulfur system completely with the present accessibility of high field NMR spectrometers. These additional studies would be of interest because, as was noted earlier, no trends can be detected in the NMR data of the phosphorus sulfides studied to date. Individual compounds should also be separated and their crystal structures determined.

The very low solubility of most of the Group VB chalconides resulting from strong intermolecular forces in the crystals has been a problem for the formation of adducts. Adduct formation might be facilitated by refluxing the chalconides and Lewis acids in solvents for long periods of time. Fusion reactions could be investigated with certain solid Lewis acids like $AlCl_3$.

It was observed during the course of this work that a 2:1:1 As:S:Se fused mixture oxidized by AsF_5 gave an orange powder the Raman spectrum of which did not appear to be the sum of those of $As_3S_4(AsF_6)$ and $As_3Se_4(AsF_6)$. It is possible that cations such as $As_3S_3Se^+$ were produced in this reaction. Selenium-containing cations could be studied by recording the ^{77}Se NMR spectra of isotopically enriched samples.

The P_4S_3/AsF_5 and P_4Se_3/AsF_5 systems will have to be studied further but in the light of the present work, oxidation of S_4N_4-shaped molecules would probably be more fruitful for attempts to produce cationic species. The compounds α and βP_4S_4 are examples of compounds that could be oxidized. Further characterization of P_4Se_4 must be undertaken before it is used in oxidative studies because this compound[89] may be a birdcage-shaped molecule with an exocyclic selenium. The selenium analogues of α and βP_4S_4 could probably be made using a synthesis analogous to Sheldrick's synthesis for the sulfur compounds:

$$P_4Se_3 + I_2 \xrightarrow[CS_2]{RT(0^\circ C)} \alpha(\beta)P_4Se_3I_2$$

$$\alpha(\beta)P_4Se_3I_2 + ((CH_3)_3M)_2Se \longrightarrow \alpha(\beta)P_4Se_4 + 2(CH_3)_3MI$$

$M = Si, Ge$

If $((CH_3)_3M)_2S$ was employed several new ternary compounds might be prepared.

The only cage anions of the Group-VB-chalconides excluding those of the sulfur-nitrogen system that have been well characterized are $P_2S_8^{-2}$,[232] $P_4S_8^{-4}$[233] and $As_4S_6^{-2}$.[172] The latter two ions, for example, are structurally interesting in relation to the neutral molecules and cations discussed in this thesis. The ion $P_4S_8^{-2}$ contains a square of phosphorus atoms while all the cations and molecules prepared for this thesis have a triangle of group VB atoms. Studies to determine whether both structural skeletons can occur in cationic, anionic and neutral species could be undertaken. Oxidation of $As_4S_6^{-2}$ may only produce As_4S_4 or As_4S_3 or alternately an arsenic atom might be removed as in the oxidation of As_4S_4 by AsF_5. It must be noted that complications might also arise because of reactions with the cations of the salts of $P_4S_8^{-4}$ and $As_4S_6^{-2}$ ions.

Some aspects of the chemistry of the VB/VIB compounds have been explored. Investigations of the chemistry of sulfur-nitrogen compounds by other workers have generally led to the syntheses of products containing rings with varying degrees of multiple bond character. However, the reactions of VB/VIB compounds of the heavier group VB elements have generally led to the production of polymeric species (As_2S_3) or molecular species exhibiting the S_4N_4 or birdcage structures possessing essentially single bonds. Oxidation of these compounds has usually led to total degradation of the molecular cage resulting in the formation of polymers (AsSI) or simple halide-containing ions and molecules (SCl_3^+ and $AsCl_3$). Whether additional studies of VB/VIB compounds will produce further analogues of the cages $As_3S_4^+$ and $As_3Se_4^+$ or other new structural types remains to be determined.

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APPENDIX I Final Structure Factors for Disordered $P_2As_2S_3$ Columns are ℓ, $10{*}F_o$, $10{*}F_c$, $10{*}\sigma(F)$ 565 Reflections with $F/\sigma F>6$ R_1 = 0.028, R_2 = 0.035.

0,0,L			
2	1297	-1232	9
4	722	593	9
6	246	-231	9
0,1,L			
1	957	986	6
3	253	246	5
5	670	648	7
7	376	-369	8
0,2,L			
0	1550	-1579	7
2	794	786	7
4	527	525	6
0,3,L			
1	1574	1626	9
3	1079	-1092	11
5	525	521	6
7	404	397	8
0,4,L			
0	502	-497	6
2	600	588	7
4	1143	-1167	11
6	162	171	13
0,5,L			
1	1044	-1070	11
3	1307	1305	13
7	174	-163	15
0,6,L			
0	1311	-1296	12
2	299	-291	6
0,7,L			
1	479	-474	6
5	360	-365	8
7	200	203	14
0,8,L			
0	1159	1191	12
2	420	-413	9
4	206	207	11
6	143	-141	18
0,9,L			
1	373	374	7
3	249	-236	9
0,10,L			
0	274	-259	8
2	231	225	11
4	172	156	14
0,11,L			
1	218	211	11
3	357	-328	9
0,12,L			
2	322	323	10
1,0,L			
1	993	-931	7
2	710	660	8
3	195	-195	6
4	819	-797	8
5	656	638	7
7	287	-290	9
8	218	-236	13
1,1,L			
1	302	289	5
2	119	120	7
3	252	254	5
4	1178	-1163	13
5	193	184	9
6	723	716	8
7	237	237	11
8	191	-199	14
1,2,L			
1	645	637	7
2	858	-870	9
3	610	-603	7
7	124	-113	17
1,3,L			
1	808	809	8
2	492	496	5
3	760	733	8
5	312	-314	7
8	253	-263	12
1,4,L			
1	725	-721	9
2	456	443	5
3	1026	1052	10
4	319	336	6
5	453	-451	6
6	192	-175	11
7	472	473	7
8	172	195	16
1,5,L			
1	196	208	7
2	514	-525	6
3	215	-214	7
5	403	406	6
6	122	-118	17
1,6,L			
1	592	597	6
2	142	-144	10
3	320	-315	6
4	220	213	9
6	246	234	10
7	142	-125	18
1,7,L			
1	138	-129	11
3	150	-160	12
4	486	492	6
5	134	-130	15
6	322	-320	9
7	146	-129	18
1,8,L			
2	392	387	7
5	332	331	9
6	127	133	20
1,9,L			
1	308	-314	9
2	124	121	16
4	358	-348	9
6	341	324	10
1,10,L			
2	192	-183	12
1,12,L			
1	158	-151	16
3	136	142	20
2,0,L			
0	1034	963	7
1	749	726	8
2	1698	-1689	9
3	1163	-1123	11
4	295	282	6
5	748	740	8
6	443	-444	6
2,1,L			
0	920	-939	7
1	810	800	8
2	912	898	9
3	185	-172	6
4	750	-740	8
5	113	-113	14
6	229	-217	9
7	172	-175	14
2,2,L			
0	902	-929	8
1	707	713	7
2	125	-115	8
3	613	621	7
4	114	-109	11
6	176	177	11
2,3,L			
0	1573	-1648	9
1	425	432	5
3	1090	-1118	11
4	287	-301	6
5	173	173	10
6	400	406	7
7	124	-140	18
2,4,L			
0	178	-175	6
1	1491	-1557	11
2	929	922	9
3	196	200	7
4	282	-277	7

(continued...)

APPENDIX I (continued)

```
       2,4,L

5    237    -241     8

       2,5,L

0    798     806     8
1    543    -544     6
2    487    -494     6
3    581     588     7
5    379    -381     7
6    306    -306     9

       2,6,L

0    177     188     8
1    366     372     5
2    292     294     6
3    108     112    14
4    139     145    13
5    232    -228     9
6    157     167    15

       2,7,L

0    328     339     6
1    349    -357     6
2    385    -375     6
3    135     126    13
4    396     404     7
7    160     135    17

       2,8,L

0    694     700     8
1    276     273     8
2    365    -366     7
3    616    -611     7
4    241     239    10
5    193     190    13
6    188    -184    15

       2,9,L

1    359     370     7
2    502     501     6
4    185    -184    13
5    124     124    20

       2,10,L

0    253    -255     9
3    154     153    15

       2,11,L

0    195    -193    12
1    134     129    17
2    140     127    17
3    133    -145    13

       2,12,L

0    232    -221    12
1    255    -251    11

       3,0,L

1   1011     957     9
2   1228    1231     9
3    107      87    10
4     98     -99    13
5    203     194     9
6    452     441     6
8    364    -370     9

       3,1,L

1   1174   -1295     8
3    658     664     7
4    101      97    13
5    217    -216     8
6    352     345     7
7    340     335     8
8    190    -185    14

       3,2,L

1    176     170     5
2    455    -452     5
3    272     285     6
4    215    -217     7
5    104     108    15
6    227     232     9
7    148    -156    15
8    150     156    17

       3,3,L

2    410     418     5
3    184    -183     8
5    668    -697     7
6    113     123    17
7    181     200    13
8    183     171    15

       3,4,L

1    217    -211     6
3    119    -125    11
4    710     731     4
5    263    -265     9
6    650    -675     8
7    202     209    13

       3,5,L

1    349    -350     5
3    197    -195     8
4    259     251     8
5    573     572     7
7    219    -207    12

       3,6,L

1    407    -410     5
2    311    -313     5
3    162    -161    11
4    417    -411     6

       3,7,L

1    509     515     6
3    214    -218     9
5    161    -157    16

       3,8,L

2    373     377     7
3    164    -158    13
4    203    -201    11
6    159     157    16

       3,9,L

1    153    -143    13
3    386     391     9
4    146    -144    16

       3,10,L

2    133    -133    16

       4,0,L

0     95    -101    10
1   1392    1363    10
3   1680   -1737    11
4    359     323     5
6    146     137    13

       4,1,L

0    590     574     6
1    655    -649     7
2    959     960     9
4    734    -739     8
5    111     -76    14
6    222     217    10
7    129     112    17

       4,2,L

0    188     193     5
1    248    -247     4
2    364     372     5
3    338     329     5
4    275    -274     7
7    363    -363     8

       4,3,L

0   1157   -1206    10
1    335     336     4
2   1254    1306    11
3    250     247     7
4    171     168    10
5    117     107    15
6    166     178    13

       4,4,L

1    909    -940     9
2    494    -511     6
3    473     477     6
4    259     263     8
5    348    -344     7
7    365     381     9

       4,5,L

0   1627    1701    12
1    172    -172     8
2    554    -562     6
3    151    -146    11
4    115     120    15
6    120    -101    18

       4,6,L

1    125     129    12
2    109     104    14
3    426     429     6
4    228    -231     9
5    229     227    10

       4,7,L

0    223    -215     8
```

(continued...)

```
        4,7,L

1     239     238     8
2     492    -499     6
4     348     346     8
6     155    -162    17

        4,8,L

0     137    -138    13
1     628     632     7
3     511    -517     7
5     230     225    12

        4,9,L

0     348    -342     8
1     205    -200    11
2     136     140    15
4     387    -382     8

        4,10,L

0     135     122    15

        4,11,L

0     391    -372     8
2     133     137    19

        4,12,L

1     267    -259    11

        5,0,L

1     592    -563     6
2     367     355     5
3     226     227     7
4     151    -127    10
5     971    -990    10
6     192     202    11
7     216     222    12
8     273    -269    12

        5,1,L

1     512    -494     6
2     615     599     7
3     695     685     7
5     315    -313     7
6     263    -269     9
7     240     227    11

        5,2,L

1     472    -477     5
3     450    -449     5
4     235    -235     8
5     493     504     6
6     139     153    15

        5,3,L

1     191     200     6
2    1072   -1117    10
5     227    -223     9
6     336    -333     8
7     176     170    14

        5,4,L

1     552     563     6
2     242    -243     7
3     152     149    11
4     613     611     7
5     103    -104    17
6     414    -424     8
7     152    -135    17

        5,5,L

1     187    -192     8
2     622     637     7
4     408    -404     7
5     230     243    10
7     167    -163    16

        5,6,L

1     195     200     8
3     131     128    13
4     231    -229    10
5     346     345     8

        5,7,L

1     158     162    11
2     262    -263     8
3     304    -306     9
5     123     122    13
6     146     143    18

        5,8,L

1     126     121    15
2     143     141    14
3     253     257     9
4     137    -135    16
5     349    -345     9

        5,9,L

1     118    -141    18
2     235     227    10
3     242     245    11
4     148     133    13
5     132    -144    21

        5,10,L

1     141    -146    16
3     150    -155    16

        6,0,L

0     712    -693     9
1     673     641     7
2     387     355     5
3     167    -159     9
5     522     524     7
6     440     448     7

        6,1,L

0     913    -753     8
1    1504   -1496    11
3     214     215     8
4     195    -197     9

        6,2,L

0     139     141     8
2     553     551     6
3     139     137    11
4     270    -272     8
5     282    -278     9

        6,3,L

0     718    -731     7
1     280     232     6
3     654     656     7
4     442    -445     5
5     217    -213    10

        6,4,L

0     559     696     7
1     461    -474     5
2     990   -1032    10
3     190     185     9
4     588     511     7
5     168    -156    13

        6,5,L

0     104     105    13
2     379    -397     6
3     427    -442     6
4     187     177    11
5     279     271     9

        6,6,L

0     171    -166     9
2     221     231     9
3     147    -146    13
4     236    -239    10
5     211    -215    12
6     199    -195    14

        6,7,L

0     406     414     6
1     649     658     8
4     144     158    16

        6,8,L

0     528    -519     7
1     224     217    10
3     220    -228    11

        6,9,L

1     506    -501     7
2     257     255    10

        7,0,L

1     506     492     6
2     176    -178     9
3     606     594     7
4     429    -426     6
5     623    -655     7
7     343     364     9

        7,1,L

1     504     486     5
2     317     318     6
3     134    -142    12
4     369     371     7
5     126    -126    16
6     172    -172    14
```

(continued...)

```
        7,2,L

 1    129    -113    11
 4    151     150    12
 5    393     391     8

        7,3,L

 2    442    -442     6
 3    369     370     6
 4    394     391     7
 5    142     140    16

        7,4,L

 1    165     156     9
 3    452    -456     6
 4    110    -123    18

        7,5,L

 1    362     371     6
 2    519     528     6
 4    207    -203    11
 6    234     229    13

        7,6,L

 1    392    -406     6
 2    121     127    15
 4    277     234    11

        7,7,L

 1    198    -206    11
 2    170    -179    12
 4    188    -189    13

        7,8,L

 3    163     157    14
 5    304    -306    11

        7,9,L

 3    133    -119    18

        8,0,L

 0   1287   -1293    14
 2    260     256     7
 3    319     313     7
 4    163    -178    13
 7    132    -191    15

        8,1,L

 0    111    -108    14
 1    580    -571     7
 2    171    -179    10
 3    230     227     9
 4    406     411     7
 5    327    -341     8

        8,2,L

 0    138     102    11
 1    264    -257     7
 3    299    -234     7
 4    315    -318     8

        8,3,L

 0    677     687     8
 1    385    -399     6
 2    189     196     9
 3    147     154    12
 4    107    -103    17
 5    170    -180    14

        8,4,L

 0    485     485     6
 1    409     414     6
 2    398    -406     6
 3    152     151    12
 4    536     555     7
 5    140     141    17
 6    149    -155    19

        8,5,L

 0    389    -395     6
 1    269     278     9
 3    340    -348     7
 4    146     141    15
 2    108      21    15

        8,6,L

 0    333     322     7
 1    149    -155    13
 2    221     233    10

        8,7,L

 1    290     281     8
 3    139    -129    16
 4    233    -225    12
 5    183     179    16

        8,8,L

 0    312    -321     9
 2    316     313     9
 3    170     174    15

        8,9,L

 0    115    -114    19
 1    195    -201    13
 2    158    -170    15
 3    196     134    14

        9,0,L

 1    172    -153    11
 2    584    -569     7
 4    429     412     7
 5    236    -206    11

        9,1,L

 2    227    -221     9
 3    114    -125    17
 5    225    -239    11

        9,2,L

 2    607     539     7

        9,3,L

 1    411    -408     6
 3    366    -367     7
 5    342     342     9
 6    171    -160    17

        9,4,L

 1    147     144    12
 2    352    -351     7
 3    150    -143    13
 4    200    -193    12
 5    185     184    14

        9,5,L

 5    361    -358    10

        9,6,L

 2    194     201    11

      \ 9,7,L

 2    119     115    19

        9,8,L

 2    310    -301    10

        9,9,L

 1    222     213    13

       10,0,L

 0    541     530     7
 2    307     319     8
 3    402     380     7
 5    238    -267    12

       10,1,L

 0    352     350     7
 1    124    -140    16
 2    518    -513     6
 3    397     388     7
 4    276     275    10

       10,2,L

 0    263    -259     9
 1    451    -437     7
 2    152     151    13
 3    121    -140    17
 4    160     127    14

       10,3,L

 0    214     213    10

       10,4,L

 0    310     319     8
 1    683     685     8
 2    262    -274     9
 3    139    -152    15

       10,5,L

 0    121    -157    18
 3    131     149    17

       10,6,L

 0    407    -416     8
 1    272    -284    10
```

(continued...)

APPENDIX I (continued)

```
        10,5,L

4     126      -20      19

        10,7,L

0     119     -107      19
2     279      272      10
3     204     -205      14

        10,8,L

3     199      215      16

        11,0,L

1     406     -405       7
2     385     -372       8
3     212     ’229      12
4     155      150      15

        11,1,L

1     176      192      13
4     330     -327       9

        11,2,L

1     266      260      10
2     146      138      15
3     301     -296       9
4     143     -140      19
```

```
        11,3,L

1     139      130      12
4     212      203      13
5     270      267      12

        11,4,L

1     278     -267      10
3     231      233      12

        11,5,L

3     151      143      17
4     209     -222      14

        11,6,L

1     257      250      11
2     143      137      17

        11,7,L

1     132     -128      19

        12,0,L

0     406      398       8
1     225     -227      11
2     305     -279       9
3     137      125      17
```

```
        12,1,L

0     125      115      19
2     154     -163      15
3     169      159      15
4     125      133      20

        12,2,L

0     454     -457       8
3     127      127      13
4     135      101      13

        12,3,L

2     221     -219      12
3     340     -324      10

        12,4,L

0     312      321      10
1     146      149      18
2     123      115      20
3     226     -224      13

        12,5,L

0     168     -134      16
3     293      297      15
```

```
        13,0,L

2     135      153      19

        13,1,L

1     136     -114      18
2     131     -114      19

        13,2,L

1     142      152      18

        13,3,L

2     229      234      13

        13,4,L

1     141     -145      19
2     137      135      21

        14,0,L

0     135      145      20

        14,1,L

0     323      325      10
1     186      192      16
```

APPENDIX II Final Structure Factors for $SCl_3(SbCl_6)$ Columns are ℓ, $10*F_o$, $10*F_c$, $10*\sigma(F)$ Reflections with $F/\sigma F>2$ R_1 = 0.038, R_2 = 0.042.

0,0,L

1	203	-231	3
2	1775	1953	9
3	616	572	7
4	1277	1310	12
5	2901	3067	13
6	1129	1113	11
7	418	420	5
8	991	970	10
9	865	-891	8
10	1845	1879	17
12	486	483	7
13	183	-197	13
14	238	159	11
15	219	211	13
16	127	137	20

0,2,L

0	1985	2011	11
1	162	-159	8
2	1707	1716	12
3	310	289	5
4	1477	1503	14
5	541	-537	6
6	1049	1025	10
7	789	788	9
8	790	805	8
9	462	-453	6
10	534	534	7
12	763	759	8
13	234	-221	12
14	372	374	9
15	143	-154	19
16	107	131	26

0,4,L

0	3140	3293	15
1	289	-251	7
2	1425	1387	14
3	527	491	5
4	985	949	9
5	956	976	10
6	568	587	6
7	474	492	6
8	806	822	8
9	498	-497	7
10	1060	1065	10
11	110	-83	20
12	458	481	8
13	103	-94	22
14	222	235	13
15	90	104	27

0,6,L

0	1651	1652	17
1	103	121	19
2	711	709	7
3	175	171	12
4	903	888	9
5	327	315	9
6	687	682	7
7	180	184	12
8	484	499	8
9	152	-167	16
10	608	585	8
11	127	130	19
12	252	270	13
13	80	-93	32

0,8,L

0	556	540	8
1	153	-160	17
2	522	518	8
3	132	142	18
4	422	423	9
5	96	-110	25
6	208	202	13
7	247	264	12
8	327	349	11
9	133	-104	20
10	274	290	13

0,10,L

0	667	663	9
2	315	323	12

1,1,L

0	635	652	7
1	2739	2932	9
-1	1662	1640	9
2	953	-943	9
-2	401	-335	5
3	452	450	6
-3	1974	2001	7
4	156	139	9
-4	385	392	5
5	1116	1117	11
-5	1601	1605	14
6	162	129	9
-6	551	569	6
7	940	910	9
-7	1688	1715	16
8	449	-435	6
-8	153	-170	10
9	400	413	7
-9	866	872	8
10	442	-436	7
-10	391	402	7
11	1020	1032	10
-11	798	922	8
13	100	122	21
-13	621	623	7
14	166	-131	14
-14	74	21	26
15	248	252	13
-15	323	322	10
-16	140	-124	13
-17	392	345	11

1,3,L

0	1410	1410	14
1	1132	1137	10
-1	2155	2163	14
2	431	-413	5
-2	771	750	8
3	1554	1633	15
-3	2027	2021	15
4	754	722	8
-4	738	-700	7
5	1568	1534	16
-5	1363	1342	16
6	592	-565	6
-6	1108	1093	10
7	699	695	7
-7	1676	1727	17
8	303	237	8
-8	115	114	15
9	595	586	7
-9	226	202	10
10	101	-114	13
-10	507	432	7
11	600	536	7
-11	993	957	9
12	138	-151	17
-12	66	43	27
13	370	350	9
-13	616	639	8
14	106	-43	21
-14	160	-132	17
15	304	395	12
-15	278	319	12

1,5,L

0	325	-311	7
1	1777	1757	10
-1	597	575	6
2	481	-458	6
-2	530	-530	6
3	91	56	13
-3	1003	989	10
-4	571	559	6
5	333	321	8
-5	487	492	7
6	237	254	10
-6	81	30	21
7	589	627	7
-7	804	820	8
8	430	-415	8
-8	197	-181	12
9	337	341	9
-9	883	854	9
10	342	-370	9
-10	114	116	19
11	737	758	8
-11	409	407	9
12	75	45	27
13	81	20	27
-13	361	362	10
14	115	-20	21
-14	151	165	18
-15	191	212	17

1,7,L

0	565	565	7
1	584	579	7
-1	792	768	8
2	132	117	16
-2	277	290	10
3	807	802	7
-3	1097	1066	11
4	255	275	11
-4	211	-190	12
5	760	777	7
-5	867	846	8
6	249	-241	11
-6	326	303	10
7	532	531	8
-7	716	727	8
8	224	238	13
-8	154	151	16
9	297	298	11
-9	172	158	15
-10	323	303	10
11	287	283	12
-11	424	416	10

1,9,L

0	84	-50	28

(continued...)

1,9,L

1	511	518	9
-1	371	382	10
2	136	-126	19
3	218	223	14
-3	406	403	10
4	199	169	15
-4	99	102	24
5	180	203	17
-5	146	188	20
-6	127	134	21
7	216	230	16
-7	358	352	11

2,0,L

0	1268	1246	6
1	471	507	4
-1	530	-569	4
2	1910	1973	8
-2	3070	3118	7
3	128	140	7
-3	887	980	6
4	869	864	6
-4	967	1028	7
5	62	89	14
-5	523	-525	4
6	1146	1114	7
-6	2116	2201	10
-7	607	562	4
8	1491	1474	10
-8	1411	1447	10
9	546	-525	4
10	449	441	5
-10	705	725	5
11	185	175	13
-11	172	169	9
12	792	784	8
-12	804	829	8
13	156	156	16
-13	518	507	7
14	64	36	29
-14	441	463	8
-15	300	-296	11
16	377	383	11
-16	463	456	9
-17	73	110	34

2,2,L

0	135	156	10
1	1373	1397	13
-1	393	413	5
2	1404	-1433	13
-2	1152	1143	12
3	1455	-1478	14
-3	2489	-2509	13
4	1724	1740	15
-4	2094	2056	14
5	451	-441	5
-5	915	-911	9
6	1545	1551	16
-6	2366	2423	16
7	1428	-1457	14
-7	68	61	13
8	565	551	6
-8	311	-319	7
9	184	174	11
-9	725	719	7
10	305	298	8
-10	643	631	6
11	392	411	8
-11	315	318	8
12	264	281	11
-12	749	752	7
13	170	-167	14
-13	149	-153	15
14	314	333	11
-14	719	723	7
15	94	32	24
-15	237	-238	12
16	437	432	11
-16	475	455	9
-17	163	143	17

2,4,L

0	1001	974	10
1	425	410	6
-1	197	-211	9
2	813	796	8
-2	1485	1454	14
3	332	-336	7
-3	149	-14	18
4	879	855	9
-4	952	916	9
5	181	170	11
-5	142	-125	11
6	832	840	8
-6	1459	1446	15
7	272	-264	9
-7	161	193	12
8	796	811	8
-8	645	663	6
9	192	-188	12
-9	110	128	18
10	450	430	8
-10	727	718	7
11	129	132	18
12	488	515	8
-12	538	562	8
-13	222	217	12
14	100	120	24
-14	370	381	10
15	104	35	25
-15	104	-117	23
-16	347	338	11

2,6,L

0	304	295	9
1	445	466	7
2	458	479	7
-2	1021	1058	11
4	729	739	7
-4	874	865	9
5	153	-157	15
-5	381	-395	8
6	684	697	7
-6	1099	1053	11
7	279	-259	10
-7	150	120	15
8	752	752	7
-8	451	410	8
-9	331	293	9
10	208	143	14
-10	341	319	10
11	146	142	19
-11	169	115	15
12	277	295	13
-12	381	372	10
13	129	33	21
-13	128	103	20
-14	399	333	11

2,8,L

0	356	340	9
1	187	172	13
-2	414	401	9
3	290	-295	11
-3	277	-271	11
4	465	473	9
-4	435	437	9
-5	106	-32	20
6	331	349	11
-6	559	543	9
7	232	-222	14
8	243	243	14
9	78	65	31
-9	130	130	20
-10	397	391	11

2,10,L

0	318	302	12
-2	450	451	11

3,1,L

0	825	-847	8
1	872	877	9
-1	1769	1811	11
2	577	-559	6
-2	185	191	7
3	749	741	7
-3	161	151	8
-4	1367	-1338	13
5	1655	1656	16
-5	1044	1037	10
6	141	-137	12
-6	319	313	6
7	644	627	6
-7	1103	1100	11
8	147	-132	14
-8	639	-631	6
9	1061	1079	11
-9	859	866	8
10	170	139	16
-10	378	-397	7
11	498	483	7
-11	624	630	6
12	266	252	10
-12	339	327	8
13	421	417	9
-13	572	586	7
14	95	-46	24
-14	119	-108	19
15	325	357	12
-15	197	298	14
-17	447	410	10

3,3,L

0	480	490	5
1	1401	1431	13
-1	931	947	9
2	704	677	7
-2	315	-317	6
3	496	476	5
-3	1491	1408	15
4	545	-536	6
-4	499	-436	5
5	2050	2032	10
-5	1512	1599	17
6	276	288	9
7	976	998	10
-7	411	386	6

(continued...)

APPENDIX II(continued)

3,3,L

8	155	-169	13
-8	104	85	15
9	557	539	7
-9	333	327	9
10	391	398	8
11	589	580	8
-11	511	492	7
12	304	325	11
13	330	344	10
-13	721	711	7
14	170	-210	18
15	390	392	11
-15	224	229	12
-16	118	95	21
-17	258	247	14
-6	81	10	18

3,5,L

0	890	-895	9
1	523	519	6
-1	1032	999	10
2	519	-521	6
-2	362	349	7
3	724	691	7
4	136	112	15
-4	569	-567	6
5	538	534	7
-5	414	402	7
6	204	-187	11
-6	138	148	14
7	239	253	11
-7	875	869	9
-8	588	-568	7
9	841	832	8
-9	675	651	7
10	108	-138	22
-10	255	-259	10
11	250	246	12
-11	405	383	9
12	77	107	29
-12	320	316	10
13	338	339	12
-13	277	265	11
-15	163	175	18

3,7,L

0	327	327	9
1	528	527	7
-1	525	529	8
2	397	414	9
3	392	399	9
-3	805	784	7
4	115	-124	20
-4	154	-176	16
5	1029	1032	10
-5	884	874	9
-6	64	34	23
7	491	500	9
-7	273	257	11
-8	156	143	16
9	370	343	10
-9	437	440	9
10	249	235	14
-10	83	76	27
11	252	228	13
-11	263	252	12
-12	105	-29	23
-13	427	398	10

3,9,L

0	193	-190	15
1	404	408	10
-1	282	301	12
-2	140	119	13
3	305	246	12
-3	199	186	13
5	273	267	13
-5	264	261	13
6	102	73	25
-7	294	280	12
-8	111	-107	25

4,0,L

0	3506	3730	9
1	1462	-1523	10
-1	1939	2021	9
2	2625	2697	10
-2	574	596	4
3	667	-633	5
-3	585	529	5
4	2042	2152	11
-4	571	-559	4
5	1819	1856	12
-5	1563	1549	10
6	941	918	6
-6	1812	1937	11
7	297	281	6
-7	1196	-1221	9
8	259	261	7
-8	1716	1761	12
9	600	607	5
-9	1068	-1113	7
10	1405	1417	14
-10	852	846	6
11	151	-175	17
-11	82	95	16
12	549	523	8
-12	364	371	8
-13	260	261	10
14	382	366	10
-14	97	-17	20
15	101	105	26
-15	72	43	27
-16	414	427	10
-17	197	-205	14

4,2,L

0	410	425	5
1	337	-317	5
-1	228	213	7
2	1768	1797	15
-2	1375	1409	15
3	159	-153	10
-3	395	-397	5
4	1031	1015	10
-4	714	539	7
5	277	-258	7
-5	465	-442	5
6	1408	1439	14
-6	758	712	7
7	176	191	12
-7	241	-230	7
8	439	433	7
-8	1120	1111	11
9	289	258	9
-9	306	-327	8
10	428	463	8
-10	211	200	10
11	151	130	14
-11	268	-301	8
12	584	534	8
-12	855	845	8
14	306	236	12
-14	176	177	13
-15	91	-90	22
-16	216	223	13

4,4,L

0	1533	1543	15
1	749	-755	7
-1	734	713	7
2	1880	1852	19
-2	823	795	8
3	165	-132	12
-3	351	343	6
4	1220	1191	12
-4	102	76	15
5	624	617	6
-5	574	586	6
6	672	687	7
-6	973	966	10
7	312	325	9
-7	581	-561	6
8	317	340	9
-8	1241	1254	12
9	400	382	8
-9	589	-581	7
10	752	751	7
-10	593	581	7
11	142	-159	19
-11	95	-99	22
12	484	489	9
-12	421	411	8
13	82	2	29
-13	201	192	12
-16	286	279	12

4,6,L

0	872	886	8
-1	402	402	8
2	904	927	9
-2	612	600	7
4	699	699	7
-4	540	514	7
5	326	338	9
-5	296	261	9
6	740	762	7
-6	720	695	7
-7	281	-302	10
8	290	277	11
-8	658	621	7
9	246	203	12
10	497	507	9
-10	338	317	10
-12	370	353	10
-13	107	-10	21
-14	166	158	17

4,8,L

0	197	207	14
1	147	-150	17
2	669	666	8
-2	421	432	9
4	275	292	12
-4	250	263	12
5	116	-109	21
-5	64	23	29
6	361	368	11
-6	210	223	14

(continued...)

4,8,L

7	139	137	20
8	167	192	19
-8	451	466	10
-10	234	231	14
-11	132	-119	21

5,1,L

0	396	397	5
1	1547	1510	15
-1	2125	2150	14
2	303	-298	6
-2	316	297	6
3	1653	1644	17
-3	336	917	9
-4	429	422	5
5	1046	1036	10
-5	1465	1465	14
6	628	624	6
-6	237	-220	7
7	568	551	7
-7	1360	1359	13
8	259	-244	10
-8	222	215	9
9	529	536	7
-9	657	685	7
10	184	183	14
-10	341	-355	8
11	615	637	9
-11	634	642	6
12	249	-256	12
13	299	311	11
-13	458	464	8
-14	224	-193	11
-15	404	383	9
-16	176	-173	15
-17	144	161	19
4	69	52	22

5,3,L

0	556	539	5
1	568	561	6
-1	2353	2433	17
2	358	363	7
-2	556	549	6
3	1870	1887	19
-3	1471	1439	14
4	509	507	6
-4	249	-252	8
5	1097	1076	10
-5	1287	1245	13
-6	405	396	6
7	702	731	7
-7	1141	1170	11
8	129	158	17
-8	539	531	6
9	646	655	7
-9	303	299	8
10	231	240	12
-10	397	-390	8
11	256	283	12
-11	924	983	9
12	170	-178	17
13	447	430	10
-13	525	518	9
-14	256	-245	11
-15	253	268	11
-17	142	103	19
6	65	21	27

5,5,L

1	1170	1165	11
-1	868	862	8
2	413	-432	8
-2	75	-68	23
3	778	757	8
-3	264	245	9
4	209	-196	11
-4	590	572	6
5	457	454	8
-5	834	829	8
6	546	579	7
-6	390	-379	9
7	244	247	11
-7	790	763	9
8	282	-265	10
-8	125	-88	16
9	324	318	10
-9	712	681	7
10	80	56	28
-10	116	-136	19
11	490	524	10
-11	330	322	10
12	195	-187	17
-12	106	105	20
-13	190	139	14
-15	349	334	11

5,7,L

0	204	221	13
1	343	364	9
-1	990	978	9
2	378	344	9
-2	142	125	17
3	819	822	8
-3	828	803	9
4	144	162	18
5	491	473	9
-5	620	628	8
-6	131	137	18
7	550	546	9
-7	425	430	9
8	86	92	29
-8	329	335	10
9	329	313	12
-9	210	213	14
-10	144	-105	18
-11	455	467	10
-13	287	296	14

5,9,L

1	356	352	11
-1	415	430	10
2	97	-115	29
-2	81	45	27
3	429	396	10
-3	130	143	21
-4	200	171	14
-5	297	302	12
-7	345	325	12

6,0,L

0	1978	1933	11
1	244	-245	5
-1	148	114	7
2	1591	1563	14
-2	1919	1879	11
3	667	664	7
-3	957	951	7
4	787	775	9
-4	1713	1692	11
5	75	76	22
-5	62	-35	14
6	642	624	6
-6	1078	1045	7
7	416	415	9
-7	859	844	6
8	617	609	7
-8	1569	1553	11
9	528	-432	7
-9	79	-51	14
10	695	696	9
-10	512	543	5
-11	113	131	12
12	394	357	10
-12	738	772	7
13	104	-67	23
-13	76	64	24
-14	638	639	8
-15	156	-149	15
-16	198	191	14

6,2,L

0	1551	1552	14
1	100	-102	15
2	639	-654	7
-2	2040	2076	17
3	669	672	6
-3	1382	-1379	13
4	840	834	8
-4	1775	1770	17
5	103	-118	18
-5	68	25	20
6	665	647	6
-6	721	695	7
7	741	-746	7
-7	1371	1331	13
8	561	561	7
-8	261	247	8
9	223	-218	12
-9	142	142	13
10	599	597	8
-10	754	745	7
-12	1122	1103	12
-13	452	-448	9
-14	644	659	8
-17	145	105	19

6,4,L

0	1394	1413	14
1	96	-99	20
2	749	704	7
-2	1108	1086	11
3	291	277	9
-3	149	174	10
4	639	651	7
-4	1209	1209	12
-5	107	113	18
6	499	528	8
-6	681	706	7
7	133	102	17
-7	475	496	7
8	355	348	9
-8	919	930	9
9	251	-254	12
-9	119	-70	16
10	544	554	9
-10	602	589	7
12	206	211	15
-12	569	565	8

(continued...)

6,4,L

-14	446	433	9
-16	157	161	19

6,6,L

0	734	771	7
2	342	390	9
-2	962	956	9
3	453	468	9
-3	92	-44	22
4	371	392	9
-4	935	965	10
5	84	-92	26
6	385	414	9
-6	438	430	8
7	75	29	28
-7	480	481	8
8	484	482	9
-8	481	468	8
9	177	-192	18
-9	131	115	17
10	307	311	12
-10	345	328	10
-11	69	48	28
-12	495	495	9
-13	142	-153	20
-14	415	411	11

6,8,L

0	520	532	9
2	100	62	23
-2	364	381	10
3	102	54	23
-3	182	-182	15
4	326	338	11
-4	459	487	9
-5	90	79	24
6	201	241	16
-6	269	264	11
-7	173	191	16
-8	236	248	14
-9	123	-42	21
-10	311	350	13

7,1,L

0	222	-229	8
1	513	479	6
-1	1032	1013	10
2	639	-641	6
-2	101	-66	15
3	683	689	6
-3	1179	1163	11
4	312	321	8
-4	361	-364	6
5	454	432	7
-5	506	449	6
6	500	-519	7
7	517	505	7
-7	1575	1566	16
8	159	-138	14
9	484	492	8
-9	642	633	6
10	80	-81	26
11	376	379	10
-11	662	695	7
-12	110	120	19
-13	598	536	7
-14	168	179	15
-15	347	351	10
-16	205	-171	13
-17	372	384	11

7,3,L

0	316	326	8
1	754	768	7
-1	980	994	10
-2	606	-605	6
3	270	241	9
-3	1483	1489	15
4	247	260	10
5	771	809	7
-5	700	694	7
6	204	-214	12
-6	262	248	9
7	691	732	7
-7	812	810	8
8	272	-297	11
-8	211	217	10
9	337	335	10
-9	646	694	7
10	91	137	26
11	441	423	9
-11	785	763	8
-12	153	-166	14
-13	551	569	9
-14	237	229	12
-15	249	259	13
-16	76	-57	27
-17	253	257	14

7,5,L

0	308	-292	9
1	314	343	9
-1	400	412	8
2	491	-534	7
-2	164	155	13
3	659	644	7
-3	532	541	7
4	50	39	23
-4	170	-133	13
-5	293	320	9
6	325	-322	10
-6	153	-145	14
7	294	391	11
-7	1140	1132	11
8	89	55	25
-8	157	-156	14
9	320	395	11
-9	391	279	8
10	190	-178	15
-10	106	97	13
-11	333	352	10
-12	191	174	13
-13	317	314	11
-14	96	53	24
-15	290	239	12

7,7,L

0	251	270	12
1	405	494	9
-1	529	559	9
2	93	42	22
-2	258	-253	11
3	189	188	14
-3	727	765	8
4	220	229	13
5	444	473	10
-5	422	436	9
-6	157	131	15
7	424	423	10
-7	326	345	10
-8	134	131	13
-9	306	245	10
-10	85	74	26
-11	440	434	10
-12	111	-131	25

7,9,L

-1	171	140	17
-3	294	290	13

8,0,L

0	548	621	6
1	308	-312	8
-1	870	851	9
2	888	877	9
-2	263	242	8
3	677	-616	5
-3	490	472	5
4	1758	1784	13
-4	195	234	9
5	158	176	14
-5	889	-874	8
6	313	236	9
-6	2017	1993	12
7	105	-48	18
-7	779	-782	8
8	445	455	9
-8	1064	1079	11
9	454	446	9
-9	303	-261	8
10	429	446	10
-10	306	336	8
11	69	46	33
-11	395	398	8
12	294	283	12
-13	351	366	9
-14	459	501	8
-15	297	-295	10
-16	488	500	9
-17	101	-144	25

8,2,L

0	156	141	12
1	160	154	12
-1	544	-529	6
2	363	351	8
-2	833	838	8
3	252	-261	10
-3	105	-113	17
4	706	704	7
-4	661	626	6
5	304	-306	10
-5	831	-851	9
6	626	618	7
-6	742	734	7
7	198	-213	13
9	554	552	8
-9	617	593	6
10	149	168	18
-10	533	490	7
11	253	240	14
-11	224	-244	11
-12	387	391	9
-13	189	190	14
-14	493	486	9
-15	82	-129	26
-16	227	220	13

(continued...)

APPENDIX II (continued)

8,4,L

0	326	328	8
1	96	-83	22
-1	275	267	9
2	670	684	7
-2	389	364	8
3	376	-332	9
-3	342	338	8
4	1062	1062	11
-4	302	313	9
5	75	-78	27
-5	588	-573	7
6	282	303	11
-6	1148	1172	12
-7	407	-404	8
8	417	424	10
-8	724	738	7
9	261	223	12
-9	167	-175	14
10	213	204	16
-10	350	360	9
-11	165	163	14
-13	281	269	11
-14	347	341	11
-15	184	-163	15
-16	357	342	11

8,6,L

0	397	421	9
1	126	119	18
2	290	296	11
-2	418	389	8
3	149	-167	17
4	577	597	9
-4	425	409	8
-5	231	-240	11
6	332	330	11
-6	694	686	8
8	350	324	12
-8	334	295	10
-10	339	333	10
-11	75	30	28
-12	192	196	15

8,8,L

-1	160	-118	16
2	306	270	11
-2	245	265	13
3	132	-100	20
-3	66	91	33
-4	260	241	12
-5	164	-162	17

-6	309	327	12
-8	262	285	14

9,1,L

0	109	-118	17
1	870	851	9
-1	549	527	6
2	114	-81	17
-2	416	404	7
3	837	827	8
-3	688	619	5
-4	452	-455	7
5	953	944	9
-5	725	704	7
-6	257	-266	9
7	257	254	11
-7	669	643	6
8	178	297	16
-8	248	-226	9
9	443	426	9
-9	595	609	7
10	105	110	25
-10	138	-165	15
11	290	287	13
-11	140	124	15
-12	104	-146	20
-13	545	559	8
-14	102	-121	21
-15	219	223	13
-16	88	-91	25
-17	172	194	18

9,3,L

0	210	-198	11
1	589	594	7
-1	851	870	8
2	299	297	9
-2	356	348	8
3	791	820	8
-3	950	922	9
4	218	219	12
-4	432	-442	7
5	754	779	7
-5	419	409	7
6	134	-135	18
-6	142	173	14
7	463	442	9
-7	460	432	7
8	283	288	12
-8	130	-60	14
9	479	478	10
-9	553	557	7
-10	358	-338	9

-11	351	356	9
-12	170	-163	14
-13	514	493	9

9,5,L

0	92	7	24
1	647	657	9
-1	173	159	13
2	248	-253	11
-2	227	234	11
3	475	456	9
-3	236	240	11
4	177	-192	15
-4	174	-177	13
5	619	620	9
-5	640	632	7
-6	263	-274	11
7	94	69	26
-7	472	485	8
8	111	93	24
-8	283	-271	10
-9	436	438	9
-10	78	51	25
-11	65	59	30
-13	390	371	12

9,7,L

0	144	-90	17
1	429	414	9
-1	429	442	10
2	260	239	13
-2	151	193	15
3	358	349	11
-3	538	525	9
4	172	92	21
-4	109	-102	21
-5	247	252	12
-6	145	149	17
-7	183	203	16
-9	337	339	11
-10	137	-125	20
-11	274	251	12

10,0,L

0	809	757	8
1	64	-75	29
-1	234	223	11
2	1441	1445	15
-2	1018	1031	11
-3	483	433	7
4	586	602	8
-4	558	641	7

5	267	255	11
-5	165	137	13
6	476	458	9
-6	642	647	7
7	249	247	13
-7	279	-293	10
8	247	260	13
-8	1003	997	10
9	105	118	25
-9	99	59	21
10	362	343	11
-10	371	353	8
-11	363	-341	9
-12	410	443	9
-14	281	279	11
-15	93	-106	26
-16	165	195	18
-17	108	-116	24

10,2,L

0	909	905	8
1	357	-348	8
-1	202	-229	12
2	622	619	7
-2	1432	1445	15
3	365	349	9
-3	222	-229	10
4	347	344	9
-4	304	304	9
5	291	277	10
-5	523	539	7
6	257	259	11
-6	119	133	17
7	232	-211	12
-7	325	306	9
8	393	403	11
-8	553	550	7
9	110	89	24
-9	168	-184	14
-10	686	725	7
-11	631	-642	8
-12	757	705	8
-14	87	105	27
-15	71	120	31
-16	87	33	25

10,4,L

0	611	636	8
1	83	-64	24
-1	95	132	22
2	860	854	8
-2	711	737	7

(continued...)

APPENDIX II (continued)

10,4,L

-3	177	154	13
4	437	443	9
-4	440	432	9
5	219	215	13
-5	229	231	11
6	330	366	11
-6	443	481	8
-7	158	-140	15
8	173	183	18
-8	625	652	8
-9	66	-22	27
-10	391	381	9
-11	258	-226	11
-12	349	354	10
-14	164	163	17

10,6,L

0	430	442	10
1	113	-62	21
-1	87	-48	25
2	583	586	9
-2	663	676	8
3	135	133	20
-3	87	34	26
4	208	202	15
-4	344	322	9
5	81	124	33
-5	210	185	13
-6	246	232	12
-7	92	61	24
-8	377	368	10
-10	324	314	11
-11	224	-228	15
-12	360	385	12

11,1,L

0	247	-261	11
1	430	418	8
-1	898	889	9
-2	174	155	13
3	633	633	8
-3	675	666	7
-4	114	133	19
5	167	155	15
-5	670	676	7
-6	126	-109	16
7	213	211	15
-7	700	698	7
-8	293	264	9
-9	647	646	7
-10	113	-134	20
-11	367	379	9
-12	90	81	24
-13	361	359	10
-15	262	361	11
-16	118	-101	24

11,3,L

0	140	-140	16
1	505	527	8
-1	979	984	9
2	153	161	17
-2	124	-120	18
3	346	358	10
-3	597	640	8
4	135	126	18
-4	286	285	10
5	271	270	11
-5	528	534	8
6	107	108	23
-6	160	128	14
7	265	277	14
-7	392	409	8
-8	169	139	15
-9	646	704	8
-10	227	-228	12
-11	473	478	9
-12	73	-3	28
-13	255	261	12
-15	241	240	14

11,5,L

0	188	-144	14
1	249	244	12
-1	386	427	10
-2	134	159	18
3	473	482	10
-3	389	375	9
4	163	-117	17
-5	504	524	9
-6	195	-195	13
-7	510	516	9
-8	160	144	16
-9	336	324	10
-11	202	295	15
-12	109	95	24
-13	267	262	14

11,7,L

-1	535	555	10
-3	299	315	12
-4	130	113	22
-5	281	290	13
-6	146	125	13
-7	178	178	16

12,0,L

0	143	135	16
-1	387	356	9
2	289	265	10
-2	394	373	9
-3	157	-163	15
4	596	553	9
-4	943	977	9
5	337	-232	11
-5	613	-573	7
6	280	286	13
-6	820	793	8
-8	592	549	9
-9	283	315	11
-11	350	349	10
-12	357	301	10
-13	166	-153	16
-14	599	605	9
-15	261	-150	15

12,2,L

0	351	345	9
1	96	-129	23
-1	285	-257	10
2	137	133	18
-2	509	533	9
3	150	154	17
-3	215	-221	12
-4	765	747	7
5	210	-212	14
-5	136	-157	16
6	290	300	13
-6	204	195	12
-7	143	141	15
-8	521	539	8
-9	88	73	24
-10	374	355	9
-12	364	317	10
-14	497	335	11
-15	89	42	25

12,4,L

0	151	157	17
-1	109	142	22
2	229	225	14
-2	326	318	10
3	112	31	22
-3	191	-194	22
4	356	337	11
-4	629	649	8
5	253	-239	14
-5	341	-333	10
-6	475	500	9
-7	71	-28	28
-8	434	449	9
-9	141	144	17
-10	113	92	19
-11	172	207	17
-12	250	237	13
-13	74	-80	33

12,6,L

0	276	283	13
-2	287	276	12
-3	88	-127	29
-4	442	451	10
-6	236	260	14
-7	90	59	25
-8	276	264	13

13,1,L

1	147	151	17
-1	151	135	15
2	137	-105	17
-2	171	-192	15
3	401	372	10
-3	591	512	9
4	131	-72	19
-4	164	-181	15
5	274	278	13
-5	342	325	9
-6	321	-332	10
-7	441	423	9
-9	216	233	13
-11	301	301	11
-12	142	-171	19
-13	292	235	12

13,3,L

0	104	-58	22
1	209	199	14
-1	278	293	11
2	84	5	27
-2	159	-163	17
3	350	342	11
-3	492	485	9
4	88	50	27
-5	109	138	22
-6	135	-133	18
-7	359	383	10

(continued...)

APPENDIX II (continued)

13,3,L

-8	80	-52	25
-9	305	313	11
-10	123	-121	20
-11	331	344	11
-12	165	-113	16
-13	197	196	16

13,5,L

1	97	116	28
-1	87	65	28
-2	110	-95	23
-3	295	311	12
-4	143	-150	20
-5	354	347	11
-6	228	-243	14
-7	313	331	12
-9	126	100	20
-10	88	95	29

14,0,L

0	285	246	12
1	85	91	27
2	442	463	10
-2	151	174	16
3	169	-123	18
-3	189	207	14
-4	360	362	10
-5	274	-309	12
-6	415	408	9
-7	275	-243	11
-8	309	332	11
-9	91	-99	24
-10	292	274	11
-11	112	-103	22

14,2,L

0	390	416	11
1	180	-148	16
-1	214	-214	14
2	364	356	12
-2	300	288	11
-3	231	194	13
-6	137	174	14
-7	110	-133	22
-8	421	405	10
-9	371	-354	11
-10	446	505	10
-11	207	-231	16
-12	93	74	26

14,4,L

0	254	250	14
-1	87	-13	27
-2	126	153	23
-3	103	113	25
-4	230	235	14
-5	152	-164	13
-6	287	326	13
-7	163	-157	17
-8	244	266	14
-9	128	-118	21
-10	256	252	14

15,1,L

0	94	-85	31
-1	224	244	15
-2	107	119	25
-3	284	369	11
-4	76	3	29
-5	274	283	12
-6	71	-29	31
-7	295	286	12
-8	103	-118	24
-9	342	339	11
-10	94	-18	25
-11	143	128	19

15,3,L

-2	131	67	20
-3	276	276	13
-5	184	195	17
-7	267	258	13
-9	198	-176	16