ADDITION COMPLEXES OF 8-HYDROXYQUINOLINE
AND
DERIVATIVES WITH U(VI) AND Th(IV)

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SCOPE AND CONTENTS:

The position of the proton in the addition complexes formed between 8-hydroxyquinoline and U(VI) and Th(IV) has been located by infrared studies. On the basis of these studies and experiments involving the use of C^{14}—8-hydroxyquinoline, it is proposed that the additional molecule of 8-hydroxyquinoline in the Th(IV) complex is coordinated to the metal-ion, and is not a lattice component.

Several new addition complexes of U(VI) and Th(IV) with derivatives of 8-hydroxyquinoline have been synthesized and characterized, and have been shown to be structurally similar to the corresponding complexes of 8-hydroxyquinoline.

The composition and thermal conversion of the U(VI) and Th(IV) addition complexes of 8-hydroxyquinoline have been re-examined, and their interaction with solvents and solutions containing other ligands has been studied.

The addition of 8-hydroxyquinoline to the normal complexes formed between 8-hydroxyquinoline and U(VI) and Th(IV) has also been re-examined.

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GENERAL INTRODUCTION

The organic reagent, 8-hydroxyquinoline (8-quinolinol, oxine), reacts with metal-ions to form chelate compounds which are of considerable analytical importance. Indeed, no organic reagent has been more widely investigated than 8-hydroxyquinoline for analytical purposes. The literature pertaining to analytical applications of this reagent is extensive (e.g., 1), and studies relating to quantitative determinations, qualitative detections, or separations of metal-ions continue to appear regularly in the literature.

The analytical emphasis given to 8-hydroxyquinoline stems from the unusual versatility of this compound. Gravimetric, absorptiometric, fluorimetric and polarographic methods have all been developed for the determination of one metal-ion or another. A variety of titrimetric methods have also been developed: these include oxidimetric, bromometric, photometric, potentiometric, coulometric and amperometric titrations.

Because 8-hydroxyquinoline is unselective in its reactions with metal-ions, its usefulness is often limited. Among organic reagents, unselectivity is not peculiar to 8-hydroxyquinoline, although it can be a more serious limitation with this reagent than with others. The selectivity of 8-hydroxyquinoline can be increased, however, by appropriate control of pH, or by the use of suitable complexing agents to mask interfering ions.

During approximately the last twenty years, a significant effort has been made to determine factors that govern the (solution) stability of metal chelates and the selectivity of the chelating ligand. Stability and selectivity have been found to depend upon such factors as the basicity of the ligand donor atoms, steric interactions arising from suitably placed substituent groups in the parent ligand, the polarizability of the donor atoms, and metal-ion properties such as charge, size and polarizability (e.g., 2-7). Much of this information has been obtained from studies involving the metal chelates of 8-hydroxyquinoline and its derivatives. For example, Irving and Rossotti (8) and Williams et al. (9) have demonstrated a direct relationship between the proton and chelate formation constants for sterically unhindered 8-hydroxyquinoline derivatives. Irving et al. (10) have shown that because of the lower basicity of the oxygen and nitrogen donor atoms, 5-nitroso-8-hydroxyquinoline is more selective than the parent compound, 8-hydroxyquinoline. Also, Irving and Rossotti (8), Kaneko and Ueno (11), and Billo (12) have shown that the stability of metal complexes derived from 2-substituted-8-hydroxyquinolines is lower than that of the corresponding complexes of 8-hydroxyquinoline (even on addition of the first ligand). This reduced stability has been attributed to steric effects, and is the primary reason advanced (13) to explain the analytically significant observation that 2-methyl-8-hydroxyquinoline does not precipitate aluminium(III)-ion from aqueous solution. Such studies as these have led to a much better understanding of the solution chemistry of metal-chelate compounds, and have given direction to the development of analytically useful reagents.

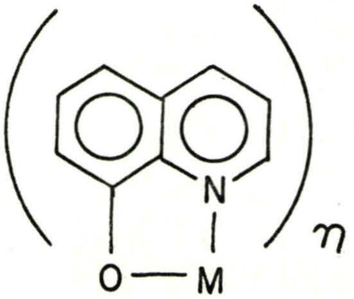
More recently, interest has been growing in the molecular structure of metal 8-hydroxyquinolinates in the solid state, and in the past few years, several X-ray structural determinations have been reported (14-22).

Normally, 8-hydroxyquinoline reacts with a metal-ion with charge

+n according to the reaction:

$$M^{+n} + nC_9H_6NOH = M(C_9H_6NO)_n + nH^+$$

The number of reacting ligands and of released protons are equal to the metal-ion charge, and the metal chelate formed contains n 5-membered rings (I):



I

With several metal-ions, however, 8-hydroxyquinoline reacts as follows:

$$M^{+n} + (n+1)\ C_9H_6NOH = M(C_9H_6NO)_n \cdot C_9H_6NOH + nH^+$$

The number of reacting ligands is one more than the charge on the metal-ion, and the resulting complex has an additional molecule of reagent, which retains its proton to preserve charge neutrality. These complexes have been termed addition compounds, adducts or solvates of 8-hydroxyquinoline.

This thesis is concerned with the addition compounds that are formed between 8-hydroxyquinoline (and its derivatives) and uranium(VI) and thorium(IV), two of the several metal-ions that form such compounds. In particular, study is given to (i) the composition of the addition compounds, (ii) the thermal preparation of the normal compounds, (iii) reactions of the adducts and normal compounds in solvents of different coordinating ability, (iv) the reaction between 8-hydroxyquinoline and the normal compounds, and (v) structural aspects of the adducts.

Although the uranium(VI) and thorium(IV) adducts of 8-hydroxyquinoline have been known for over 35 years and have been used in chemical analysis for many years, the chemical behaviour and structural nature of these compounds have not been fully investigated. In view of the current emphasis on high coordination-number polyhedra (23), any investigation yielding structural information is of particular interest.

HISTORICAL INTRODUCTION

The metal-ions known to yield solid addition compounds with 8-hydroxyquinoline are listed in Table I, together with appropriate literature references.

TABLE I

SOLID ADDITION COMPOUNDS OF 8-HYDROXYQUINOLINE

Ion	Compound	Reference
Ag(I)	$Ag(C_9H_6NO)\cdot C_9H_6NOH$	(22,24-30)
Co(II)	$[Co(C_9H_6NO)\cdot 2C_9H_6NOH]NO_3$	(31)
Mn(II)	$Mn(C_9H_6NO)_2\cdot 2C_9H_6NOH$	(32)
Sc(III)	$Sc(C_9H_6NO)_3\cdot C_9H_6NOH$	(33-42)
Th(IV)	$Th(C_9H_6NO)_4\cdot C_9H_6NOH$	(37-40,43-53)
U(IV)	$U(C_9H_6NO)_4\cdot C_9H_6NOH$	(53)
Zr(IV)	$Zr(C_9H_6NO)_4\cdot C_9H_6NOH$	(54)
Zr(IV)	$ZrO(C_9H_6NO)_2\cdot C_9H_6NOH$	(54)
Pu(VI)	$PuO_2(C_9H_6NO)_2\cdot C_9H_6NOH$	(55)
U(VI)	$UO_2(C_9H_6NO)_2\cdot C_9H_6NOH$	(20,21,37-40,43, 49,52,56-68)

Solid addition complexes have also been reported with a number of derivatives of 8-hydroxyquinoline (Table II).

TABLE II

SOLID ADDITION COMPOUNDS OF 8-HYDROXYQUINOLINE DERIVATIVES

8-Hydroxyquinoline Derivative	Compound	Reference
2-methyl	$Sc(C_{10}H_8NO)_3 \cdot C_{10}H_8NOH$	(39,40,69-72)
	$UO_2(C_{10}H_8NO)_2 \cdot C_{10}H_8NOH$	(39,40,69-72)
3-methyl	$Th(C_{10}H_8NO)_4 \cdot C_{10}H_8NOH$	(73)
5,7-di-X (X=Cℓ,Br)	$Sc(C_9H_4X_2NO)_3 \cdot C_9H_4X_2NOH$	(36,37,39)
	$Th(C_9H_4X_2NO)_4 \cdot C_9H_4X_2NOH$	(37,39,40,74)
	$UO_2(C_9H_4X_2NO)_2 \cdot C_9H_4X_2NOH^{*}$	(37,39,40,62)
5,7-diiodo	$UO_2(C_9H_4I_2NO)_2 \cdot C_9H_4I_2NOH^{**}$	(75)
5-chloro-7-iodo	$Sc(C_9H_4C\ell INO)_3 \cdot C_9H_4C\ell INOH$	(36)
	$Th(C_9H_4C\ell INO)_4 \cdot C_9H_4C\ell INOH$	(74)
	$UO_2(C_9H_4C\ell INO)_2 \cdot C_9H_4C\ell INOH^{**}$	(62)

[*] The reported composition of these compounds has been shown to be in error (76). The reaction product is $UO_2(C_9H_4X_2NO)_2 \cdot CO(CH_3)_2$, contaminated with coprecipitated reagent.

[**] The reported composition of these compounds is almost certain to be in error (see(76)).

In addition, 8-hydroxyquinoline forms solid adducts with covalent halides. Examples are $MX_4 \cdot nC_9H_6NOH$, where M = Sn(IV) or Ti(IV), X = F, Cℓ, Br or I and n = 1 or 2 (19,77,78), $SiF_4 \cdot C_9H_6NOH$, $SnF_4 \cdot 2C_9H_6NOH$ and $TiF_4 \cdot C_9H_6NOH$ (79

The existence of adducts in solution, particularly in solvent extraction systems, has also been reported (Table III).

A more detailed account of the uranium(VI) and thorium(IV) adducts follows.

PART A Uranium(VI) Complexes of 8-Hydroxyquinoline and Derivatives

Under appropriate conditions, reaction between uranium(VI) and 8-hydroxyquinoline in aqueous solution yields a brick-red compound with the assigned formula, $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$. This compound has been used for the quantitative determination of uranium for many years (e.g., 56,90,91). It was prepared and its composition determined first by Hecht and Reich-Rohrwig (56) and later by Frere (43) and Fleck (57). Since this early work, the compound has been reported in the literature many times (e.g., 37-40,49, 52, 58-68).

Although the 3:1 ratio for HQ:U* has become accepted, Claassen and Visser (58) found the 8-hydroxyquinoline content in the compound to be slightly low, giving a ratio that was not precisely 3:1. In many of the studies referred to above, the method of Moeller and Wilkins (61) was used to prepare the compound. In the present study, it will be shown that the compound obtained by this method is slightly deficient in 8-hydroxyquinoline.

Although the normal compound, bis(8-hydroxyquinolinato)dioxouranium(VI), cannot be precipitated directly, Frere (43) has shown that it can be prepared by controlled heating of the 3:1 compound, according to the reaction,

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*Throughout this thesis, HQ is used as an abbreviation for 8-hydroxyquinoline.

TABLE III

ADDITION COMPOUNDS OF 8-HYDROXYQUINOLINE IN SOLUTION

Ion	Compound	Reference
Ag(I)	$Ag(C_9H_6NO)\cdot C_9H_6NOH$	(80-82)
Ca(II)	$Ca(C_9H_6NO)_2\cdot C_9H_6NOH$	(81)
Sr(II)	$Sr(C_9H_6NO)_2\cdot 2C_9H_6NOH$	(81,83)
Ba(II)	$Ba(C_9H_6NO)_2\cdot 2C_9H_6NOH$	(81,84)
Co(II)	$Co(C_9H_6NO)_2\cdot 2C_9H_6NOH$	(81)
Zn(II)	$Zn(C_9H_6NO)_2\cdot 2C_9H_6NOH$	(81)
Zn(II)	$Zn(C_9H_5XNO)_2\cdot C_9H_5XNOH$ (X = H, 4-methyl, 5-Cℓ, 5-Br or 5-NO_2)	(85,86)
Cd(II)	$Cd(C_9H_6NO)_2\cdot 2C_9H_6NOH$	(81)
Sc(III)	$Sc(C_9H_6NO)_3\cdot C_9H_6NOH$	(81)
V(V)	$VO(OH)(C_9H_6NO)_2\cdot C_9H_6NOH$	(87)
V(V)	$VO_2(C_9H_6NO)\cdot C_9H_6NOH$	(88)
U(VI)	$UO_2(C_9H_6NO)_2\cdot C_9H_6NOH$	(81)
U(VI)	$M[UO_2(C_9H_6NO)_3]$ (M = sodium or quaternary ammonium ion)	(64,89)

$$\underset{\text{(brick red)}}{UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH} \xrightarrow[\text{2 hrs.}]{\sim 200°C} \underset{\text{(dark green)}}{UO_2(C_9H_6NO)_2} + \underset{\text{(sublimate)}}{C_9H_6NOH}$$

The thermal reaction has also been studied by thermogravimetric and differential thermal analysis (40,49,59,66). Van Tassel and Wendlandt (40,49), and Bordner and Gordon (66) found the 3:1 compound to be stable up to 200°C. However, Duval (59) reported the 3:1 compound was thermally stable up to only 157°C. All workers found that the bis compound began to decompose further at about 370°C towards U_3O_8. The mechanism of the thermal loss of 8-hydroxyquinoline has not been determined, although Horton and Wendlandt (40) have proposed that a molecular rearrangement (corresponding to a DTA endothermic peak at 150°C) occurs before evolution of the extra ligand. In the present study, additional information on the thermal reaction is presented.

The preparation of the bis compound by thermal conversion of the tris compound has been reported often (21,38,49,52,57,58,61,62,64,68). Surprisingly, however, the degree of experimental control required for the preparation of the <u>pure</u> bis complex has received little attention, and analytical data supporting the reported composition of the product are scanty. Claassen and Visser (58) stated that the duration of the heating period at a temperature (∿200-215°C) suitable for the conversion depends on the amount of the tris compound initially taken, and that too lengthy a period causes decomposition below the 2:1 level. This precaution seems to have been ignored by several subsequent workers, who most often have used a procedure (61) which recommends a heating period of 48 hours (in air) at 210-215°C.

It will be shown below that this procedure leads to appreciable decomposition of the bis compound, and a superior method for its preparation is described.

The structure of the bis compound is not known, although Bullwinkel and Noble (64) have speculated that it is an "infinite-type" complex with extensive polymerization of the uranyl groups.

Frere (43) has reported that on treatment with a solution of 8-hydroxyquinoline, the bis compound is converted to the tris complex (∿97% conversion*). Few experimental conditions were given. A more detailed study (involving C^{14}—8-hydroxyquinoline) is described in this thesis.

In acetone, chloroform or absolute ethanol, the bis compound undergoes disproportionation (64) according to the following reaction:

$$3\ UO_2(C_9H_6NO)_2 \xrightarrow{\text{solvent}} UO_2^{++}(\text{solvated}) + 2\ UO_2(C_9H_6NO)_3^{-1}$$

The formation of a red residue or a red colour in solution was taken as evidence for the occurrence of the above reaction. The authors also reported the formation of the tris compound by the action of dilute acid or alkali on the bis compound. The interaction of the bis compound with various solvents is given further study in the present work.

Until recently, two views were prevalent on the structural nature of the 3:1 uranium(VI)—8-hydroxyquinoline compound. In one view, the extra molecule of 8-hydroxyquinoline was considered to be merely a component of the crystal lattice, in which it is held by weak lattice forces between molecules of bis(8-hydroxyquinolinato)dioxouranium(VI). In the other view, all three 8-hydroxyquinoline molecules were considered to be bidentate ligands

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* This yield is in error. Correct calculation gives 89%.

coordinated to the central uranium atom. The evidence leading to these views follows.

Moeller and Ramaniah (62) found that the ultraviolet absorption spectrum of the 3:1 compound dissolved in chloroform is identical, except for intensity, to the spectrum for an equivalent amount of the 2:1 compound. The authors concluded that in solution, the uranium(VI) adduct dissociated to give the 2:1 compound, and that in the solid, the extra molecule of 8-hydroxyquinoline is a lattice component. According to Bullwinkel and Noble (64), however, the spectrophotometric data could be explained by disproportionation of the 2:1 compound, and not dissociation of the 3:1 compound.

By calorimetric and vapour-pressure measurements, Wendlandt et al. (49,39) determined the heat of interaction for the reaction,

$$UO_2(C_9H_6NO)_2(\text{solid}) + C_9H_6NOH(\text{solid}) = UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH(\text{solid})$$

The low values obtained (-4.9 and -4.2 kcal mole^{-1}, by the two methods) suggested that the additional molecule is only weakly held and, therefore, likely a lattice component. This interpretation has been criticized, since it ignores the energy required for the rearrangement of the bis compound (92). Wendlandt et al. (39,40) also determined the heat of dissociation for the following reaction:

$$UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH(\text{solid}) = UO_2(C_9H_6NO)_2(\text{solid}) + C_9H_6NOH(\text{gas})$$

(ΔH = 21.8 and 20±2 kcal mole^{-1}, by vapour-pressure measurements and differential thermal analysis, respectively) but no conclusion regarding the bonded nature of the extra molecule was drawn.

The only evidence for the coordination structure before the work of Bullwinkel and Noble (64) was that of Venkateswarlu and Rao (60), which indicated that in very dilute aqueous solution, the stoichiometry of the uranium(VI)—8-hydroxyquinoline complex was 3:1. Later, in a more convincing study, Bullwinkel and Noble (64) showed that the proton in the 3:1 complex (dissolved in acetonitrile) was considerably more acidic than the proton in free 8-hydroxyquinoline. Salts with the composition $M[UO_2(C_9H_6NO)_3]$, where $M = Na^+$, $(C_2H_5)_4\overset{+}{N}$, $(C_6H_5)_4\overset{+}{As}$, could be prepared in alkaline solution, indicating the presence of the anion $UO_2(C_9H_6NO)_3^-$ in solution. The anion was also indicated in the extraction of uranium(VI) into chloroform as the ion-pair species, $(M^+, UO_2(C_9H_6NO)_3^-)$, where M = quaternary ammonium-ion (89). Thus, these workers concluded that in the 3:1 complex (both in the solid and in solution), all three molecules of 8-hydroxyquinoline are coordinated to the central uranium atom (coordination number 8), and are essentially equivalent. Furthermore, it was proposed that in the solid compound, the acidic hydrogen is intermolecularly hydrogen-bonded between two uranyl oxygen atoms, resulting in long chains of the type $\text{---O{=}U{=}O---H---O{=}U{=}O---H---O{=}U{=}O---}$.

Van Tassel et al. (38) also found that the 3:1 compound is a stronger acid than 8-hydroxyquinoline, and concurred with the suggestion of Bullwinkel and Noble that all three molecules of 8-hydroxyquinoline are coordinated to the uranium atom.

Although the infrared spectra of the 2:1 and 3:1 complexes have been examined in the ranges 5000-250 cm^{-1} (68,93), 1200-700 cm^{-1} (63) and 900-400 cm^{-1} (52), little direct evidence has been found for the coordinated nature of the extra molecule. In the range 1200-700 cm^{-1}, the absence of vibrational bands of free 8-hydroxyquinoline was interpreted as evidence that the forces binding the 8-hydroxyquinoline moieties are sufficiently strong to modify the vibrational frequency of all 3 groups (63). Similarly, absence of free 8-hydroxyquinoline bands in the range 900-400 cm^{-1} led to the conclusion that the extra molecule is bonded to the central atom (52).

In all the infrared studies, no attempt was made to locate the acidic proton present in the 3:1 complex. In the present work, the infrared spectra are examined more closely, and the position of the proton in the 3:1 complex is located.

Recently (20,94), Hall, Rae and Waters determined the structure of the tris (i.e., the 3:1) compound by three-dimensional X-ray analysis. This definitive work proved that the extra molecule is coordinated to the uranium atom but, unlike the two bidentate ligands, through the phenolate oxygen only. Furthermore, it was shown that all three molecules of 8-hydroxyquinoline lie approximately in a plane perpendicular to the linear uranyl group, and that the monodentate ligand is twisted away from the uranium atom. The authors speculated that the proton is located on the uncoordinated nitrogen atom, and is probably hydrogen-bonded to the donor oxygen atom of a neighbouring bidentate ligand. In a similar X-ray study, Fleming and Lynton (21) also concluded that the extra molecule is bonded to the uranium atom through oxygen only.

Several uranium(VI) complexes with derivatives of 8-hydroxyquinoline have been described. Moeller and Ramaniah (62) reported the formation of complexes between U(VI) and 5,7-dichloro- and 5,7-dibromo—8-hydroxyquinoline. According to these workers, it is possible to precipitate both the 3:1 and 2:1

compounds if the initial ligand-to-metal ratio in solution is adjusted accordingly. Subsequently, Wendlandt et al. (37,39,40) studied the compounds by thermogravimetric, differential thermal analysis and X-ray diffraction methods. It was reported that the 3:1 and 2:1 compounds are crystallographically different (monoclinic and triclinic, respectively) and that the 2:1 compounds could not be prepared thermally from the 3:1 compounds. The 3:1 5,7-diiodo—8-hydroxyquinoline complex was observed to behave similarly (75).

Thompson (76,95) demonstrated, however, that the 5,7-dihalo derivatives form compounds with the composition $UO_2(C_9H_4X_2NO)_2 \cdot CO(CH_3)_2$, where x = Cℓ or Br)*. He found that the dihalo reagents were extremely insoluble, and that the excess amounts precipitated nearly quantitatively under the conditions reported by earlier workers, thus giving an apparent 3:1 stoichiometry for the compounds isolated from solution. Both X-ray diffraction and microscopic examination demonstrated the presence of large amounts of coprecipitated reagent.

With 2-methyl—8-hydroxyquinoline, a 3:1 compound is formed (39,40,69-72). This compound has been examined by thermogravimetric, X-ray diffraction, DTA and calorimetric methods.

The preparation of tris complexes with 5-substituted 8-hydroxyquinolines is described in this thesis. These complexes are shown to be structurally similar to the tris 8-hydroxyquinoline complex.

An unusual compound, $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$, has been described by Bordner et al. (65). To date, this compound has only been prepared by precip-

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* The compounds were precipitated from 30% V/V aqueous acetone, as prescribed by Moeller and Ramaniah (62).

itation from homogeneous solution. Its infrared spectrum is essentially identical to that of the tris compound (68,93). Magee and Woodward (96) have speculated that the compound is polymeric, containing units of the tris and bis compounds, but no definitive evidence is yet available.

PART B Thorium(IV) Compounds of 8-Hydroxyquinoline and Derivatives

In hot aqueous solution, thorium(IV) and 8-hydroxyquinoline react under appropriate conditions of pH and concentration to give an orange precipitate. Hecht and Reich-Rohrwig (56) appear to have been the first to prepare this compound, to which they ascribed the formula $Th(C_9H_6NO)_4 \cdot xH_2O$. Frere (43) showed subsequently that the ratio HQ:Th was 5:1, i.e., the compound contained one molecule of 8-hydroxyquinoline in excess of the normal valence requirement of thorium(IV). In a later paper, Hecht and Ehrman (44) substantiated this finding. Since Frere's work, the compound has usually been formulated as $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$.

At least three groups of workers have claimed, however, that the orange compound is not stoichiometric (48,50,51); the ratio HQ:Th is about 4.8:1 and the orange compound contains water.

Recently, Thomson (73) claimed to have prepared a compound having the stoichiometric composition. His conclusions were based only on the 8-hydroxyquinoline content of the compound, however. More extensive analytical data reported in the present thesis show that the stoichiometric 5:1 compound could not be obtained, at least by a procedure similar to Thompson's.

When thorium(IV) is precipitated by 8-hydroxyquinoline from cold aqueous solution (i.e., 50°C and lower), the precipitate is yellow and more voluminous than the orange precipitate obtained from hot aqueous solution.

Hecht and Reich-Rohrwig (56) considered this yellow compound to be the normal 4:1 compound, $Th(C_9H_6NO)_4$, without water of crystallization, but no analytical data to support this view was given. Corsini (97) has provided analytical data to show that the HQ:Th ratio is just less than 5:1.

Recently, Cardwell et al. (98) prepared a lime-green compound corresponding to the formula $Th_2(C_9H_6NO)_7\cdot OH\cdot 4H_2O$. The anhydrous compound was obtained on heating at 70°C. Also, Thomson (73) has reported the preparation of a yellow compound, $Th(C_9H_6NO)_3\cdot OH$.

The normal tetrakis compound, $Th(C_9H_6NO)_4$, can be obtained by controlled heating of the orange compound. The thermal reaction has been reported many times (37-40,43-47,49-52,97,99), but there is considerable disagreement on the temperature conditions required for the preparation (see (97) for a discussion). A simple procedure for the preparation of the <u>pure</u> tetrakis compound is described in the present work.

According to Wendlandt et al. (40,49), the thermal reaction is a two-step process:

$$2Th(C_9H_6NO)_4\cdot C_9H_6NOH = [Th(C_9H_6NO)_4]_2\cdot C_9H_6NOH + C_9H_6NOH$$

$$[Th(C_9H_6NO)_4]_2\cdot C_9H_6NOH = 2Th(C_9H_6NO)_4 + C_9H_6NOH$$

Borrel and Paris (46) also suggested a two-step process — an intramolecular dehydration to give $Th(C_9H_6NO)_4\cdot(C_9H_6NO)_2O$ and H_2O, and the subsequent volatilization of $(C_9H_6NO)_2O$ to yield $Th(C_9H_6NO)_4$.

The structure of the tetrakis compound has not yet been determined, although Dyrssen (100) has suggested that it is based on the square antiprism. In the light of current information on high coordination-number polyhedra (23), the suggestion appears reasonable.

Frere (43) has observed that when the tetrakis compound is in contact with a solution of 8-hydroxyquinoline, an orange compound approaching a 5:1 composition is obtained.* Few experimental details were recorded. A more detailed investigation of the addition reaction is described in the work to follow.

The structure of the 5:1 compound has not been determined. The additional 8-hydroxyquinoline molecule is thought to be either a crystal-lattice component, or a coordinated ligand equivalent to the other four ligands. The evidence leading to these views follows.

Moeller and Venkataramaniah (47) studied the ultraviolet absorption spectra of the 4:1 and 5:1 compounds in chloroform. They found that the addition of an equivalent quantity of 8-hydroxyquinoline to a chloroform solution of the 4:1 chelate gives a spectrum nearly identical to that of the 5:1 compound, suggesting that upon dissolution of the 5:1 compound, the extra molecule of 8-hydroxyquinoline is lost.

In the same study, the interplanar "d" spacings for both the 5:1 and 4:1 compounds were determined by X-ray diffraction. From the data, it was concluded that in the solid state, the two compounds are different. The 5:1 compound is not a physical mixture of the 4:1 compound and 8-hydroxyquinoline. The investigators concluded that although in the solid state the two compounds are different, in solution they become indistinguishable

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* Frere reported the extent of addition to be 97%. Recalculation of his data gave 85%.

and that, probably, the additional molecule in the 5:1 compound is only a lattice component.

Wendlandt et al. (39,49) determined the heat of solvation for the following reaction:

$$Th(C_9H_6NO)_4(solid) + C_9H_6NOH(solid) = Th(C_9H_6NO)_4 \cdot C_9H_6NOH(solid).$$

According to the investigators, the low value (-5.6 and -6.5 kcal mole^{-1}, by two different methods) for the heat of interaction supports the view that the additional molecule of 8-hydroxquinoline is held in the crystal lattice by weak electrostatic forces, similar to those binding chloroform in the chloroform-bearing chromium, iron and aluminium acetylacetonates. This interpretation of the measured heat of interaction has been criticized (92) on the basis that it ignores any energy involved in the rearrangement of the 4:1 complex.

Van Tassel and Wendlandt (38) found that the titration curve for the 5:1 compound dissolved in acetonitrile is different from that for the tris uranium compound in that it is very broad, with no discernible buffer region that could be ascribed to the proton in the complex. This suggested that the additional molecule of 8-hydroxyquinoline in the thorium compound is held in a different manner than the extra molecule in the uranium compound. According to the investigators, the formation of a complex anion in basic solution would require the "unlikely coordination number of ten for thorium". The authors apparently favour the view that the additional molecule is a lattice component. Although decacoordination for thorium has not been rigorously established, it is reasonably certain that coordination ten exists in at least a few thorium complexes (e.g., in the tropolonate anion, $Th(C_7H_5O_2)_5^-$ (23,101)).

In an infrared study of the 900-400 cm^{-1} region, Tackett and Sawyer (52) concluded that the extra molecule of 8-hydroxyquinoline is coordinated to the central thorium atom, since they were unable to detect any vibrational bands of free 8-hydroxyquinoline in the spectrum of the 5:1 compound. This conclusion can be criticized since it is unlikely that the vibrational bands of 8-hydroxyquinoline would be unperturbed by lattice forces even if the extra molecule is a lattice component.

By analogy to the tris uranium(VI) compound in which it was proposed that the proton is bonded between two uranyl oxygen atoms, Bullwinkel and Noble (64) have pointed out that if the additional molecule is coordinated in the 5:1 thorium adduct, the perplexing problem arises of where the proton is located.

Experimental evidence is provided in this thesis for the coordinated nature of the additional molecule of 8-hydroxyquinoline, and for the location of the acidic proton in the thorium adduct.

Thorium compounds of several substituted 8-hydroxyquinolines have also been studied. It has been reported that both the 4:1 and 5:1 compounds can be precipitated from aqueous solution by 5,7-dichloro—, 5,7-dibromo— and 5-chloro—7-iodo—8-hydroxyquinoline (74). The 4:1 complexes cannot be prepared thermally (37). 5,7-Diiodo—8-hydroxyquinoline apparently precipitates only the 4:1 complex (70). Moeller and Ramaniah (74) found that the spectra of chloroform solutions of the 5:1 complexes resemble those of solutions containing an equivalent amount of the 4:1 complexes and the free 8-hydroxyquinoline, and concluded that the additional molecule is not coordinated in solution. 2-Methyl—8-hydroxyquinoline forms only the 4:1 complex with thorium (69,102).

The synthesis of thorium complexes with 7-methyl—, 7-phenyl—, 7-t-butyl— and 5-phenyl—8-hydroxyquinoline are described in this thesis.

EXPERIMENTAL AND RESULTS

Apparatus

Certified volumetric ware was used when appropriate.

Weighings were made on a conventional balance using calibrated weights and, when necessary, on a semimicro balance. The milligram quantities of samples for carbon-14 measurement were weighed on a microbalance.

Measurements of pH were made with a Radiometer Model PHM_4 pH meter (Radiometer, Copenhagen) equipped with Beckman saturated calomel and E-3 (low sodium-ion error) glass electrodes.

Infrared spectra were recorded with a Beckman IR-5 infrared spectrophotometer (Beckman Instruments Inc., Fullerton, California). Spectra in the visible range were recorded with a Cary Model 14 spectrophotometer (Applied Physics Corporation, California). Absorbance measurements at particular wavelengths in the visible region were made using a Hitachi Perkin-Elmer Model 139 Spectrophotometer (Perkin-Elmer Corp., Norwalk, Connecticut), the cell compartment of which was maintained at 25°C.

The apparatus for the wet-oxidation of compounds containing carbon-14 and the collection of radioactive carbon dioxide from the oxidation has been described elsewhere (103). The carbon dioxide was collected in a stainless-steel Borkowski ionization chamber (Applied Physics Corporation, Pasadena, California). Measurements of carbon-14 radioactivity were made by the "rate-of-drift" method (104), using a vibrating-reed electrometer (Model 30E, Applied Physics Corporation). A combination of these techniques for carbon-

14 determinations has been reported (105) to yield results with a precision of 0.2 percent.

The apparatus for the conversion of the addition compound to the normal chelate consisted of a 40-ml flat-bottomed flask connected to the bent arm of a U-tube by a clamped ground-glass ball joint. The other arm of the U-tube was connected to an evacuating pump. In use, the apparatus was evacuated, the U-tube was then immersed in a dry-ice bath, and the flask was immersed in an oil bath and heated under vacuum (0.1 mm Hg). The sublimed 8-hydroxyquinoline was collected in the initial portion of the U-tube.

Sieves (U.S. Standard Sieve Series, A.S.T.M. Specifications, Dual Manufacturing Company, Chicago, Illinois) were used to control the initial particle size of the normal chelates in the addition reaction with 8-hydroxyquinoline.

Reagents

All common laboratory chemicals were either analyzed grade or of sufficient purity for the purpose intended, and were obtained from reputable suppliers.

The uranyl nitrate hexahydrate (Analar grade, British Drug Houses, Toronto) was used without further purification. For the work described in Section (g), PART A (below), a stock solution (1.53×10^{-4} M) was prepared and standardized by precipitation of ammonium uranate and ignition to U_3O_8 (106). 8-Hydroxyquinoline (Certified Grade, Fisher Scientific Company, Toronto) was purified by sublimation prior to use. The C^{14}-glycerol (0.5 mc, Volk Radiochemical Company, Chicago, Illinois) used for the synthesis of

C^{14}—8-hydroxyquinoline was 99% radiochemically pure. Stock solutions containing 1.4 mg Th/ml were prepared from thorium nitrate hexahydrate (Analar grade, British Drug Houses, Toronto) and adjusted to about pH 1.5 with freshly boiled nitric acid. Ethylenediammine (Certified Grade, Fisher Scientific Company, Toronto) was used without purification. 1,2-Dichloroethane (Certified Grade, Fisher Scientific Company, Toronto) was dried before use for at least 48 hours over molecular sieves (Fisher Scientific Company, Toronto). Reagent-grade 1,4-dioxane (Fisher Scientific Company, Toronto) was purified by refluxing over sodium for at least 24 hours, followed by fractional distillation through a 1-meter column packed with glass helices. The fraction boiling in the range 100.5-101.0°C was collected as required and used within 24 hours. Dimethylsulfoxide (Certified Grade, Fisher Scientific Company, Toronto) was used without further purification. The deuterium oxide (Columbia Organic Chemicals Company, Inc., Columbia, S.C.) used in infrared studies was 99.7% pure. Hexachloro-1,3-butadiene (Eastern Chemical Corporation, Newark, N. J.), used for preparing infrared samples, was of spectral purity. Derivatives of 8-hydroxyquinoline used in this work were available in the laboratory and were suitably pure.

C^{14}—8-hydroxyquinoline was prepared by a Skraup reaction between C^{14}-glycerol and O-aminophenol. The procedure was identical to that used by Corsini (97). The yield of crude C^{14}—8-hydroxyquinoline was 70 percent. The crude 8-hydroxyquinoline was steam-distilled and recrystallized from aqueous ethanol. The product was white and melted over a temperature range of 73.5-74°C (lit, 72-74°C, 73-74°C (107)).

The activity of the C^{14}—8-hydroxyquinoline was determined using the wet-oxidation and "rate-of-drift" technique referred to earlier. The specific activity of the 8-hydroxyquinoline was found to be 3.58±0.02 mv/sec/mg (9 determinations; the error is standard error). It is customary to express specific activity either as the number of disintegrations per minute per gram of substance, or as millicuries per mole of substance. In the present work, the specific activity in the above units can be converted to the customary units by either determining the head capacitance of the vibrating-reed electrometer and the efficiency of the ion-chamber, or by calibrating the instrument with compounds of known C^{14}— activity. As far as the work in this thesis is concerned, only relative, not absolute, values of specific acticity are required and hence, for convenience, the specific activity is expressed as mv/sec/mg.

Elemental Analyses

The elemental analyses reported in this thesis were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Max Planck Institut für Kohlenforschung, Mulheim (Ruhr), Germany. Some of the elemental metal analyses and the bromometric analyses were done in this laboratory.

PART A Uranium(VI) Complexes of 8-Hydroxyquinoline and Derivatives

(a) Syntheses

(i) The C^{14}—tris uranium(VI)—8-hydroxyquinoline complex: Uranyl nitrate hexahydrate (100 mg) was dissolved in 50 ml of water containing 2 drops of concentrated nitric acid. Then, one ml of a solution of C^{14}—8-hydroxyquinoline (100 mg in one ml glacial acetic acid) was added. To the resulting yellow solution, 5 g of urea were added and the solution heated to boiling. The solution was then placed on a steam bath for 4 hours. The red crystals which formed were removed by filtration, washed once with 5 ml ethanol (95 per cent) and several times with water, and then dried in a stream of air for one hour and at 110°C for one hour.

(ii) The tris uranium(VI)—8-deuteroxy-quinoline complex: 50 mg of uranyl nitrate hexahydrate were dissolved in 25 ml of deuterium oxide containing one drop of concentrated nitric acid. To this solution were added 50 mg of 8-hydroxyquinoline dissolved in 4 drops of glacial acetic acid and diluted with 2 ml of deuterium oxide. The solution was heated to 70°C and the pH raised to about 5.5 by the dropwise addition of a deuterium oxide solution of sodium hydroxide (0.5 M). After digesting for two hours, the precipitate which formed was filtered, washed with three 2-ml portions of deuterium oxide and dried in a stream of air for 10 hours, and finally, at 110°C for one hour.

(iii) The tris uranium(VI)—5-nitro—8-hydroxyquinoline complex: 100 mg of uranyl nitrate hexahydrate were dissolved in 50 ml of water containing one ml of nitric acid. Next, a solution of 5-nitro—8-hydroxyquinoline (130 mg dissolved in 5 ml of warm glacial acetic acid) was added dropwise with continuous stirring. Then 5.2 g urea were added, the solution heated to boiling and transferred to a steam bath for 4 hours. A yellow flocculent precipitate was formed. The pH of the supernatant liquid (after cooling to room temperature) was 5.2. The precipitate was filtered, washed once with ethanol and several times with hot water, and was then dried in a stream of air for 17 hours and at 70-75°C for 3 hours in vacuo (5 cm Hg).

Calculated for $UO_2(C_9H_5N_2O_3)_2 \cdot C_9H_6N_2O_3$: C, 38.67; H, 1.93; N, 10.03; U, 28.38.

Calculated for $UO_2(C_9H_5N_2O_3)_2$: C, 33.34; H, 1.55; N, 8.64; U, 36.70.

Calculated for $UO_2(C_9H_5N_2O_3)_2 \cdot H_2O$: C, 32.44; H, 1.81; N, 8.41; U, 35.71.

Calculated for $UO_2(C_9H_5N_2O_3)_2 \cdot NH_3$: C, 32.49; H, 1.97; N, 10.54; U, 35.77.

Found: C, 37.60; H, 2.04; N, 10.03; U, 29.70.

Clearly, the data are in best agreement with the tris complex, although a closer correspondence would have been desirable. The infrared spectrum (Section (d), below) leaves little doubt that the compound is essentially the tris complex. No attempts to prepare a purer compound were made.

(iv) The tris uranium(VI)—5-acetyl—8-hydroxyquinoline complex: This complex was prepared initially exactly as the 5-nitro—8-hydroxyquinoline complex, but the results of the elemental analyses were poor. The infrared spectrum, however, showed the characteristic $\overset{+}{N}H$ bands of the 3:1 complex (see Section (d), PART A, EXPERIMENTAL AND RESULTS). Therefore, the procedure was modified as follows. The amount of 5-acetyl—8-hydroxyquinoline was increased to 230 mg (i.e., 100 percent excess) and the pH of the solution was raised to 5.2 by adding aqueous ammonia (1.0 M). A red crystalline precipitate formed. The solution was filtered while hot. The precipitate was washed once with ethanol and several times with water and then dried in a stream of air for 2 hours and at 105°C for 2 hours.

Calculated for $UO_2(C_{11}H_8NO_2)_2 \cdot C_{11}H_9NO_2$: C, 47.74; H, 3.04; N, 5.06; U, 28.67.

Calculated for $UO_2(C_{11}H_8NO_2)_2$: C, 41.12; H, 2.51; N, 4.36; U, 37.04.

Calculated for $UO_2(C_{11}H_8NO_2)_2 \cdot H_2O$: C, 39.99; H, 2.75; N, 4.24; U, 36.03.

Calculated for $UO_2(C_{11}H_8NO_2)_2 \cdot NH_3$: C, 40.05; H, 2.90; N, 6.37; U, 36.08.

Found: C, 46.81; H, 2.86; N, 4.91; U, 27.59.

The data are in best agreement with the tris compound. The infrared spectrum (Section (d), below) confirms that the compound is essentially the tris complex. Attempts to prepare a purer compound were not made.

(b) Composition of the tris uranium(VI)—8-hydroxyquinoline complex prepared by the method of Moeller and Wilkins

In the present work, the tris compound was prepared by the widely used method of Moeller and Wilkins (61).

In the several preparations made, the pH of the supernatent liquid (cooled to room temperature) was in the range 4.9 to 5.2. The precipitate was collected in a sintered-glass crucible (medium porosity), washed with a 15-ml portion of ethanol and ten 15-ml portions of water, dried in a stream of air for one hour, and then kept for 24 hours in a dessicator containing anhydrous magnesium perchlorate. A few samples were further dried at 110°C for 3 hours prior to analyses. In one preparation, the procedure was slightly modified by increasing the ratio of 8-hydroxyquinoline to uranium from 3.4 to 4.5. The precipitate was washed with three 15-ml portions of ethanol and then with water as above, and dried without heating.

Samples from each preparation were taken for estimation of the uranium and 8-hydroxyquinoline content by ignition to U_3O_8 (108) and by bromometric titration (102), respectively. In the uranium determination, oxalic acid was not used as a covering layer. The ignition was completed by placing the crucible and its contents in a muffle furnace at 950°C for one hour. For the bromometric titration, a carefully weighed sample of the tris compound was transferred to an iodine flask, dissolved in 50 ml of 4 M hydrochloric acid, and then diluted to 100 ml with de-ionized water. The titration procedure was the same as that described by Corsini and Graham (102). The accuracy of the method was tested by titrating known amounts of purified 8-hydroxyquinoline under the conditions prevailing in the analysis of uranium-containing compound. From the percent uranium and 8-hydroxyquinoline, the HQ:U molar ratio in the tris compound was calculated (Table IV).

TABLE IV

ANALYSIS OF THE RED COMPOUND FORMED BETWEEN URANIUM(VI) AND 8-HYDROXYQUINOLINE

(For $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$, %U = 33.84 and %HQ, expressed as Q^- = 61.47)

Condition	%U	%HQ (as Q^-)	Molar Ratio HQ:U
Dried without heating	33.94* ±0.03	60.88* ±0.04	2.963 ±0.003
Dried at 110°C	33.96**	60.76† ±0.06	2.957 ±0.002
50% excess HQ; dried without heating	33.88† ±0.03	60.88‡ ±0.08	2.968 ±0.006

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* Average of 11 results; error is the standard error $(\sigma/\sqrt{n})$ (109).

**Single result.

† Two results.

‡ Three results.

Samples of the tris compound were also taken for the determination of the ratio of sublimed 8-hydroxyquinoline to the bis compound remaining after thermal conversion. The conversion was effected quantitatively by heating in vacuo at 210-215°C for 4 hours, as described in the next section. In all cases, a very small droplet of moisture was noticed below the deposit of 8-hydroxyquinoline in the U-tube. This deposit and the residual bis compound were separately dissolved in 4M HCℓ, determined bromometrically, and the ratio $HQ:UO_2Q_2$* calculated (Table V).

TABLE V

MOLAR RATIO $HQ:UO_2Q_2$ IN THE RED COMPOUND

Red Compound taken (mg)	HQ Sublimed (mg)	UO_2Q_2 Residue (mg)	Molar Ratio $HQ:UO_2Q_2$
307.9	61.1	245.5	0.957
152.5	30.6	121.2	0.969

In a similar experiment, only the percent sublimed 8-hydroxyquinoline was determined, based on the weight taken of the red compound (Table VI).

The data of all three experiments are consistent in showing that the tris compound is slightly deficient in 8-hydroxyquinoline, at least by the method used for the preparation (see Section (a), PART A, DISCUSSION).

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* $UO_2Q_2 = UO_2(C_9H_6NO)_2$

TABLE VI

PERCENT SUBLIMED HQ IN THE RED COMPOUND

Red Compound Taken (mg)	HQ Sublimed (mg)	% HQ Sublimed
881.4	176.6	20.04
533.6	105.9	19.85
535.9	106.2	19.82
535.1	106.9	19.97
	Average:	19.92±0.05*

* Error is standard error.

(c) Thermal preparation of pure bis-(8-hydroxyquinolinato)dioxouranium(VI) and thermal ligand exchange

Initial attempts to prepare the pure bis compound thermally were based on Moeller and Wilkins' procedure (61) involving heating the tris uranium(VI)—8-hydroxyquinoline compound in air at 210-215°C for 48 hours. Analyses of the product gave the following results: %U, 44.63±0.06 (2 results; theoretical, 42.64%); %HQ as Q^-, 46.86±0.06 (3 results; theoretical, 51.63%). These results show that appreciable decomposition of the bis compound occurred. The use of shorter heating times (30, 14 and 2 hours) resulted in compositions progressively closer to the theoretical. In one experiment, the bis compound was obtained in reasonably pure form on heating for two hours (%U, 42.38, and %Q^-, 51.61), although in general, the samples appeared to be somewhat red after this heating time.

Further experimentation showed that the thermal conversion can readily be made by heating in vacuo in the assembly described earlier. Several experiments were carried out to determine a suitable time and temperature range for the complete conversion of the tris compound to the pure bis compound. The residue in the flask was analyzed for uranium and 8-hydroxyquinoline as described earlier.

The data of Table VII show that the pure bis compound can be easily prepared thermally by heating the red compound (500-900 mg) in vacuo at 210-215°C for 4 hours. A red colour was still discernible after 2 hours. Heating periods of up to 37 hours have little effect on the composition of the bis compound.

Based on the above results, all subsequent thermal conversions of the tris compound were carried out by heating in vacuo at 210-215°C for 4 hours.

The possibility of intra and intermolecular ligand exchange* during the thermal reaction was investigated as follows. Known amounts of the C^{14}-tris uranium(VI)—8-hydroxyquinoline complex and of the inactive bis complex were mixed thoroughly and carried through the thermal conversion procedure. The specific activity of the residual bis compound and of the sublimed 8-hydroxyquinoline was determined. The data (Table VIII) were used to estimate the amount of ligand exchange that occurred during the thermal conversion (see Section (b), PART A, DISCUSSION).

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* A knowledge of whether ligand exchange occurs has a bearing on the interpretation of the data obtained in the C^{14} experiments described later.

TABLE VII

THERMAL PREPARATION OF PURE BIS(8-HYDROXYQUINOLINATO)DIOXOURANIUM(VI) IN VACUO

(For $UO_2(C_9H_6NO)_2$, %U = 42.64; %HQ as Q^- = 51.63)

Temperature = 210-215°C

Pressure = 0.1 mm Hg

Heating time	Analysis of residual bis compound		Molar Ratio
(Hrs)	%U	$\%Q^-$	Q^-:U
3	42.47[*]	51.40[*]	1.997
4	42.52[**] ±0.04	51.50[†] ±0.04	2.001 ±0.002
9	42.33 ±0.00	51.70 ±0.08	2.016 ±0.003
12	42.53 ±0.04	51.47 ±0.08	1.997 ±0.004
22	42.34 ±0.00	51.74 ±0.06	2.017 ±0.002
37	42.40 ±0.00	51.62 ±0.07	2.009 ±0.003

[*] Single determination.

[**] Average of 10 results; error is the standard error.

[†] Average of 15 results; all other values are the average of 2 results.

TABLE VIII

LIGAND EXCHANGE IN THERMAL REACTION

	Expt. I	Expt. II
Inactive bis compound taken	= 90.7 mg	58.7 mg
Active tris compound taken	= 60.5 mg	64.6 mg

Original activity of tris compound = 3.58 mv/sec/mg

	Expt. No.	Measured Sp. Act. (mv/sec/mg)	Sp. Act. for Complete Exch. (mv/sec/mg)	Sp. Act. for No Exch. (mv/sec/mg)	Percent Exchange
Sub. HQ	I	2.99	1.58	3.58	30
	II	3.16	2.02	3.58	27
Resid. bis compd.	I	1.30	1.58	1.24	18
	II	1.79	2.02	1.68	32

Average = 25±7

(d) Infrared spectra of the uranium(VI) complexes

The main purpose of the infrared studies was to attempt location of the acidic proton in the tris uranium(VI) complexes. Certain considerations prior to the recording of the infrared spectra of the uranium(VI) complexes led to the preparation of samples as mulls in hexachloro-1,3—butadiene. For example, in the absence of long pathlength cells, solution spectra in spectroscopic solvents such as $CC\ell_4$, $CHC\ell_3$ and CS_2 were precluded because of the very low solubility of the uranium complexes (particularly of the bis complex). Furthermore, because of solvent absorption in the proton region 3500-1600 cm^{-1}, perfectly matched cells would be required. The KBr disc technique was restricted because of the invariable presence of the absorption band due to water at about 3400-3450 cm^{-1}. The use of nujol as a mulling agent was similarly restricted because of absorption, particularly in the 3300 and 2000 cm^{-1} region. Accordingly, the samples were prepared as mulls in hexachloro—1,3-butadiene, which is transparent in the range 3600-1800 cm^{-1}. Sodium chloride windows (6 mm) were used and the spectra were calibrated against a polystyrene film.

All spectra were recorded from 5000-630 cm^{-1}. The spectra of the tris complexes of 8-hydroxyquinoline (A, Figure 1, APPENDIX I*) and 5-acetyl- and 5-nitro—8-hydroxyquinoline (A and B, Figure 2) exhibit two bands of primary interest; an unusually broad band of medium intensity centered at about 2650 cm^{-1} and a weaker one at 2050 cm^{-1}. These bands are not present in the sodium salt of the tris 8-hydroxyquinoline complex, or in bis(8-hydroxyquinolinato)dioxouranium(VI) (C, Figure 1), or in free 8-hydroxyquinoline (A, Figure 3). They are present, however, in the hydro-

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* **All infrared spectra are recorded in Appendix I.** For all addition complexes described in this thesis, about 15-25 mg of the compound was used in preparing the mull.

chloride salts of 8-methoxyquinoline (D, Figure 1), 2-methyl—8-hydroxyquinoline (C, Figure 2), 8-hydroxyquinoline and quinoline (B and C, Figure 3), and pyridine (Figure 4). In some instances the bands are better resolved and somewhat shifted.

In the spectrum of the tris complex of 8-deuteroxyquinoline (B, Figure 1), the intensity of the band at 2650 cm^{-1} is extremely weak, the band at 2050 cm^{-1} is broader and more intense, and a new band (sharp, moderate intensity) is present at 1524 cm^{-1}.

These and other features of the spectra are discussed further in Section (c), PART A, DISCUSSION.

(e) Interaction of the tris uranium(VI)—8-hydroxyquinoline complex with solvents

The general procedure was as follows. A saturated solution of the tris complex was prepared at the boiling point of the solvent. The excess solid was removed by filtration and the filtrate cooled to yield a crystalline solid. Further concentration of the solvent was sometimes necessary to obtain sufficient solid for examination. The solid was removed by filtration, dried first in a stream of air for one hour and finally at 105°C for 3 hours, and then identified by its infrared spectrum.

The compounds isolated from 1,2-dichloroethane, absolute ethanol and 1,4-dioxane were similar in appearance to the original red tris compound, and their infrared spectra had the characteristic absorption bands of the tris complex at 2650 and 2050 cm^{-1}. Thus, the tris complex is stable in these solvents, i.e., the extra molecule of 8-hydroxyquinoline is not displaced by the solvent.

In dimethylsulfoxide, the solubility of the tris complex was very high. Concentration of the solution to 1/4 of its original volume yielded no solid. On standing for one week at room temperature, the concentrated solution yielded a gum-like material which was removed by filtration and dried at 105°C for 6 hours. The infrared spectrum of the material showed the complete disappearance of the bands at 2650 and 2050 cm^{-1} and a new strong band at $1015cm^{-1}$. After one week, blood-red crystals appeared in the filtrate. These were removed and dried in a stream of air for one hour and at 105°C for 3 hours. The infrared spectrum of the crystals (A, Figure 5) was identical to that of the gum-like material. The results of elemental analyses were:

Calculated for $UO_2(C_9H_6NO)_2 \cdot OS(CH_3)_2$: C, 37.71; H, 2.85; N, 4.40; S, 5.04.

Found: C, 37.85; H, 2.99; N, 4.35; S. 4.85.

In similar experiments, it was found that pyridine and dimethylformamide also displaced the extra ligand (partially or wholly), as indicated by preliminary data (bromometric analysis). Further attempts to obtain pure pyridine and dimethylformamide adducts should be made.

(f) Exchange reaction between the tris uranium(VI)—8-hydroxyquinoline complex and C^{14}—8-hydroxyquinoline

The following experiment was carried out to determine whether the tris complex undergoes facile exchange in solution with free (C^{14}- labelled) 8-hydroxyquinoline. It was hoped that the result of this experiment might provide the basis for determining the bonded nature (i.e., coordination or lattice forces) of the extra molecule in the addition complexes of ions other than uranium(VI).

1,2-Dichloroethane was chosen as the solvent because of the stability (previous section) of the tris compound in it. Since, however, the solubility of the tris compound is limited in dichloroethane (Section (i), below), the reaction system to be described was heterogeneous.

The unlabelled tris compound (126 mg, 0.19 millimoles) was placed in 5.0 ml of a 1,2-dichloroethane solution* containing C^{14}—8-hydroxyquinoline (52 mg, 0.36 millimoles, specific activity = 3.58 mv/sec/mg), and the mixture was stirred continuously at 25°C. At the end of the reaction time, the product was filtered quickly (∿ 20 seconds) through a fritted-glass crucible (porosity M), washed with five 2-ml portions of dichloroethane to remove contaminating C^{14}—8-hydroxyquinoline, and dried in a stream of air for one hour and at 75-80°C for one hour. The product was then thermally converted to the bis compound and sublimed 8-hydroxyquinoline. The latter was dried at 50-55°C for 2 hours. The specific activity of the residual bis compound and of the sublimed 8-hydroxyquinoline were determined by the method described earlier.

The reaction times used were 5, 10, 15, 30 and 180 minutes. For reaction times of 30 minutes or less no activity was found in the bis compound and the sublimed 8-hydroxyquinoline. Even after 180 minutes, the specific activity was very small (∿ 0.1 mv/sec/mg). For complete exchange of all three ligands, the specific activity should be 1.44 mv/sec/mg. (Since 126 mg of the tris compound contains 77.3 mg of inactive 8-hydroxyquinoline and 52 mg active 8-hydroxyquinoline were dissolved in the dichloroethane, the specific activity of the tris compound, after exchange equilibrium is reached, should be $[52.0/(77.3 + 52.0)] \times 3.58 = 1.44$ mv/sec/mg.)

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* The dichloroethane solution was previously equilibrated at 25°C.

In a similar experiment, the amount of the tris compound was reduced to 33 mg (0.047 millimoles), and the C^{14}—8-hydroxyquinoline concentration kept as before. After 3 hours, the specific activity of the tris compound was only 0.36 mv/sec/mg (2.58 mv/sec/mg for complete exchange).

The data are interpreted in Section (e), PART A, DISCUSSION.

(g) Stoichiometry of the uranium(VI)—8-hydroxyquinoline complex in 50% V/V aqueous dioxane

The solution experiments described below were undertaken to complement the infrared and carbon-14 studies on the solid tris compound.

Since the solubility of the uranium(VI) complex in water is extremely small, the following studies were made in 50% V/V aqueous dioxane (i.e., 17.4 mole percent dioxane).

(i) Mole-ratio study: Solutions for the measurement of absorbance were prepared in 50-ml flasks by pipetting in the following order: x ml of an 8-hydroxyquinoline solution (1.57 x 10^{-4} M, in dioxane, Table XI), (25-x) ml of dioxane and 2.0 ml of the uranyl nitrate solution. Each solution was than diluted to the mark at 25.0±0.1°C with de-ionized water and the pH adjusted to 6-7 by the addition of one or two drops of sodium hydroxide (1.0 M). The absorbance of each solution was measured at 500 and 475 mμ. At these wavelengths, absorbance due to free 8-hydroxyquinoline and hydrated uranyl-ion is negligible (Figure 1, APPENDIX II). For each wavelength, a plot (Figure 2, APPENDIX II) of the molar ratio of reagent to metal yields a sharp break at 2.3 (see Section (f), PART A, DISCUSSION).

(ii) Potentiometric titration: A measure of the ligand-to-metal

TABLE IX

DATA FOR MOLE-RATIO STUDY

Volume of HQ Solution, x ml	HQ/U Molar Ratio	Absorbance at 475 mμ	Absorbance at 500 mμ
0.50	0.26	0.085	0.070
1.00	0.52	0.127	0.106
2.00	1.03	0.264	0.230
3.00	1.55	0.410	0.362
3.50	1.80	0.480	0.432
4.00	2.06	0.549	0.492
5.00	2.58	0.600	0.540
6.00	3.09	0.602	0.540
8.00	4.12	0.610	0.549
10.00	5.15	0.610	0.549

ratio in the metal complex formed in 50% V/V aqueous dioxane was obtained potentiometrically by determining the number of protons released per uranyl ion in the complexation reaction.

The potentiometric titration was performed in a 200-ml jacketed titration cell maintained at 25.0±0.1°C by water circulated from a constant-temperature bath through the jacket. The cell was fitted with a lucite cover, into which were bored holes for the glass and reference electrodes, nitrogen inlet tubes, thermometer and burettes. Purified-grade nitrogen was bubbled through and above the solution prior to and during the titration. The contents of the cell were stirred magnetically. The tip of the burette containing the standard sodium hydroxide solution (0.1 M) was drawn into a fine capillary and kept below the surface of the solution. The burette was filled by gravity from a 4-ℓ polyethylene bottle, the contents of which were protected from atmospheric moisture and carbon dioxide by guard tubes filled with Drierite and Ascarite. The pH meter was standardized at pH 4.01 and 7.00 before use with standard buffers.

Solutions of three different compositions were titrated (Table X). To maintain the dioxane-water composition at 50% V/V, each incremental addition of sodium hydroxide solution was followed by the addition of an equal volume of dioxane. The titration curves are presented in Figure 3, APPENDIX II.

Two buffer regions are evident in curve C (HQ:U(VI) = 3:1). The first region (pH 4-6) corresponds to the release of two protons (2.07) per uranyl ion, and the second region (pH 7-10) to one proton (1.02) per uranyl ion. Since identical behaviour is observed in Curve B (HQ:U(VI) = 2:1) the second region must be due to proton release from a coordinated water molecule (i.e., hydrolysis), and not to proton release from a coordinated 8-hydroxyquinoline molecule. These data suggest that the formula of the complex in 50% V/V aqueous dioxane is $UO_2(C_9H_6NO)_2 \cdot H_2O$ (see Section (f), PART A, DISCUSSION).

(iii) Precipitation of the uranium(VI)—8-hydroxyquinoline complex from 50% V/V aqueous dioxane: In view of the results of the two preceeding experiments, it was interesting to determine whether precipitation from 50%

TABLE X

COMPOSITION OF SOLUTIONS FOR POTENTIOMETRIC TITRATION

Standard Solutions: (a) 8-hydroxyquinoline in dioxane, 1.06×10^{-2}M

(b) U(VI) in water, 1.01×10^{-2}M

(c) $HC\ell O_4$ in water (0.21 M in $NaC\ell O_4$), 1.0×10^{-2}M

Titration No.	Solution(a) (ml)	Solution(b) (ml)	Solution(c) (ml)	Molar Ratio HQ:U(VI)	Dioxane (ml)
1	0.00	5.00(H_2O)	50.00	-	55.00
2	10.00	5.00	50.00	2:1	45.00
3	15.00	5.00	50.00	3:1	40.00

V/V aqueous dioxane would yield a bis or tris compound. The procedure was: 100 mg (0.2 millimoles) of $UO_2(NO_3)_2 \cdot 6H_2O$ were dissolved in 50 ml of 50% V/V aqueous dioxane containing 3 drops of concentrated nitric acid. To this were added 100 mg (0.7 millimoles) of 8-hydroxyquinoline dissolved in one ml of dioxane. Then 5 g of urea were added, the solution was heated to boiling and transferred to a steam bath for 3 hours. The red needle-like crystals which formed were removed by filtration and washed with water. The crystals were dried in a stream of air for 1/2 hour and at 105°C for 2 hours. The pH of the cooled filtrate was 7.

Bromometric analysis for the 8-hydroxyquinoline content (expressed as Q^-) gave 46.39±0.04% (two determinations), in agreement with the formula $UO_2(C_9H_6NO)_2 \cdot CO(NH_2)_2$ (theoretical % Q^-, 46.63). The composition was further confirmed by elemental analyses:

Calculated for $UO_2(C_9H_6NO)_2 \cdot CO(NH_2)_2$: C, 37.25; H, 2.61; N, 9.06; U, 38.48.

Found: C, 37.59; H, 3.05; N, 9.06; U, 38.80.

The infrared spectrum (B, Figure 5) supports the composition (i.e., absorption bands at 3450, 3300 and 3150 cm^{-1}; a strong band at 1625 cm^{-1}; and the absence of bands at 2650 and 2050 cm^{-1}; see Section (f), PART A, DISCUSSION).

(h) Interaction of bis(8-hydroxyquinolinato)-dioxouranium(VI) with solvents

Bullwinkel and Noble (64) have reported that the bis compound undergoes disproportionation in solution to yield the tris compound and uranium(VI) species. The experiments below were done to gain further knowledge about the proposed disproportionation reaction, particularly with regard to the role of solvent.

The action of various solvents (95% ethanol, methanol, acetone and chloroform) was investigated qualitatively on a "small beaker" scale using about 50 mg of the bis compound and 10 ml of the solvent. The mixture was stirred continuously for 3 hours at room temperature. Because of the various colours involved, the course of the reaction could be followed visually. Each solution and the surface of the undissolved residue became red in moments, and darker red on standing. Visual observation was not sufficient to distinguish between the red tris compound, i.e., the product of the disproportionation reaction, and compounds such as $UO_2(C_9H_6NO)_2 \cdot H_2O$ and

$UO_2(C_9H_6NO)_2 \cdot CO(CH_3)_2$, etc., i.e., products of solvolysis reactions. Accordingly, solid compounds* were isolated from solution and their infrared spectra taken (Figure 6).

The important features of the spectrum for each isolated compound are noted in Table XI. The infrared data suggest that both disproportionation and solvolysis reactions have occurred in these solvents. Attempts to obtain purified samples for analyses were not made.

TABLE XI

FEATURES OF INFRARED SPECTRA OF COMPOUNDS ISOLATED FROM INTERACTION OF THE BIS COMPOUND WITH SOLVENTS

Solvent**	Features of Infrared Spectrum
Ethanol (95%)	Bands at 2650 and 2050 cm^{-1}. A sharp band at 3550 cm^{-1}.
Methanol	Band at 2650 cm^{-1}. Weak bands at 2900 and 3500 cm^{-1}.
Acetone	Bands at 2650 and 2050 cm^{-1}. A sharp band at 1700 cm^{-1}. Weak bands at 2900 and 3500 cm^{-1}.
Chloroform	Bands at 2650 and 2050 cm^{-1}. Strong band at 750 cm^{-1}. Weak band at 2950 cm^{-1}.

** The solvents were deliberately used as supplied commercially, without further purification.

The action of 1,2-dichloroethane was also investigated and is singled out here. After 3 hours, the solution was yellow, not red, and

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* The compounds were isolated by evaporation to dryness of the filtrate obtained after filtration of the original solution to remove undissolved bis compound.

the undissolved residue remained black (the colour of the bis compound). The solid was then removed by filtration, dried in a stream of air for 1/2 hour and heated for 4 hours at 210-215°C (0.1 mm Hg), in the assembly used for the thermal preparation of the bis compound. From the (bromometric) determination of the residual bis compound and the sublimed 8-hydroxyquinoline, the amount of the tris compound in the undissolved solid was about one percent. This can be taken as the approximate extent of disproportionation of the bis compound in dichloroethane.

The small extent of interaction in dichloroethane was also shown by the fact that the bis compound could be dissolved in hot dichloroethane and recovered unchanged. The infrared spectrum of the recrystallized material was identical to that of the thermally prepared bis compound.

The presence of a small amount of water in the dichloroethane has a marked effect. For example, the addition of 4 drops of water to the mixture caused the solution and the surface of the undissolved residue to become red.

In a further experiment, a saturated solution of the bis compound was prepared at the boiling point of dichloroethane saturated with water. The hot mixture was filtered to remove the excess solid. The red filtrate appeared identical to a solution of the tris complex in dichloroethane. Concentration of the solution to 1/4 of the original volume and subsequent cooling yielded red crystals, which were filtered and dried for 30 minutes in air and 2 hours at 105°C. The infrared spectrum was identical to that of the tris compound. The identity was confirmed by elemental analyses.

Calculated for $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$: C, 46.09; H,2.72; N, 5.97.

Found: C, 45.04; H. 2.74; N, 5.37.

The low values for C and N may be due to the presence of small amounts of $UO_2(C_9H_6NO)_2 \cdot H_2O$ and unreacted bis compound.

The results are dealt with in Section (g), PART A, DISCUSSION.

(i) Addition of 8-hydroxyquinoline to bis(8-hydroxyquinolinato)dioxouranium(VI)

As mentioned in the INTRODUCTION, the addition of 8-hydroxyquinoline to the bis compound was first reported by Frere (43), but he failed to give the conditions of the reaction. The experiments described below constitute a more detailed examination of the reaction than that reported by Frere.

(i) Choice of solvent: Based on the results of the previous section and of Section (e), it is clear that in order to avoid the disproportionation and other complicating reactions, the solvent must be dry, only weakly protonic or non-protonic, and non-polar. 1,2-Dichloroethane appeared suitable (both the bis and tris compounds are stable in it) and was used as the solvent for the addition reaction.

(ii) Solubility of 8-hydroxyquinoline and of the bis and tris compounds in dichloroethane: The solubility of the components of the addition reaction were determined as follows. An excess of the solid was added to 25 ml of dichloroethane and the mixture was stirred continuously at 25°C. After a specified period of time, the solution was filtered through a fine-porosity fritted-glass crucible. An aliquot volume of the filtrate was taken and treated with 50 ml of warm 4 M HCℓ in an iodine flask. The 8-hydroxyquinoline content of the solution was determined bromometrically and the solubility of the compound calculated. The solubility of the tris compound was 2.1 mg/ml dichloroethane (after 5 minutes and 12 hours). It was not noticeably affected by the presence of 8-hydroxyquinoline (10.5 mg/ml) in the solvent. The solubility of the bis compound was 1.5 and 2.3 mg/ml, after 5 minutes and 12 hours, respectively. The equilibrium solubility of 8-hydroxyquinoline was very high (344 mg/ml).

(iii) Addition reaction — effect of time, reagent concentration and initial particle size: Because of the limited solubility* of the bis and tris compounds in dichloroethane, the addition reaction was carried out heterogeneously, and the percent addition was obtained by examination of the excess solid rather than of the species in solution. Because of the large amount (100 mg) of the bis compound initially taken, the small volume (5 ml) of dichloroethane, and the small difference in solubility between the bis and tris compounds, the error introduced by the above procedure was thought to be tolerable. Certainly, it is outweighed by the convenience afforded for rapid quenching of the reaction (by quick filtration).

The effect of reaction time, reagent concentration and the initial particle-size of the bis compound were examined. The general procedure was as follows: 100±0.2 mg of the bis compound (of known particle size) were weighed into a 15-ml bottle with a ground-glass cover. Then, 5.0 ml of a solution of 8-hydroxyquinoline in dichloroethane were added. The mixture was maintained at 25.0±0.1°C and stirred (magnetically) during the reaction. At the end of the reaction time, the mixture was quickly filtered (about 20 seconds) through a fritted-glass crucible (porosity F). The collected solid was washed with five 2-ml portions of dichloroethane, and dried in a stream

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* The solubility of the bis and tris compounds are much greater in solvents such as dimethylsulfoxide, dimethylformamide and pyridine, but their strong coordinating ability prohibited their use.

of air for 30 minutes and at 85-90°C (at 5-6 cm Hg) for 3 hours. Elemental analyses of the solid showed the presence of chlorine and, therefore, of unremoved solvent in the solid. Since more drastic drying conditions could cause some volatilization of the added ligand, the percent addition was obtained by determining the relative amounts of the bis compound and added 8-hydroxyquinoline by the thermal and analytical procedures described earlier in Section (b). The amount of solvent associated with the solid could then be determined from a mass balance for the original weight of the solid. From the data, a formula was established for the addition product. This formula was used for calculating the specific activity of the solid when the reaction was carried out with C^{14}—8-hydroxyquinoline (see below).

The effect of time on the addition reaction was studied, using an initial particle size of less than 74 μ and a two-fold excess of 8-hydroxyquinoline. The reaction time was varied from 3 hours to 5 minutes. The results are given in Table XII.

TABLE XII

ADDITION REACTION -- EFFECT OF TIME

Bis compound taken = 100.0±0.2 mg

Particle size < 74 μ

HQ taken = 52.0±0.1 mg (100% excess)

Time (min)	Percent Addition
180	100
30	100
15	100
10	100
5	92

Similarly, the effect of concentration of 8-hydroxyquinoline (i.e., the percent excess 8-hydroxyquinoline) on the percent addition was determined. The particle size was less than 74 μ and the reaction time was 5 minutes (Table XIII).

TABLE XIII

ADDITION REACTION -- EFFECT OF HQ CONCENTRATION

Bis compound taken = 100.0±0.2 mg
Particle size < 74 μ
Reaction time = 5 minutes

Percent Excess HQ	Percent Addition
1000	100
500	100
100	92
0	67

The effect of particle size was also determined. A two-fold excess of 8-hydroxyquinoline was used and the reaction time was 5 minutes (Table XIV).

(iv) Addition reaction using C^{14}—8-hydroxyquinoline: The addition reaction was also studied using C^{14}—8-hydroxyquinoline. It was hoped that in the absence of complicating reactions, the experimental data could be unambiguously interpreted in terms of coordination of the extra molecule of 8-hydroxyquinoline, thus providing another experimental test* for other

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* As discussed later, the bands at 2650 and 2050 cm^{-1} in the infrared spectrum provide a test for coordination of the extra molecule.

TABLE XIV

ADDITION REACTION -- EFFECT OF PARTICLE SIZE

Bis compound taken = 100.0±0.2 mg

HQ taken = 52.0±0.1 mg (100% excess)

Reaction time = 5 minutes

Particle Size (μ)	Percent Addition
< 74	92
74-149	77
149-250	73

8-hydroxyquinoline adduct compounds.

The effect of time on the specific activity of the isolated reaction product was studied. The initial conditions are recorded in Table XV. After isolation and thermal conversion of the solid, the specific activity of the bis compound and sublimed 8-hydroxyquinoline* were determined as described earlier. The specific activity of the isolated solid was also determined (before thermal conversion) for the 5-minute reaction. This provided a successful check for radiobalance. The data are presented in Table XV.

The effect of excess 8-hydroxyquinoline was also studied; the reaction time was constant at 5 minutes. The results are given in Table XVI.

An attempt to interpret the C^{14} data is made in Section (h), PART A, DISCUSSION.

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* Dried at 50-55°C for 2 hours.

TABLE XV

ADDITION REACTION WITH C^{14}—8-HYDROXYQUINOLINE: EFFECT OF TIME ON SPECIFIC ACTIVITY

Bis compound taken = 100.0±0.2 mg

Particle size range = 74-149 μ

HQ taken = 52.0±0.1 mg (100% excess)

Specific activity of initial HQ = 3.58 mv/sec/mg

Reaction Time (min)	Percent Addition	Sp. Act. of Isolated Prod. (mv/sec/mg)	Sp. Act. of Bis Compound (mv/sec/mg)	Sp. Act. of Sub. HQ (mv/sec/mg)
180	-	-	1.84 ±0.01	1.85 ±0.01
30	100	-	2.02 ±0.01	2.04 ±0.02
15	-	-	2.13 ±0.01	2.15 ±0.01
10	98	-	2.04 ±0.01	2.17 ±0.01
5	77	1.75* ±0.03	1.59* ±0.03	2.21* ±0.02

* Average of 3 determinations; error is the standard error. All other values are an average of two determinations.

TABLE XVI

ADDITION REACTION WITH C^{14}—8-HYDROXYQUINOLINE: EFFECT OF HQ CONCENTRATION ON SPECIFIC ACTIVITY

Bis compound taken = 100.0±0.2 mg

Particle Size < 74 μ

Reaction time = 5 minutes

Specific activity of initial HQ = 3.58 mv/sec/mg

Percent Excess HQ	Percent Addition	Sp. Act. of Isolated Prod. (mv/sec/mg)	Sp. Act. of Bis Compound (mv/sec/mg)	Sp. Act. of Sub. HQ (mv/sec/mg)	Difference (Bis compd.-HQ) (mv/sec/mg)
0	67	1.39* ±0.01	1.23* ±0.02	1.69* ±0.02	0.46 ±0.03
100	92	2.03** ±0.03	1.88** ±0.03	2.20** ±0.02	0.32 ±0.04
500	100	-	2.49† ±0.03	2.88† ±0.01	0.39 ±0.03

* Average of three results; error is the standard error.

** Average of four results.

† Average of two results.

PART B Thorium(IV) Complexes of 8-Hydroxyquinoline and Derivatives

(a) Syntheses

(i) The 5:1 Thorium(IV)—7-methyl—8-hydroxyquinoline complex: 25 ml of the thorium stock solution (1.4 mg Th/ml) were diluted with 25 ml of water and heated to 70°C. Then, in order, a warm solution of the reagent (200 mg, dissolved in 2 ml acetic acid and diluted to 8 ml with water) and of ammonium acetate (2 g dissolved in 10 ml water) were added dropwise with continuous stirring. Finally, the pH was raised to 8 by the slow addition of warm IM ammonia, and the mixture allowed to stand for one hour at 70°C. The orange precipitate was filtered, washed with 100 ml of hot water, and dried in a stream of air for 20 hours.

Bromometric analysis of the precipitate for 7-methyl—8-hydroxyquinoline (expressed as the anion) gave 76.05% (calculated for the 5:1 compound, 77.21%; for the 4:1 compound, 73.16%).

The precipitate was further characterized by elemental analyses.

Calculated for $Th(C_{10}H_8NO)_4 \cdot C_{10}H_8NOH$: C, 58.64; H, 4.04; N, 6.84; Th, 22.66.

Calculated for $Th(C_{10}H_8NO)_4$: C, 55.55; H, 3.73; N, 6.48; Th, 26.83.

Found: C, 58.35; H, 4.40; N, 6.74; Th, 22.23.

(ii) The 5:1 thorium(IV)—7-phenyl—8-hydroxyquinoline complex: 20 ml of the thorium stock solution were diluted to 40 ml with water, and then 20 ml of ethanol were added (to reduce the amount of the coprecipitated reagent). The solution was heated to 80°C. In order, a warm solution of the reagent (150 mg in 6 ml of glacial acetic acid) and of ammonium acetate (2 g dissolved in 15 ml of water) were added, dropwise with stirring.

Precipitation of an orange compound occurred on addition of the acetate solution. The pH was 4.5. The precipitate was digested for 5 hours. The beaker was covered with a watch glass to minimize the evaporation of alcohol. The hot solution was then filtered, and the precipitate was washed with 200 ml of hot water and dried in a stream of air for 20 hours.

Elemental analyses of the precipitate indicated the presence of coprecipitated reagent.

Calculated for $Th(C_{15}H_{10}NO)_4 \cdot C_{15}H_{10}NOH$: C, 67.44; H, 3.85; N, 5.25; Th, 17.38.

Calculated for $Th(C_{15}H_{10}NO)_4$: C, 64.76; H, 3.62; N, 5.04; Th, 20.85.

Found: C, 69.66; H, 3.90; N, 5.48; Th, 14.34.

To remove the coprecipitated reagent, the compound was heated at 130-135°C in vacuo (0.1 mm Hg) for 45 minutes. A small amount of sublimed 7-phenyl—8-hydroxyquinoline in the U-tube confirmed the presence of coprecipitated reagent. Elemental analyses of the purified compound gave: C, 67.22; H, 4.00; N, 5.23; Th, 17.35.

(iii) The 5:1 thorium(IV)—5-phenyl—8-hydroxyquinoline complex: The method of preparation was the same as that used for the 7-phenyl—8-hydroxyquinoline complex, except that the pH was adjusted to 5 by the addition of warm IM ammonia. The orange precipitate which formed was filtered, washed and dried, and characterized by elemental analyses.

Calculated for $Th(C_{15}H_{10}NO)_4 \cdot C_{15}H_{10}NOH$: C, 67.44; H, 3.85; N, 5.25; Th, 17.38.

Calculated for $Th(C_{15}H_{10}NO)_4$: C, 64.76; H, 3.62; N, 5.04; Th, 20.85.

Found: C, 66.07; H, 3.90; N, 5.25; Th, 16.26.

The experimental data are in closer agreement with the 5:1 rather than the 4:1 composition. The low C and Th data cannot be explained by the effects of coprecipitation alone. No attempts were made to improve the conditions of the synthesis.

(iv) Tetrakis(7-t-butyl—8-hydroxyquinolinato)thorium(IV): To 15 ml of the thorium stock solution warmed to 80°C was added dropwise with stirring a warm solution of the reagent (108 mg, dissolved in 5 ml of glacial acetic acid). A small amount of reagent precipitated and was redissolved by the addition of a minimum (1 or 2 drops) of concentrated nitric acid. Then a warm solution of 1M ammonia was added very slowly until the pH was 4.5. A lemon-yellow precipitate formed. After the addition of 30 ml of water, the solution was digested for 4 hours at 80°C. The hot solution was filtered, the precipitate washed with 200 ml of hot water, and then dried in a stream of air for 20 hours.

To remove any coprecipitated reagent, the precipitate was heated in vacuum (0.1 mm Hg) at 155-160°C for 30 minutes. Elemental analyses of the pruified compound gave the following results:

Calculated for $Th(C_{13}H_{14}NO)_4 \cdot C_{13}H_{14}NOH$: C, 63.26; H, 5.99; N, 5.68; Th, 18.80.

Calculated for $Th(C_{13}H_{14}NO)_4$: C, 60.47; H, 5.46; N, 5.43; Th, 22.47.

Found: C, 60.74; H, 5.16; N, 5.49; Th, 22.30. On heating in vacuo, a small amount of sublimed 7-t-butyl—8-hydroxyquinoline (identified by melting point) was collected; the colour of the lemon-yellow precipitate remained unchanged. The amount of sublimed reagent was about 4 mg. On the basis of a 5:1 composition, this represents about one-third the amount expected for the weight (∿ 80 mg) of precipitate taken. It is likely that the precipitate is not a mixture of the 5:1 and 4:1 compounds, but a mixture of the tetrakis compound contaminated with the slightly soluble reagent.

The synthesis was repeated as above except that 10 ml of ethanol were added before the addition of ammonia to reduce the amount of coprecipitation. The lemon-yellow product, after washing with 200 ml of hot water and drying in a stream of air for 20 hours, was analysed.

Found: C, 61.62; H, 5.31; N, 5.44; Th, 21.97. It appears that a small amount of coprecipitated reagent was still present.

When the buffering agent, ammonium acetate, was used in the synthesis, a green precipitate formed which could not be identified. Elemental analyses gave: C, 44.30; H, 2.39; N, 12.69; Th, 17.65. Likely, the precipitate is a mixture of mixed-ligand complexes, containing a combination of 7-t-butyl—8-hydroxyquinolinate, acetate, hydroxide and nitrate ligands.

(v) Tetrakis(7-phenyl—8-hydroxyquinolinato)thorium(IV): This compound could not be prepared directly by precipitation. It was obtained by thermal conversion of the corresponding 5:1 compound. The assembly described previously for the thermal preparation of bis(8-hydroxyquinolinato)dioxouranium(VI) was used. The conversion was carried out in vacuo (0.1 mm Hg). At 120°C, a small amount of sublimed 7-phenyl—8-hydroxyquinoline (identified by melting point) was observed in the U-tube. The orange colour of the 5:1 compound remained unchanged. As the temperature was slowly raised to 200°C, the amount of sublimate increased and the colour of the compound in the flask slowly turned to yellow. When the temperature was raised to 230-235°C and maintained constant for one hour, the precipitate became completely yellow. Elemental analyses of this residue gave the following data:

Calculated for $Th(C_{15}H_{10}NO)_4$: C, 64.76; H, 3.62; N, 5.04; Th, 20.85.

Found: C, 64.74; H, 3.61; N, 5.11; Th, 20.63.

The 5:1 thorium(IV)—3-methyl—8-hydroxyquinoline complex and the tetrakis(2-methyl—8-hydroxyquinolinato)thorium(IV) were prepared by the method of Thompson (73) and Corsini (97), respectively.

(b) Composition of the orange thorium(IV)—8-hydroxyquinoline complex

The orange thorium(IV)—8-hydroxyquinoline complex was prepared as described by Corsini (97). It was dried in a stream of air for 3 hours and stored over P_2O_5 in a desiccator. After one week the compound became brown. Therefore, it was always freshly prepared as needed.

The composition of the compound was established in two ways. (i) The thorium and 8-hydroxyquinoline contents were determined and a ratio of thorium to 8-hydroxyquinoline was made (Table XVII). Thorium was determined by ignition to thorium dioxide at 800°C (47). 8-Hydroxyquinoline was determined by bromometric titration. (ii) The ratio of sublimed 8-hydroxyquinoline to the residual tetrakis compound obtained on thermal conversion was determined. The conversion was effected quantitatively by heating in vacuo (0.1 mm Hg) at 165-170°C for 1 1/2 hours as described in the next section. The apparatus was that used for the thermal conversion of the tris uranium(VI)—8-hydroxyquinoline compound. In all cases, a very small droplet of moisture was noticed below the deposit of 8-hydroxyquinoline in the U-tube. The sublimed 8-hydroxyquinoline and the tetrakis compound were separately dissolved in warm 4M HCℓ, determined bromometrically, and the ratio $HQ:ThQ_4$

TABLE XVII

COMPOSITION OF THE ORANGE THORIUM(IV)—8-HYDROXYQUINOLINE COMPOUND

(For $Th(C_9H_6NO)_4 \cdot C_9H_6NOH$; %Th = 24.32; %HQ as Q^- = 75.57)

Precipitation Number	Percent Q^- Found	Percent Th Found	Molar Ratio Q^-:Th
1	72.62*	24.13*	4.84
2	73.54 ±0.05	24.35 ±0.05	4.86 ±0.01
3	74.28 ±0.06	24.25 ±0.05	4.93 ±0.01

* Single determination; all other results represent the average of two determinations.

TABLE XVIII

MOLAR RATIO OF HQ:ThQ_4 IN THE ORANGE THORIUM(IV)—8-HYDROXYQUINOLINE COMPOUND

Precipitation Number	Wt. of ThQ_4* Found (mg)	Wt. of Sub. HQ Found (mg)	Molar Ratio HQ:ThQ_4
1	213.9	36.6	0.95
2	184.4	29.6	0.89
	155.3	24.8	0.89
3	136.8	23.7	0.96
	123.2	21.3	0.96

*$ThQ_4 = Th(C_9H_6NO)_4$.

calculated (Table XVIII).

The data of Tables XVII and XVIII show that the composition of the precipitate varies from one precipitation to another, i.e., that the composition is very sensitive to the experimental conditions. Since precipitation occurs during the addition of the ammonium acetate solution (97) to the acid solution of thorium(IV) and 8-hydroxyquinoline, it was felt that the composition might be dependent on the rate of addition of the former solution. The data of Table XIX represent the results obtained when the rate of addition of ammonium acetate was varied from 7 to 3 ml/min. Conclusions to the above work are drawn in Section (a), PART B, DISCUSSION.

(c) Thermal preparation of pure tetrakis(8-hydroxyquinolinato)thorium(IV) and thermal ligand exchange

The pure tetrakis compound was obtained by heating the orange compound (150-200 mg) in vacuo (0.1 mm Hg) at 165-170°C for 1 1/2 hours. Several preparations of the orange compound were used for the thermal conversion. The thorium and 8-hydroxyquinoline contents of the thermal product were determined as before. Analysis of the product gave the following results: %Th, 28.54±0.04 (4 results; theoretical, 28.69%); %Q^-, 71.37±0.05 (10 results; theoretical 71.31%); molar ratio Q^-:Th, 4.02±0.01. Close control of the upper temperature limit is essential for the preparation of the pure compound. When the temperature was 175°C, the residual yellow compound was found to be deficient in 8-hydroxyquinoline (%Q^-, 70.19±0.04, 3 results). The effect of varying the temperature and the time was not investigated further.

The possibility of intra and intermolecular exchange of ligands during the thermal conversion of the addition product was investigated as

TABLE XIX

EFFECT OF THE RATE OF ADDITION OF AMMONIUM ACETATE ON THE MOLAR RATIO HQ:ThQ_4

(Concentration of NH_4Ac = 1.7 M)

Rate of Add. of NH_4Ac (ml/min)	Wt. of ThQ_4 Found (mg)	Wt. of Sub. HQ Found (mg)	Molar Ratio HQ:ThQ_4
7	138.3	22.7	0.91
	171.3	28.2	0.92
6	159.3	25.8	0.93
5*	217.7	35.0	0.90
	121.8	19.4	0.89
3	108.2	17.2	0.89
	123.3	19.7	0.89

* Rate used for the results in Tables XVII and XVIII.

in the studies with the uranium(VI)—8-hydroxyquinoline compound.

A known amount of the orange compound (126.5 mg prepared using C^{14}—8-hydroxyquinoline) and of the (inactive) tetrakis compound (110.0 mg) were intimately mixed in the reaction flask and heated in vacuo at 165-170°C for 1 1/2 hours. The specific activity of the residual tetrakis compound and of the sublimed 8-hydroxyquinoline were determined as previously described, and the percent ligand exchange calculated (Table XX).

The data are discussed in Section (b), PART B, DISCUSSION.

TABLE XX

LIGAND EXCHANGE IN THERMAL REACTION

Inactive 4:1 compound taken = 110.0 mg

Active 5:1 compound taken = 126.5 mg

Original activity of 5:1 compound = 3.58 mv/sec/mg

	Measured Sp. Act. (mv/sec/mg)	Sp. Act. for Complete Exch.* (mv/sec/mg)	Sp. Act. for No Exch. (mv/sec/mg)	Percent Exchange
Sub. HQ	2.74	1.97	3.58	52
Resid. 4:1 Compd.	1.90	1.97	1.77	65
				Average 59±7

* Calculated on the basis of a perfect 5:1 composition for the orange compound

(d) Interaction of the orange thorium(IV)—8-hydroxyquinoline complex with solvents

(i) Absolute ethanol: A saturated solution of the orange compound in absolute ethanol was prepared at room temperature. The excess solid was removed by filtration and the filtrate was slowly evaporated under vacuum. The yellow crystals which formed were filtered, dried in a stream of air for 10 hours, and identified by elemental analyses to be $Th(C_9H_6NO)_4 \cdot C_2H_5OH$.

Calculated for $Th(C_9H_6NO)_4 \cdot C_2H_5OH$: C, 53.39; H, 3.54; N, 6.56; Th, 27.14.

Found: C, 53.05; H, 4.02; N, 6.59; Th, 27.09.

The infrared spectrum (A, Figure 7) showed weak absorption at 2950 cm^{-1} (aliphatic CH) and 3350 cm^{-1} (alcoholic OH). No bands were present at 2650 and 2075 cm^{-1} (for a comparison to the spectrum of the orange compound, see D, Figure 8).

(ii) Dimethylsulfoxide: A saturated solution of the orange compound in warm dimethylsulfoxide was prepared, and the excess solid was removed by filtration. On cooling the filtrate, a yellow precipitate was obtained which was removed and dried in a stream of air for 5 hours, and then at 100°C for 3 hours. The precipitate was characterized by elemental analyses.

Calculated for $Th(C_9H_6NO)_4 \cdot 2OS(CH_3)_2$: C, 49.68; H, 3.76; N, 5.81; S, 6.65; Th, 24.05.

Found: C, 50.03; H, 3.76; N, 5.86; S. 6.63; Th, 24.72.

The infrared spectrum (B, Figure 7) showed the complete absence of the bands at 2650 and 2075 cm^{-1}. The $>S{=}O$ vibrational band was present at 1025 cm^{-1}, and the aliphatic C—H absorption was identified as a shoulder at 2975 cm^{-1}.

(iii) Dichloroethane: A saturated solution of the orange compound was prepared in dichloroethane at room temperature. The excess solid was removed by filtration and the filtrate concentrated by slow evaporation under vacuum. On stirring the solution, an orange-yellow precipitate formed. The precipitate was removed, washed with 2 ml of dichloroethane, and dried in a stream of air for 12 hours.

The composition of the precipitate was established by determining the relative amounts of the tetrakis compound and the sublimed 8-hydroxyquinoline. The ratio ThQ_4:HQ was 1:0.26, showing that the precipitate was predominantly the tetrakis compound containing a small amount of the orange compound.

When the experiment was repeated using warm dichloroethane (∿ 70°C), a yellow precipitate was immediately obtained. This precipitate was removed and the filtrate concentrated and cooled. The yellow needle-like crystals which formed were removed and dried in a stream of air for 12 hours. Elemental analyses gave the following results:

Calculated for $Th(C_9H_6NO)_4$: C, 53.45; H, 2.99; N, 6.93; Th, 28.70.

Found: C, 53.15; H, 3.01; N, 6.84; Th, 27.53.

The infrared spectrum of the precipitate was identical to that of the thermally prepared tetrakis compound (E, Figure 8).

When the experiment was repeated using dichloroethane in which was dissolved 8-hydroxyquinoline (26 mg/ml), the orange 5:1 compound was obtained. The composition of the compound isolated was established by determining the relative amounts of the tetrakis and sublimed 8-hydroxyquinoline. The ratio ThQ_4:HQ was found to be 1:0.99, showing that the orange compound was stoichiometric.

(e) Exchange reaction between the 5:1 thorium(IV)—8-hydroxyquinoline complex and C^{14}—8-hydroxyquinoline

The results reported in previous section show that the orange compound is stable in dichloroethane which contains a sufficient excess of

8-hydroxyquinoline. Therefore, this solvent was used in experiments described below. The solubility of the orange compound in 5 ml of dichloroethane containing 130 mg of 8-hydroxyquinoline is only 7.5 mg. The exchange reaction as carried out was thus heterogeneous.

To 5.0 ml of dichloroethane (at 25°C) containing 130 mg (0.9 millimoles) of C^{14}—8-hydroxyquinoline were added 171 mg (0.18 millimoles) of the orange compound. The mixture was stirred continuously. At the end of the reaction time, the mixture was rapidly filtered through a fritted-glass crucible (porosity M), washed with 5 ml of dichloroethane, and dried in a stream of air for 30 minutes. The product was then thermally converted to the tetrakis compound and 8-hydroxyquinoline, and the specific activity of each determined. The reaction times were 1, 2, 3 and 6 hours. Even after 6 hours, the specific activity of both the tetrakis compound and the sublimed HQ was very low (< 0.1 mv/sec/mg). For complete exchange, the specific activity expected is $130 \times 3.6/130 + 130 = 1.8$ mv/sec/mg.

In further experiments, the amount of C^{14}—8-hydroxyquinoline dissolved in the dichloroethane was reduced to 52 mg (0.36 millimoles) and 26 mg (0.18 millimoles), while the amount of the orange compound was 171 mg (0.18 millimoles). Considerable activity was now found in the tetrakis compound and the sublimed 8-hydroxyquinoline. The results are presented in Table XXI.

The experiment was repeated using 30 mg (0.03 millimoles) of the orange compound and 130 mg (0.9 millimoles) of C^{14}—8-hydroxyquinoline. The reaction time was 3 hours. The product isolated had no measurable activity. The data are interpreted in Section (d), PART B, DISCUSSION.

TABLE XXI

EXCHANGE REACTION BETWEEN THE ORANGE COMPOUND AND C^{14}—8-HYDROXYQUINOLINE

Orange compound taken = 171 mg (0.18 millimoles)

Specific activity of initial HQ = 3.58 mv/sec/mg

Reaction Time (hrs)	Amt. C^{14}-HQ Taken (mg)	Sp. Act. of ThQ_4 (mv/sec/mg)	Sp. Act. of Sub. HQ (mv/sec/mg)	Sp. Act. for Complete Exch.* (mv/sec/mg)
6	52.0 (0.36 millimoles)	0.40	0.33	1.0
3	26.0 (0.18 millimoles)	0.63** ±0.04	0.38** ±0.04	0.6

* Calculated on the basis of a perfect 5:1 composition for the orange compound.

** Average of two determinations.

(f) Infrared spectra of thorium(IV) complexes of 8-hydroxyquinoline and derivatives

The purpose of the infrared study was to locate the acidic proton in the 5:1 thorium(IV)—8-hydroxyquinoline compound. All spectra were taken as mulls in hexachloro—1,3-butadiene.

The spectrum of the 5:1 thorium(IV)—8-hydroxyquinoline complex, which had been previously carefully dried and prepared for infrared analysis in a dry-box, is given by D, Figure 8. The most prominent feature is the very broad band centered at about 2650 cm^{-1}. This diagnostic band is also present in the tris uranium(VI) complexes, as discussed earlier. An extremely weak absorption is present at about 2075 cm^{-1}. This diagnostic band is more prominent in the spectra of the tris uranium(VI) complexes. In the spectrum of the thorium(IV)—8-deuteroxyquinoline complex, the 2650 and 2075 cm^{-1} bands are shifted to 2050 and 1510 cm^{-1}, respectively. The 2650 and 2075 cm^{-1} bands are absent in the spectrum of the corresponding tetrakis compound (E, Figure 8).

The resolution of the band at 2650 cm^{-1} is somewhat reduced if a significant amount of water is present in the compound. In Figure 8, spectra A, B, C and D are for samples that were dried with progressively more care. The drying conditions are given in Table XXII. The increased resolution of the 2650 cm^{-1} band (Figure 8) with improvement in the drying conditions is apparent. Also apparent is the concomitant decrease in the intensity of the band at 3350 cm^{-1} (Figure 8 and Table XXII).

The broad 2650 cm^{-1} band is also observed in the spectrum of the 5:1 complex of 3-methyl—8-hydroxyquinoline (B, Figure 9), after careful drying of the compound (50-55°C, 72 hours, 0.1 mm Hg) and preparation of the mull in a dry-box. Spectrum A, Figure 9, was obtained when the complex was dried in air (20 hrs). Spectra C and D, Figure 9, are for the 7-methyl— and 5-phenyl—8-hydroxyquinoline complexes which were also dried in air (20 hrs).

The spectrum of the 5:1 complex of 7-phenyl—8-hydroxyquinoline (E, Figure 9) clearly shows the 2650 and 2075 cm^{-1} bands. The compound had previously been heated at 130-135°C (0.1 mm Hg) for 45 minutes to remove coprecipitated reagent. The above bands are not present in the spectrum of tetrakis(7-phenyl—8-hydroxyquinolinato)thorium(IV), (F, Figure 9).

TABLE XXII

EFFECT OF DRYING CONDITIONS ON INTENSITY OF 3350 cm^{-1} BAND IN SPECTRUM OF 5:1 THORIUM(IV)—8-HYDROXYQUINOLINE COMPOUND

Spectrum	Drying Conditions	Preparation of Mull	Intensity of 3350 cm^{-1} Band*
A	not dried	in atmosphere	5.5
B	in air, 3 hrs.	in atmosphere	1.6×10^{-1}
-	50-55°C (0.1 mm Hg) 48 hrs.	in atmosphere	1.5×10^{-1}
C	50-55°C (0.1 mm Hg) 3 hrs.	in dry-box	1.2×10^{-1}
-	50-55°C (0.1 mm Hg) 53 hrs.	in dry-box	6.4×10^{-2}
D	50-55°C (0.1 mm Hg) 72 hrs.	in dry-box	0

* The "intensity of the 3350 cm^{-1} band" is actually a ratio of the integrated intensity of the 3350 cm^{-1} and 1100 cm^{-1} bands. The latter band has been attributed to a C—O vibration in the complex (63). A comparison of the intensity ratio rather than of the intensity of the 3350 cm^{-1} band is preferable because the effect due to differences in sample size are cancelled.

The spectra of the tetrakis complexes of 7-t-butyl— and 2-methyl—8-hydroxyquinoline are given by A and B, Figure 10. No absorption is observed at 2650 and 2075 cm^{-1}.

The significance of the spectra is discussed in Section (e), PART B, DISCUSSION.

(g) Stability of the 5:1 thorium(IV)—8-hydroxyquinoline complex in dichloroethane containing various ligands

The experimental work in this section was prompted by the observation that the 5:1 compound is stable in dichloroethane containing a large excess of 8-hydroxyquinoline (Section (d), above) and could be isolated unchanged.

(i) The infrared spectrum of the solution of the 5:1 compound (10 mg/ml) in dichloroethane containing 8-hydroxyquinoline (26 mg/ml) is shown in A, Figure 11. The spectrum was taken using matched solution cells (0.1 mm pathlength, NaCℓ windows) to effectively cancel absorption (B, Figure 11) due to dichloroethane in the region 3000-2000 cm^{-1}. Spectrum A indicates a broad absorption band centered at 2600 cm^{-1}. The expected low-intensity band at about 2075 cm^{-1} is not unequivocally discernible.

(ii) 5-Methyl—8-hydroxyquinoline: To a dichloroethane solution containing 5-methyl—8-hydroxyquinoline (27 mg/ml), were added about 25 mg/ml of the 5:1 thorium(IV)—8-hydroxyquinoline compound. The solution was heated to 70°C and the small amount of undissolved solid was removed by filtration. The 5:1 compound was readily soluble and no precipitation of the insoluble tetrakis compound was noticed. The filtrate was concentrated, but a precipitate (orange) was obtained only after the solution was cooled in a refrigerator for several days. The precipitate was filtered and washed with about 10 ml of dichloroethane.

Although the infrared spectrum of the solid was identical to that of the 5:1 compound, examination showed that exchange between 8-hydroxyquinoline and 5-methyl—8-hydroxyquinoline had occurred to some extent. When the isolated compound was heated at 165-170°C in vacuo, two white deposits were observed in the U-tube. The deposit closest to the reaction flask melted over the range 117-119°C, and the other at 60-65°C. The former was likely 5-methyl—8-hydroxyquinoline (m.p., 123°C (110)) contaminated with 8-hydroxyquinoline, and the latter deposit, 8-hydroxyquinoline (m.p., 73-74°C (107)) contaminated with 5-methyl—8-hydroxyquinoline. The 8-hydroxyquinoline deposit was considerably greater in amount. The analytical data for the residue in the flask did not correspond exactly to $Th(C_9H_6NO)_4$, indicating the presence of a small amount of the 5-methyl—8-hydroxyquinolinate anion in the complex.

The infrared spectrum of the solution (C, Figure 11), taken as described above, clearly showed characteristic bands at 2600 cm^{-1} and 2075 cm^{-1}.

(iii) 5-Nitro—8-hydroxyquinoline: The procedure was the same as that above. The concentration of 5-nitro—8-hydroxyquinoline was 6 mg/ml. About 10 mg/ml of the 5:1 compound were added. Again, the 5:1 compound was very soluble; a deep red solution formed. No dissociation to the tetrakis compound occurred. Only on complete removal of the solvent could a solid (dark yellow) be obtained. Since the solid was contaminated with free 5-nitro—8-hydroxyquinoline, characterization was not possible. Attempts to purify the residue by recrystallization from other solvents were not successful.

The spectrum (D, Figure 11) of the solution had an intense broad band centered at about 2700 cm^{-1} (with shoulders at 2850 and 2600 cm^{-1}), and a much weaker band at 2075 cm^{-1}.

(iv) Ethylenediammine: The 5:1 8-hydroxyquinoline complex was dissolved (25 mg/ml) in warm dichloroethane containing ethylenediammine (10 mg/ml). A yellow precipitate formed on cooling the solution. After filtration, the precipitate was washed with a small volume (8 ml) of dichloroethane and dried in a stream of air for 20 hours.

Calculated for $[Th(C_9H_6NO)_4 \cdot C_9H_6NOH]_2 \cdot C_2H_8N_2$: C, 56.12; H, 3.58; N, 8.54; Th, 23.57.

Found: C, 56.11; H, 3.63; N, 8.69; Th, 23.41.

The infrared spectrum (E, Figure 11) had a very weak band at 3350 cm^{-1} and unresolved absorption in the region 2850-2500 cm^{-1}.

(v) Quinoline and Pyridine: Quinoline (25 mg/ml) and pyridine (14 mg/ml) appeared to have no stabilising effect on the 5:1 8-hydroxyquinoline compound in solution. A yellow precipitate formed almost immediately when the orange compound was placed in warm dichloroethane. The infrared spectrum of the yellow compound was identical to that of the thermally prepared tetrakis compound. Elemental analyses of the compound gave the following result:

Calculated for $Th(C_9H_6NO)_4$: C, 53.45; H, 2.99; N, 6.93; Th, 28.70.

Found: C, 53.76; H, 3.37; N, 6.87; Th, 27.98.

An interpretation of the above data is given in Section (f), PART B DISCUSSION.

(h) Addition of 8-hydroxyquinoline to tetrakis(8-hydroxyquinolinato)thorium(IV)

The orange thorium(IV)—8-hydroxyquinoline compound is stable when dissolved in dichloroethane containing a large excess of 8-hydroxyquinoline

(Section (d) above). Also, the disproportionation of the tetrakis compound in dichloroethane is negligible (∿ 1%). Accordingly, dichloroethane was used as the solvent for the addition reaction. The concentration of 8-hydroxyquinoline was equal to 5 equivalents (i.e., in 400% excess) of the tetrakis compound and was maintained constant. Only the particle-size range < 74 microns was investigated (corresponding to the smallest screen-mesh on hand, #200), since it was difficult to prepare the tetrakis compound with a large particle size.

The experimental procedure was that used for the addition reaction involving the bis uranium(VI) compound. The amount of the tetrakis compound taken and of 8-hydroxyquinoline was 145.0±0.5 mg (0.18 millimoles) and 130.0±0.1 mg (0.9 millimoles), respectively.

The reaction times were 5, 60 and 180 minutes.

The addition reaction with C^{14}—8-hydroxyquinoline was carried out exactly as above. The data are recorded in Table XXIII, and discussed in Section (g), PART B, below.

TABLE XXIII

ADDITION REACTION BETWEEN C^{14}—8-HYDROXYQUINOLINE AND TETRAKIS(8-HYDROXYQUINOLINATO)THORIUM(IV)

Tetrakis compound taken = 145.0±0.5 mg

Particle size < 74 μ

HQ taken = 130.0±0.1 mg (400% excess)

Reaction Time (min)	Percent Add.	Sp. Act. Add. Prod. (mv/sec/mg)	Sp. Act. ThQ_4 (mv/sec/mg)	Sp. Act. Sub. HQ (mv/sec/mg)	(Sp. Act. HQ)-(Sp. Act. ThQ_4) (mv/sec/mg)
180	44	-	2.20	2.15	-
60	40	-	1.89* ±0.03	2.30* ±0.05	0.41 ±0.06
5	34	1.78**	1.68† ±0.04	2.20† ±0.01	0.52 ±0.04

* Average of two determinations.

**This result was used to determine that radiobalance existed.

† Average of three determinations.

DISCUSSION

PART A. Uranium(VI) Complexes of 8-Hydroxyquinoline and Derivatives

(a) Composition of the tris uranium(VI)—8-hydroxyquinoline complex

As outlined in the INTRODUCTION, the preparation of the red tris compound formed between uranium(VI) and 8-hydroxyquinoline has been reported in the literature several times. The method of Moeller and Wilkins (61) has been most frequently used for the preparation and was used in the present work.

Because preliminary analytical data did not indicate a strict 3:1 composition, a detailed investigation of the composition was made (Section (b), EXPERIMENTAL AND RESULTS). The data of Table IV indicate that the red compound is slightly deficient in 8-hydroxyquinoline. The data in the first row was obtained for samples that were dried without heating. This precaution was taken to ensure that not a trace of the thermally volatile neutral ligand was lost due to drying at an elevated temperature. A limited amount of data was obtained for samples that were dried for 3 hours at 110°C. Comparison with the data of the first row shows that these drying conditions did not significantly alter the results. The possibility that the deficiency was caused by hydrolysis of a small amount of the uranyl ion during precipitation was investigated by increasing the initial molar ratio HQ:U from 3.4:1 to 4.5:1 (i.e., from a 13 to 50% excess of reagent). The data was unaffected (third row); further experiments with excesses that approach the solubility limit of 8-hydroxyquinoline were not made.

Because of the mild drying conditions used, it is possible that the samples retained traces of moisture. Although the presence of moisture would lower both the percent U and Q^- in the tris compound, it would not affect the molar ratio of the species. Since the data obtained for samples that were dried at 110°C are not significantly different, the amount of moisture present cannot be substantial. The effect of the presence of coordinated water is discussed below.

The data of Table V, obtained by determining the relative amounts of sublimed 8-hydroxyquinoline and the bis compound, are in excellent agreement with the data of Table IV. As before, the presence of small amounts of unbound water in the red compound would not affect the molar ratio $HQ:UO_2Q_2$. That the red compound did retain traces of moisture, however, was confirmed by the presence of a very small droplet condensed in the U-tube below the 8-hydroxyquinoline deposit. If it is assumed that the deficient 8-hydroxyquinoline is replaced by coordinated water, the formula of the red compound can be written as $UO_2(C_9H_6NO)_2 \cdot 0.96C_9H_6NOH \cdot 0.04H_2O$. From the weights taken of the red compound (307.9 and 152.5 mg), calculation shows that the amount of coordinated water in the two samples is 0.32 and 0.15 mg. These amounts represent volumes (0.32 and 0.16 $\mu \ell$) that would hardly be discernible to visual observation. Thus, the bulk of the observed droplet must be present as moisture (0.3-0.4 mg moisture per 100 mg, by calculation).

The validity of the conclusions depends heavily on the accuracy of the analytical determinations, since the effect being sought is small. For this reason, classical elemental analysis for C, H and N were not done, since the accuracy of such determinations does not approach that of the bromometric determination. To test the accuracy of the latter method, known amounts of purified 8-hydroxyquinoline were brominated under the conditions prevailing in the analysis of the uranium-containing compound. The samples ranged in weight from 40 to 300 mg. In no case did the absolute error exceed ±0.1 mg. To obtain the data in Table IV, the weights of the red compound taken for bromination ranged from about 100 to 135 mg. When these weights are corrected for the presence of moisture (∿ 0.4 mg), it can be shown that the deficiency of 8-hydroxyquinoline being sought is 0.7-0.9 mg. The bromometric error is within this range, representing 10-15% of it. A corresponding test for the accuracy of the uranium determination (ignition of the complex to U_3O_8) could not be devised, but the experimental value (33.94%) agrees well with the expected value (33.95%) for the non-stoichiometric compound containing 0.4% moisture. The statistical student t test indicates that the difference between the experimental value and the value for a 3:1 composition (33.84%), although small, is significant.

More latitude was obtained in experiments involving the determination of the molar ratio $HQ:UO_2Q_2$ (Table V), in which the deficiency in 8-hydroxyquinoline was 2.1 and 1.0 mg for the two samples. Similarly, in experiments in which only the sublimed 8-hydroxyquinoline was determined (as percent sublimed 8-hydroxyquinoline in the red compound), the deficiency was about 3.5-6.3 mg (for sample weights of about 500-900 mg). In these experiments, the average of four results was 19.92±0.05% (Table VI). Based on a stoichiometric compound containing 0.4% moisture, the theoretical percent sublimed 8-hydroxyquinoline is 20.55; for a compound with the composition $UO_2(C_9H_6NO)_2 \cdot 0.96C_9H_6NOH \cdot 0.04H_2O$ and containing 0.4% moisture, the percent sublimed 8-hydroxyquinoline is 19.87, considerably closer to the experimental result.

Since the three methods of analysis give essentially the same result, it is concluded that the red complex is slightly deficient in 8-hydroxyquinoline, at least when prepared by the method of Moeller and Wilkins.

Of the previous workers, only Claassen and Visser (58) have reported that the red compound is slightly deficient in 8-hydroxyquinoline (see INTRODUCTION).

The deficiency can be readily explained by competition from coordinating ligands such as water or ammonia for the coordination site occupied by the neutral 8-hydroxyquinoline ligand. Competition by water or ammonia has been demonstrated in the case of uranium(VI) complexes of 7-substituted derivatives of 8-hydroxyquinoline (76). In these complexes, steric interference from the 7-substituent prevents the stable attachment of the neutral ligand. As a result, complexes with the composition $UO_2(R\text{-}C_9H_5NO)_2\cdot H_2O$ (R = 7-methyl or 7-t-butyl), and $UO_2(R\text{-}C_9H_5NO)_2\cdot NH_3$ (R = 7-methyl, pH adjusted by urea hydrolysis) are obtained.

With an initial reagent concentration much higher than that used in this study, and with different pH conditions, it should be possible to prepare the stoichiometric red compound.

Whether pH values below or above the range (4.9-5.2) used in this study would be more suitable depends on the mechanism of attachment of the neutral ligand. If this ligand reacts in its fully protonated form (H_2Q^+) and the phenolic proton is released during the formation of the U—O bond, preparation of a stoichiometric compound would be favoured by a lower pH, since the concentration of H_2Q^+ would be higher. On the other hand, if reaction is by the neutral species, HQ, and the phenolic proton is transferred to the nitrogen atom during the formation of the U—O bond, the stoichiometric compound would be favoured by a higher pH. Judging from the observation (65) that at pH 6.8, an orange-red compound with the composition $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ is precipitated, while at pH 5.0. the red tris compound is obtained, it appears that the formation of the stoichiometric compound would be favoured by a lower pH.

The data presented in this study suggest that one in about 25-30 uranium atoms is deficient in 8-hydroxyquinoline. This effect is too small to allow detection of the competing ligand by infrared or X-ray methods.

(b) Thermal preparation of pure bis(8-hydroxyquinolinato)dioxouranium(VI) and thermal ligand exchange

Initial attempts to thermally prepare the pure bis compound were based on the frequently used procedure of Moeller and Wilkins (61), who did not report supporting analytical data. This method involves heating the red compound in air at 210-215°C for 48 hours.

The results obtained (Section (c), PART A, EXPERIMENTAL AND RESULTS) clearly show that appreciable decomposition of the bis compound occurred. The use of shorter heating periods resulted in improved results. For the shortest heating period (2 hours), the results were non-reproducible, probably because variability in the thickness of the sample layer and in particle-size distribution are important at such short times.

The pure bis compound was easily prepared by heating about 500-900 mg of the red compound in vacuo at 210-215°C for 4 hours. (For smaller samples, complete conversion would likely require less than 4 hours.) In vacuo, the length of the heating period beyond 4 hours is not critical (Table VII). In air, the duration of the heating period is critical (58). The advantage in preparing the bis compound in vacuo rather than in an oxidizing atmosphere is readily apparent.

These results do not contradict those of earlier TGA and DTA studies (37,40,49), in which it was shown, for example, that no weight loss occurs up to 220°C. The experimental conditions of TGA and DTA are much different than those used in the present study, and an exact correspondence in the temperature of a thermal reaction is not to be expected.

A mechanism by which 8-hydroxyquinoline is thermally removed from the tris complex has not been proposed. Whatever the mechanism, the data of Table VIII show that intermolecular ligand exchange occurs ($\sim$ 25%) at the temperature of the thermal reaction. This is evidenced by the fact that the specific activity of the sublimed HQ is lower than 3.58 mv/sec/mg, and the specific activity of the bis compound, higher than 1.30 mv/sec/mg (1.68 mv/sec/mg for Expt. II). These results could be obtained only if an intermolecular exchange of ligands occurred between the active tris and inactive bis compounds, intimately mixed in the reaction flask.* Thus, extensive bond-breakage must occur under the conditions of the thermal reaction.

Experiments that duplicate the exact conditions of the thermal reaction could not be devised because the tris compound could not be prepared with specific C^{14}— labelling of only the additional molecule (or of only the two bidentate ligands).

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* It is reasonable to assume that intramolecular exchange must occur to an even greater extent than intermolecular exchange.

(c) Infrared spectra of the uranium(VI) complexes

Several workers (52,63,68) have examined the tris uranium(VI)—8-hydroxyquinoline complex by infrared spectroscopy, but little structural information has been obtained. Charles et al. (63) assigned the strong band at 1114 cm^{-1} to a diatomic vibration associated with the C—O bond in the ═C—O—M grouping, and the intense band at 890 cm^{-1} to the UO_2 group.

No attempt has been previously made to assign absorption bands due to the proton in the tris complex. The purpose of this work was to identify the protonic vibrational bands and from these, to locate the position of the proton in the tris complex. As stated earlier (Section (d), PART A, EXPERIMENTAL AND RESULTS), the samples were prepared as mulls in hexachloro—1,3-butadiene.

The spectrum of the tris compound (A, Figure 1) has an unusually broad band of medium intensity centered at about 2650 cm^{-1}, and a weaker band at 2050 cm^{-1}. These bands, which have been overlooked by previous investigators, are not present in the bis complex (C, Figure 1) or free 8-hydroxyquinoline (A, Figure 3).

That these bands arise from protonic vibrations is proved by the facts that (i) the bands are absent in the sodium salt* of the tris complex, and (ii) in the deuterated complex (B, Figure 1), the 2650 cm^{-1} band is shifted to 2050 cm^{-1} (broader than the 2050 cm^{-1} band in the undeuterated complex), and the 2050 cm^{-1} band to 1524 cm^{-1}, giving $\nu_H/\nu_D = 1.29$ and 1.35, respectively.

Since the spectra of the hydrochloride salts of 8-hydroxyquinoline

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* Prepared by the procedure described by Bullwinkel and Noble (64).

(B, Figure 3), 8-methoxyquinoline (D, Figure 1), and 2-methyl—8-hydroxyquinoline (C, Figure 2) also exhibit similar bands (although somewhat shifted from 2650 and 2050 cm^{-1}), it is concluded that in the tris complex, the proton is located on the N atom of the extra ligand - i.e., the ligand is a zwitter-ion.

The spectra of pyridine hydrochloride (Figure 4) and 6-aminoquinoline hydrochloride hydrate (III) also contain these bands (2450*, 2100 cm^{-1} and 2630, 2090 cm^{-1}, respectively). In the spectrum of quinoline hydrochloride (C, Figure 3), the broad band has a shoulder at 2350 cm^{-1} and the 2050 cm^{-1} band exhibits fine structure. In all these spectra, the intensity of the bands is much higher than observed in the tris uranium(VI) complex. This is undoubtedly related to the large molecular size of the uranium(VI) complex, in which the infrared active $>\overset{+}{\mathrm{N}}\mathrm{H}$ group is dilute.

These bands have also been observed in the spectra of the acid salts of many organic bases, and have been the subject of several investigations (112-118). In these investigations, the bands were attributed to the vibrational modes of the $>\overset{+}{\mathrm{N}}\mathrm{H}$ group. The displacement of the broad 2450 cm^{-1} band in pyridine hydrochloride from the normal $>\overset{+}{\mathrm{N}}\mathrm{H}$ stretching frequency (3200 to 3360 cm^{-1}) has been attributed (112,115,118) to strong hydrogen bonding of the type N—H---Cℓ. Kynaston et al.(115,118) has shown that in the spectra of pyridinium tetrachloroborate, pyridinium mercurichloride $[(C_5H_5NH)^+(HgC\ell_3)^-]$ and 2,6-di-t-butyl pyridinium mercurichloride, no absorption occurs in the range 2200-2800 cm^{-1}, but strong sharp bands are obtained in the range 3164-3362 cm^{-1}. In 2,6-di-t-butyl pyridinium mercurichloride, hydrogen bonding is sterically prevented, and the 3362 cm^{-1} band is believed to represent the stretching frequency of the free $>\overset{+}{\mathrm{N}}\mathrm{H}$ group.

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* This frequency is quoted in reference (112).

It is apparent, then, that in the tris uranium(VI)—8-hydroxyquinoline complex, the proton is strongly hydrogen bonded.

The extreme band width has been attributed to the composite nature of the band, in which the band components are unresolved because of intermolecular interactions (112,114). Considerable structure is observed, however, with the hydrochloride salts of aliphatic ammines. The broadness (i.e., high integrated intensity) of the 2500 cm^{-1} band is characteristic of H—bonding. This characteristic has not been satisfactorily explained on a theoretical basis. Theoretical explanations have appealed to the superposition of the symmetrical stretching frequency on the antisymmetrical stretching frequency, to coupling of the stretching vibrations with vibrations of lower frequency, and to the double-minima potential model (114). The 2100 cm^{-1} band may represent a combination band between the scissoring frequency ($\sim$ 1600 cm^{-1}) and a low internal frequency or lattice frequency ($\sim$ 400 cm^{-1})(114). However, it may merely represent the perpendicular (i.e., in-plane) bending vibration, the frequency of which has been predicted by Bader (119) to increase on hydrogen bonding.

In the tris uranium(VI)—8-hydroxyquinoline complex, the deuterium isotope effect was 1.29 and 1.35 for the high- and low-frequency bands, respectively (theoretical, 1.41). Lord and Merrifield (112) obtained 1.29 for the 2450 cm^{-1} band of pyridine hydrochloride and attributed this low value to the anharmonicity of the vibration. Pimentel and McClellan (120) have pointed out, however, that the data of Lord and Merrifield are not conclusive evidence for anharmonicity. Anharmonic effects are minor and account only partly for the difference observed.*

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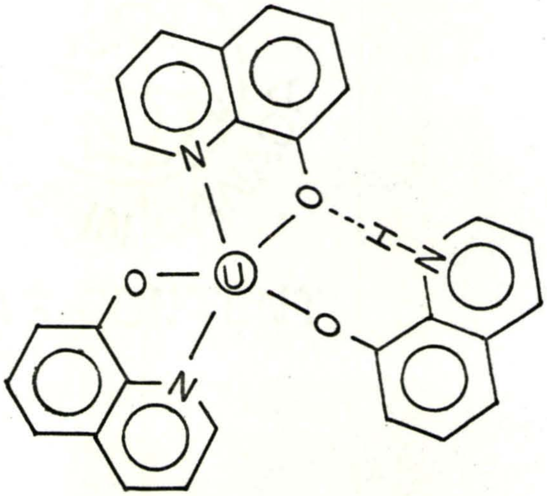
* The fact that isotope-effect theory applies strictly to gases also accounts for part of the difference. The most important effect, however, is the contribution of the masses of the basic atoms involved in the hydrogen bond to the reduced mass of H and D. This contribution reduces the experimental ratio.

The isotope effect for the 2050 cm^{-1} band in the tris compound is in closer agreement with 1.41. This is expected for a bending vibration.*

The foregoing evidence leaves little doubt that the proton is on the nitrogen atom of the monodentate ligand and is hydrogen bonded. Examination of Courtauld models (based on the X-ray structure) shows that the hydrogen bond must involve the phenolate oxygen of the neighbouring bidentate ligand, to which the proton makes a very close approach (II). In this respect, the ligand can be termed "pseudo-bidentate". A survey of about 40 compounds in which $\overset{+}{N}—H---O$ bonding occurs shows that the most probable N—O distance is 2.8-2.9 Å (121). In the tris compound, the N—O distance is 2.71 Å (20), which suggests a strong hydrogen bond.



II

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* The basic atoms contribute little to the bending motion.

The present work proves the suggestion of Bullwinkel and Noble (64) to be incorrect. These investigators speculated that the proton is intermolecularly hydrogen bonded to uranyl oxygens, resulting in the formation of long chains of the type ---O=U=O---H---O=U=O---H---O=U=O---.

The structure of the sodium salt of the tris compound has not been determined,* but would be of considerable interest. Bullwinkel and Noble (64) have proposed that in the complex anion, all three ligands are bidentate.

The spectra of the tris uranium(VI) complexes of 5-acetyl— and 5-nitro—8-hydroxyquinoline (A, B, Figure 2) are essentially identical to the spectrum of the 8-hydroxyquinoline complex, and it is likely that the structures are also similar.

It is interesting that the spectra of U(VI) compounds derived from 7-CH_3—, 2,7-dimethyl—, 5,7-dichloro—, 5,7-dibromo— and 7-t-butyl—8-hydroxyquinoline do not exhibit the 2650 and 2050 cm^{-1} bands (76). These sterically hindering ligands yield complexes shown in Table XXIV.

The introduction of substituent groups in the 7-position of the quinoline ring sterically prevents coordination of the additional reagent molecule, and smaller ligands present in solution occupy the open position (76). When the substituent is away from the coordinating site, as in the 5-substituted 8-hydroxyquinolines, the tris complex is again formed.

The identification of the infrared bands for the hydrogen bonded $>\overset{+}{N}H$ group is obviously an important diagnostic test for studies on the addition complexes of other metal ions.

In view of the foregoing, it is worth commenting on the DTA endothermic peak observed by Horton and Wendlandt (40) at 150°C. These workers

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* An attempt to determine the structure by X-ray analysis was not successful (122)

TABLE XXIV

U(VI) COMPLEXES OF 7-SUBSTITUTED DERIVATIVES OF 8-HYDROXYQUINOLINE*

Ligand	Complex
7-Me	$UO_2(C_{10}H_8NO)_2 \cdot H_2O$ $UO_2(C_{10}H_8NO)_2 \cdot NH_3$
2,7-di-Me	$UO_2(C_{11}H_{10}NO)_2 \cdot H_2O$
7-t-Bu	$UO_2(C_{13}H_{14}NO)_2 \cdot H_2O$
5,7-di-Cℓ	$UO_2(C_9H_4Cl_2NO)_2 \cdot CO(CH_3)_2$
5,7-di-Br	$UO_2(C_9H_4Br_2NO)_2 \cdot CO(CH_3)_2$

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* Data of reference (76).

suggested that it was due to a rearrangement reaction of the complex rather than to a reaction (e.g., a decomposition) involving the elimination of a gas, since a gaseous product could not be detected. It is suggested here that this interpretation is basically correct, and that the endothermic absorption corresponds to rupture of the hydrogen bond followed by a rearrangement (of this ligand or of the complex as a whole) prior to the elimination of the 8-hydroxyquinoline ligand.

Also, it is worth commenting on the compound $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$ first prepared by Bordner et al. (65), and later examined by Magee and Gordon

(68,93) and Magee and Woodward (96).

Magee and Woodward (96) have suggested that this compound is an amorphous polymer since no X-ray powder lines could be obtained. They proposed that the basic polymeric unit is composed of the 3:1 and 2:1 compounds held together by a bond between the N atom of the monodentate ligand and the U atom of the 2:1 compound. In turn, the basic polymeric units are bonded by a proton bridge between the uranyl oxygens of the 2:1 compound in adjacent units. This suggestion is not likely correct since the infrared spectrum of the compound is essentially identical to that of the tris compound, with the characteristic bands present at 2650 and 2050 cm^{-1}. Therefore, in $[UO_2(C_9H_6NO)_2]_2 \cdot C_9H_6NOH$, the proton is located on the N atom, and the structure is not as proposed by Magee and Woodward. Some other form of bonding is required to hold the 3:1 and 2:1 components together in a unit, and to expand the unit polymerically.

It is interesting that the compound has been prepared only by a PFHS method (involving a slow hydrolysis of 8-acetoxyquinoline). Also, a low reagent concentration and a relatively high pH value (6.8) were used. One might consider the compound to be an equimolar mixture of $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$ and $UO_2(C_9H_6NO)_2 \cdot H_2O$ (or $.NH_3$). The analytical data of Bordner et al. (65), however, preclude this possibility.

All of the more important structural details of the tris compound are now known. For the newly reported tris complexes of 5-nitro— and 5-acetyl—8-hydroxyquinoline, it will be interesting to see if future X-ray work bears out the structural similarities suggested by the infrared studies. Of particular interest would be the structural determination of the uranium(VI) compounds of the sterically hindering derivatives, and of the bis 8-hydroxyquinoline complex.

Finally, no further interpretation of the infrared spectra were attempted. Most of the bands in the spectrum remain unassigned.

(d) Interaction of the tris uranium(VI)—8-hydroxyquinoline complex with solvents

From the results described in Section (e), PART A, EXPERIMENTAL AND RESULTS, it is clear that polar coordinating solvents such as dimethylsulfoxide, dimethylformamide and pyridine interact strongly with the tris complex. The compound isolated from dimethylsulfoxide was shown to be $UO_2(C_9H_6NO)_2 \cdot OS(CH_3)_2$ by elemental analysis. In the infrared spectrum, there was no absorption at 2650 and 2050 cm^{-1}, and a new strong absorption band appeared at 1015 cm^{-1}. This band is present in dimethylsulfoxide complexes such as $Hg(SCN)_2 \cdot 2OS(CH_3)_2$ and $[Co\{OS(CH_3)_2\}_6]^{2+}$ (124), and is due to absorption by the coordinated $>$S=O group. Thus, interaction of the tris compound with polar solvents is by displacement of the monodentate ligand. Dimethylformamide and pyridine also appear to displace this ligand but the experimental data are not complete. This is the first reported preparation of a 2:1 uranium(VI)—8-hydroxyquinoline complex with a different ligand occupying the remaining coordination position. Like other 7-coordinated uranium(VI) complexes (23), its structure is expected to approximate the pentagonal bipyramid.

Less polar solvents such as dichloroethane, dioxane and absolute ethanol do not displace the monodentate ligand.

(e) Exchange reaction between the tris uranium(VI)—8-hydroxyquinoline complex and C^{14}—8-hydroxyquinoline

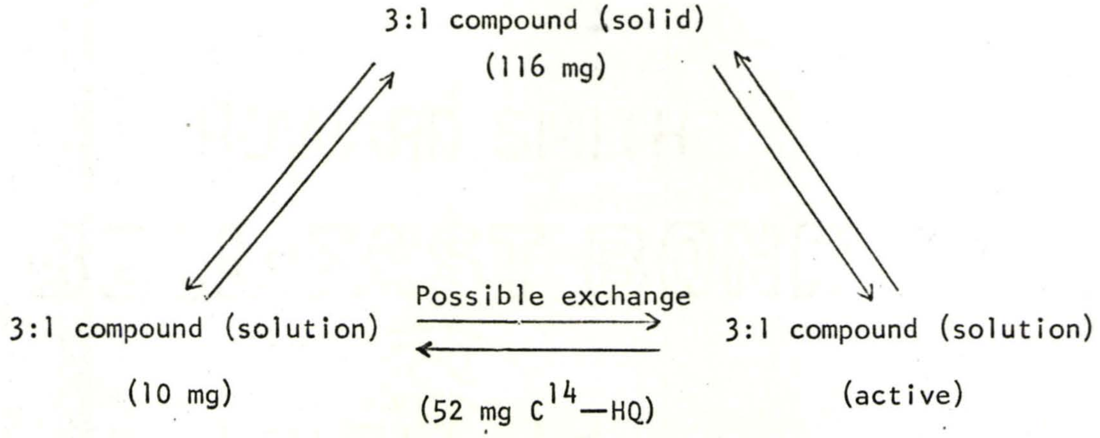
The low specific activity (0.1 mv/sec/mg) found in the bis compound and the sublimed 8-hydroxyquinoline (Section (f), PART A, EXPERIMENTAL AND RESULTS) after reaction for 30 and 180 minutes indicates that all ligands of the tris compound are resistant to exchange with C^{14}—8-hydroxyquinoline. For complete exchange, the specific activity would have been 1.44 mv/sec/mg.

This result could be used as the basis for determining whether, in the addition complexes of other metal-ions, the extra 8-hydroxyquinoline molecule is coordinated to the central atom, or is a lattice component. If the extra molecule in the U(VI) compound was a lattice component, the compound isolated from the reaction mixture would have been highly active in a relatively short period of time. This follows because on dissolution, the adduct compound would have dissociated into 8-hydroxyquinoline and the bis compound. As shown in Section (h), below, the bis compound undergoes rapid exchange and addition to the 3:1 compound in the presence of free 8-hydroxyquinoline. Since, in the present experiment, the solution contained a large excess of C^{14}—8-hydroxyquinoline, a high level of activity would have been expected in the adduct compound obtained from the reaction mixture. That this was not found is proof that the uranium(VI) addition compound exists in solution as a stable molecular entity.

This test, together with infrared data, could yield considerable information when applied to other addition complexes of 8-hydroxyquinoline. The results of experiments with the 5:1 thorium compound are given in Section (d), PART B, DISCUSSION.

A limitation of the test is that it likely would not distinguish between a very weakly coordinated molecule and a lattice-component molecule.

The solubility of the tris uranium(VI) compound in 5 ml of dichloroethane is about 10 mg. Since the initial amount taken was 126 mg, the reaction system was heterogeneous. Since the solubility equilibrium is attained in about 5 minutes (Section (i), PART A, EXPERIMENTAL AND RESULTS), however, all or most of the tris compound would have had the opportunity to participate in the relevant solution equilibria after 180 minutes. The equilibria can be depicted as follows:



As a precaution against non-attainment of the solubility equilibrium, the experiment was repeated using 33 mg of the tris compound and the same amount (52 mg) of C^{14}—8-hydroxyquinoline. After 180 minutes, the specific activity of the isolated tris compound was 0.36 mv/sec/mg (2.58 for complete exchange). Considering the relative amounts of the tris compound taken in the two experiments, this result is consistent with the first, and shows that the heterogeneous reaction system does not invalidate or unduly complicate the interpretation of the results.

(f) Stoichiometry of the uranium(VI)—8-hydroxyquinoline complex in 50% V/V aqueous dioxane

The mole-ratio graphs at each wavelength (475 and 500 mμ) show a sharp break at a ligand-to-metal ratio of 2.3 (Figure 2, APPENDIX II). It is difficult to reconcile this result in terms of a solution species in 50% V/V aqueous dioxane.

It is not likely that the non-integral value is a result of extensive dissociation* of the monodentate ligand. If this were the case, a gradually increasing rather than a constant absorbance would have been observed as the ligand-to-metal ratio was increased above 3:1. Furthermore, The degree of curvature below the point of intersection of the extrapolated lines would have been substantially greater than observed. Indeed, the low degree of curvature indicates that the complex formed in solution is appreciably stable. Since the data from the potentiometric titrations show that the HQ:U ratio of the species in solution is 2:1 (2.07:1), the non-integral ratio can likely be ascribed to an indeterminate experimental error. Furthermore, the high value of log β_2 (20.89) for the formation of the 2:1 complex in 50% V/V aqueous dioxane (126) is consistent with the low degree of curvature in the mole-ratio plot.

As shown in Figure 3, APPENDIX II, the important features of the titration curves representing a 2:1 and 3:1 ratio of ligand-to-metal are identical. In each, two buffer regions in the pH ranges 4 to 6 and 7 to 10, are present. In each curve, the lower buffer region corresponds to a release of two protons per U(VI) ion (curve B, 2.07; curve C, 2.07), and the higher one to one proton per U(VI) ion (curve B, 1.02; curve C, 1.02). The two-proton release is due to the addition of two ligands to a U(VI) ion. For Curve B, the ligand-to-metal ratio was 2:1 and the release of the single

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* The mole-ratio and related methods are known to be unreliable for the determination of the composition of weak complexes (125).

proton corresponds to hydrolysis, i.e.,

$$UO_2(C_9H_6NO)_2 \cdot H_2O \rightleftarrows [UO_2(C_9H_6NO)_2 \cdot OH]^- + H^+$$

Since Curve C is identical to Curve B, the release of the lone proton must also correspond to hydrolysis. This is confirmed by noting that in the pH range 10-12, Curve C is lower than Curve B because of the titration of uncomplexed 8-hydroxyquinoline in the solution.

From the data just presented, it is concluded that in 50% V/V aqueous dioxane, U(VI) and 8-hydroxyquinoline react to form the soluble species, $UO_2(C_9H_6NO)_2 \cdot H_2O$. Coordination of the polar solvent component prevents attachment of the additional ligand.

In apparent contradiction is the fact that in a purely aqueous solution, U(VI) and 8-hydroxyquinoline react to give the solid, $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$. The difference in behaviour between the two reaction systems could be accounted for as follows. (i) Because of the presence of a significant amount of dioxane, considerable break-down of the hydrogen-bonded water structure occurs, allowing water to compete more effectively for the remaining coordination site after attachment of the two bidentate ligands. (ii) Assume that in water, the following equilibria exist:

$$UO_2(H_2O)_5^{++}(\text{soln.}) + 2C_9H_6NOH(\text{soln.}) \rightleftarrows UO_2(C_9H_6NO)_2 \cdot H_2O(\text{soln.}) + 4H_2O + 2H^+ \quad (1$$

$$\begin{array}{r} UO_2(C_9H_6NO)_2 \cdot H_2O(\text{soln.}) + C_9H_6NOH(\text{soln.}) \rightleftarrows UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH(\text{soln.}) + H_2O \quad (2 \\ \downarrow\uparrow \qquad\qquad\qquad \\ UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH(\text{solid}) \qquad\qquad\quad \end{array}$$

Because the energy of crystallization is greater than the energy of solvation, precipitation of the tris compound occurs. Although the solution concentration of the tris compound may be low, its crystallization causes the equilibria to shift and, therefore, precipitation to be essentially quantitative. In 50% V/V aqueous dioxane, the solvation energy, and thus, the solubility, of the tris compound is increased. Therefore, crystallization does not occur and the predominant species in solution is the aquated bis complex.

Interestingly, when precipitation from 50% V/V aqueous dioxane was promoted by using high concentrations of reactants, the complex $UO_2(C_9H_6NO)_2 \cdot CO(NH_2)_2$ was obtained. The source of the urea ligand was the relatively large amount of urea added to raise the pH through hydrolysis (as in the precipitation of the tris compound from water). When, however, dilute sodium hydroxide was used to raise the pH and the solution was concentrated by prolonged heating (5 hours) on a steam bath, the tris compound precipitated.

Because of the greater affinity of uranium(VI) for oxygen rather than nitrogen donor atoms, the urea is likely bonded to the central uranium atom through the carbonyl oxygen, as in $UO_2(OH)_2[CO(NH_2)_2]_2$ (123), rather than through one of the terminal nitrogen atoms, as in $[Pt\{CO(NH_2)\}_2C\ell_2]$ (127,128). Evidence of this is provided in the infrared spectrum of urea-bis(8-hydroxyquinolinato)dioxouranium(VI) (B, Figure 5). The absorption band due to the coordinated carbonyl group is at 1625 cm^{-1}, and is considerably shifted from the carbonyl absorption at 1683 cm^{-1} in free urea (see (123)).

Like the complex $UO_2(C_9H_6NO)_2 \cdot OS(CH_3)_2$, the compound

$UO_2(C_9H_6NO)_2 \cdot CO(NH_2)_2$ is a further example of a uranium(VI)—8-hydroxyquinoline complex in which coordination of the additional 8-hydroxyquinoline ligand is prevented by a secondary ligand. The properties of the secondary ligand which appear to determine the displacement of the 8-hydroxyquinoline ligand are smaller size[*] and the presence of a neutral oxygen donor.[**]

(g) Interaction of bis(8-hydroxyquinolinato)dioxouranium(VI) with solvents

Table XI summarizes the important features of the infrared spectra of the compounds isolated from the interaction of bis(8-hydroxyquinolinato)-dioxouranium(VI) with 95 percent ethanol, methanol, acetone and chloroform.

The presence of the 2650 and 2050 cm^{-1} bands shows that disproportionation of the bis to the tris compound occurred on interaction with all solvents except dichloroethane. The infrared spectrum of the compound isolated from dichloroethane was identical to that of the bis compound. When a small amount of water was added to the dichloroethane, however, the tris compound was isolated (infrared and elemental analyses).

Each of the solvents were used as obtained commercially (except the dichloroethane, which was dried over molecular sieves), and contained different amounts of water. Thus, the disproportionation reaction can be depicted in a manner similar to that reported by Bullwinkel and Noble (64), i.e., $3UO_2(C_9H_6NO)_2 + 2H_2O \rightleftharpoons 2UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH + (\underset{\substack{\downarrow \\ \text{formation of uranates}}}{UO_2^{++}} + 2OH^-)$

Fleming and Lynton also found (21) that recrystallization of the bis

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[*] With three 8-hydroxyquinoline ligands, the equatorial plane of the uranyl ion is crowded (20).

[**] Coordination by a neutral rather than an anionic oxygen donor would cause less transfer of negative charge to the highly coordinated uranium atom.

compound from chloroform yielded the tris compound. (The tris compound was said to contain a molecule of lattice-held chloroform. In the present work, the bands at 2950 (D, Figure 6) and 750 cm^{-1} in the infrared spectrum confirm the presence of chloroform.)

It appears that a role of water is the disproportionation reaction is to protonate 8-hydroxyquinolinate anions for the formation of the tris compound.

The infrared spectra (A, B, C, Figure 6) also provide evidence for the following solvolysis reactions:

$$UO_2(C_9H_6NO)_2 + C_2H_5OH = UO_2(C_9H_6NO)_2 \cdot C_2H_5OH$$

$$UO_2(C_9H_6NO)_2 + CH_3OH = UO_2(C_9H_6NO)_2 \cdot CH_3OH$$

$$UO_2(C_9H_6NO)_2 + (CH_3)_2CO = UO_2(C_9H_6NO)_2 \cdot CO(CH_3)_2$$

Since the mixture of reaction products was dried at 105°C for 1 hour, it is not likely that acetone, methanol and ethanol are present in the indicated quantities as contaminants. In the acetone complex, the carbonyl stretching frequency is at the same frequency as in $UO_2(C_9H_4X_2NO)_2 \cdot CO(CH_3)_2$ ($X = C\ell$ or Br) (95).

(h) Addition of 8-hydroxyquinoline to bis(8-hydroxyquinolinato)dioxouranium(VI)

Dichloroethane was used as the solvent because of the stability of the bis and tris compounds in it. Consequently, the addition reaction was not complicated by the occurrence of disproportionation and solvolysis. As stated in Section (i), PART A, EXPERIMENTAL AND RESULTS, the reaction system was heterogeneous.

The data of Tables XII, XIII and XIV show the effect of reaction time, concentration of 8-hydroxyquinoline, and the initial particle size of the bis compound, on the extent of addition. It is possible to obtain quantitative addition after 5 minutes if a sufficient excess (i.e., 500%) of 8-hydroxyquinoline and a small particle size (< 74 μ) are used.

As mentioned previously, the addition reaction was first reported by Frere (43) but his investigation was only qualitative. He reported none of the important reaction conditions, did not study the reaction as a function of the reaction variables, and also miscalculated the extent of addition (INTRODUCTION).

The addition reaction can be conceived as occuring by one or both of the following mechanisms.

(i) Addition in solution: On dissolution of a small amount of the bis compound in dichloroethane, addition occurs to yield the tris compound, which precipitates after saturation of the solution. Further dissolution of the bis compound and further formation and precipitation of the tris compound occur. Given sufficient time, all of the bis compound would have an opportunity to dissolve and to react with the 8-hydroxyquinoline in solution, and the final reaction mixture would consist of a solution saturated with the tris compound and the tris compound present as a solid.

The process can be depicted by the following equilibria:

$$\begin{tikzcd}
\text{bis compound (solid)} \arrow[d, shift right] & & \text{tris compound(solid)} \arrow[d, shift right] \\
\text{bis compound (soln.)} \arrow[u, shift right] \arrow[rr, shift left, "\text{HQ(soln.)}"] & & \text{tris compound(soln.)} \arrow[u, shift right] \arrow[ll, shift left]
\end{tikzcd}$$

(ii) Heterogeneous addition: In this mechanism, it is considered that the 8-hydroxyquinoline in solution interacts with the external and internal surface of the small particles, the latter by penetration of the solution. This mechanism implies that the size of the particle is important in determining the rate of addition. Indeed, the data of Table XIV show that for a reaction time of 5 minutes, the percent addition increases as the size of the particle decreases. This observation can also be readily explained, however, by the first mechanism, i.e., as the size of the particle is decreased, the rate of dissolution of the bis compound, and therefore of the addition reaction, is increased.

A more sophisticated attempt to determine whether a relationship exists between the extent of addition and the initial mean particle-size may not prove fruitful, since the initial mean size would soon be altered by operation of the solubility equilibrium involving the bis compound.

The structure of bis(8-hydroxyquinolinato)dioxouranium(VI) is unknown, but Bullwinkel and Noble (64) have suggested that it is polymeric. Other complexes in which the central U(VI) atom is coordinately unsaturated are known (i.e., bis(acetylacetonato)uranium(VI)) and it has been suggested (129) that these are probably dimeric, with bridging donor atoms.

If the bis compound is dimeric or polymeric, the detailed mechanism for the addition reaction must provide for the breakup of the polymer into units*. The detailed mechanism is undoubtedly complex but would be interesting to pursue, after the structure of the bis compound becomes known.

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* For example, into units in which the coordination number of the central U(VI) atom is 6, followed by the addition of the extra ligand, or into units of the tris compound, during or after addition of the ligand.

The data for the addition reaction with C^{14}—8-hydroxyquinoline are given in Tables XV and XVI, in which are shown the effect of reaction time and 8-hydroxyquinoline concentration, respectively.

Examination of the data reveals three interesting features.

(i) There is more activity in the addition product than is expected from the amount of active 8-hydroxyquinoline added. This point is illustrated, for example, by the data corresponding to a 5-minute reaction time in Table XV. Under the conditions of the addition reaction, 100 mg of the bis compound add 20 mg (i.e., 77% addition) of the active 8-hydroxyquinoline (original specific activity = 3.58 mv/sec/mg). In the absence of complicating reactions, the specific activity of the isolated addition product should be 1.0 mv/sec/mg. Since 100 mg of the bis compound contain 52 mg of 8-hydroxyquinoline, the specific activity of the addition product should be $[20/(52 + 20)] \times 3.6 = 1.0$ mv/sec/mg. The measured specific activity, however, is 1.75 mv/sec/mg. The higher specific activity could only result if an exchange reaction involving the originally inactive ligands of the bis compound and the active 8-hydroxyquinoline in solution is occurring together with the addition reaction. This exchange could occur only before or during the addition step (in which, presumably, a rearrangement of the existing ligands, and therefore bond-rupture, occurs), since the tris compound, once formed, exchanges relatively slowly (Section (e), above).

(ii) The specific activity of the bis compound and of the sublimed 8-hydroxyquinoline are equal for reaction times of 15 minutes and longer. Only for a reaction time of 5 minutes (Tables XIV and XV) is there a substantial difference. This observation could be explained by either one or both of the following processes.

1. At the end of 5 minutes, a quantity of the bis compound remains unreacted and simply acts as a diluent to the activity of the reaction products. The specific activity of the sublimed 8-hydroxyquinoline would then be higher than that of the residual bis compound from the thermal reaction, since the latter is radioactively diluted. As the reaction time is increased, however, the amount of reacted bis compound also increases, and when sufficient time* has elapsed for all reactions (exchange and addition) to have reached equilibrium, the specific activity of the sublimed 8-hydroxyquinoline and the residual bis compound are equal.

If it is assumed that the exchange reaction occurs at the time of addition, a correction can be applied for the specific activity of the bis compound in Tables XV and XVI. Table XXV gives the corrected values. These values are not very different from those for the sublimed 8-hydroxyquinoline. If the correction is valid, the C^{14} data would not allow one to conclude that the extra molecule of 8-hydroxyquinoline is different from the other two. This interpretation is not entirely correct, however, because even for 100 percent addition, the specific activity of the bis compound and of the sublimed 8-hydroxyquinoline are significantly different (Table XVI).

2. Since, for 100 percent addition, the specific activities are significantly different, it appears that the exchange and addition reaction are independent of one another and proceed with different rates. Therefore, the data for a reaction time of 5 minutes show that one ligand is different from the other two. The same conclusion was drawn previously, of course, from X-ray and infrared analyses.

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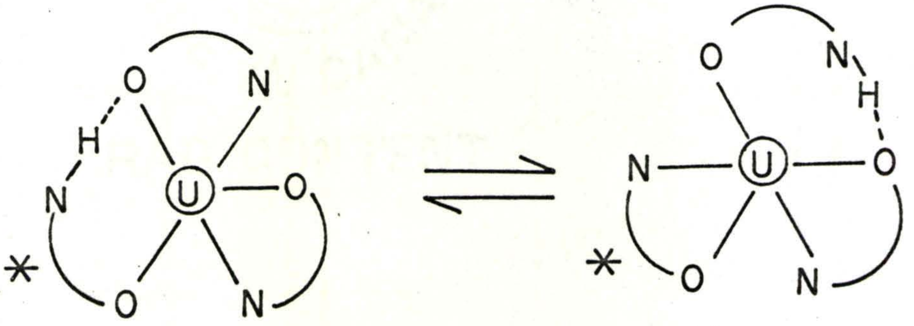
* Fifteen minutes or more.

TABLE XXV

SPECIFIC ACTIVITY -- CORRECTED FOR UNREACTED BIS COMPOUND

Percent Addition	Measured Sp. Act. of Bis Compound (mv/sec/mg)	Corrected Sp. Act. of Bis Compound (mv/sec/mg)	Measured Sp. Act. of Sub. HQ (mv/sec/mg)
67	1.23	1.84	1.69
77	1.59	2.06	2.21
92	1.88	2.05	2.20

After sufficient time has elapsed (≥ 15 minutes), the specific activity of the 8-hydroxyquinoline and the bis compound are equal. This could be due to randomization of the activity by an intramolecular exchange equilibrium such as is shown below.



(iii) The specific activity of bis compound (Table XV) exceeds the equilibrium value of 1.79 mv/sec/mg for reaction times of 15 and 30 minutes.

This is likely associated with the fact that as the exchange reaction proceeds, the specific activity of the 8-hydroxyquinoline in solution is decreased. Consequently, the tris compound which precipitates early in the reaction has a higher activity than the tris compound which precipitates later. When, however, the solid in the reaction mixture has had sufficient time to equilibrate homogeneously with the solution, the specific activity of the tris compound and therefore, of the bis compound, should approach the equilibrium value. This was observed after a reaction time of 3 hours.

The data for 77 percent addition in Table XV was used to prove the existence of radiobalance. The specific activity of the addition product can be calculated to be (2.00 x 1.59 + 0.77 x 2.21)/2.77 = 1.8 mv/sec/mg, which agrees with the experimentally determined value (1.75 mv/sec/mg).

Finally, the C^{14} data is complicated by the occurrence of ligand exchange during the thermal conversion of the reaction products to 8-hydroxyquinoline and the bis compound (see Section (b), above). The effect of this exchange reaction is to randomize the activity acquired by the tris compound in the addition reaction and, therefore, to reduce the difference in specific activity between the sublimed 8-hydroxyquinoline and the bis compound. This difference is still finite, however, as shown by the data for a reaction time of 5 minutes.

PART B Thorium(IV) Complexes of 8-Hydroxyquinoline and Derivatives

(a) Composition of the orange thorium(IV)—8-hydroxyquinoline complex

The data of Tables XVII and XVIII indicate that the orange compound is deficient in 8-hydroxyquinoline. Furthermore, the composition of the orange compound varies from one preparation to another (the range was 4.84:1

to 4.96:1), even though the experimental conditions were not intentionally altered. The samples were dried without heating to ensure that not a trace of the thermally volatile 8-hydroxyquinoline molecule was lost. (Thermal loss is reported to begin at about 80°C (37,45,46,49).) Because of the mild drying conditions used, it is likely that the samples retained a small amount of moisture. Although the presence of moisture would lower both the percent Th and Q^- in the orange compound, it would not affect the molar ratio of the species.

The presence of water in the orange compound was confirmed by the condensation of a small droplet of water in the U-tube (below the 8-hydroxyquinoline deposit) during the thermal conversion. Also, infrared spectra obtained on samples of orange compound dried under increasingly rigorous conditions show that the absorption band centered at 3350 cm^{-1} is due to the presence of water (Section (e), below).

If, as in the case of the uranium(VI) complex, the extra molecule is coordinated to the central atom, it can be assumed that the deficient 8-hydroxyquinoline is replaced by coordinated water. It is not possible to assign a formula, however, because of variation in the composition from one precipitation to another. The composition is obviously very sensitive to slight changes in experimental conditions. From the data of Table XIX, it is difficult to conclude whether the rate of addition of ammonium acetate is an important experimental variable. Variables such as temperature, pH, time of digestion and percent excess 8-hydroxyquinoline should be investigated. In this work, the precipitations were made using a 64% excess of 8-hydroxyquinoline. This percent excess may not be sufficient to suppress hydrolysis of thorium(IV) as the pH is raised to the final value of 5.5.

With a much higher concentration of reagent, and perhaps with different pH conditions, it should be possible to prepare the stoichiometric orange compound.

It is interesting to note the observation of Cardwell et al. (98) that when the pH of the solution containing thorium(IV) and 8-hydroxyquinoline (in the ratio 1:4) is raised rapidly with concentrated ammonia, a compound of the formula $Th_2(C_9H_6NO)_7 \cdot OH \cdot 4H_2O$ is formed, whereas when the pH is raised slowly, the 5:1 composition is more closely approached. This would indicate that widely varying rates of addition of base should be tried.

The non-stoichiometry (∿ 4.8:1) and the varying composition of the orange compound have been reported by other workers (48,50,51). Crouthamel and Johnson (51) also found an appreciable amount of water in the compound. A claim has been made recently (73) that when the last traces of water are removed, the resulting composition is exactly 5:1. This claim is based on the determination of only the 8-hydroxyquinoline content of the dried material. When the compound prepared in this work was dried under identical conditions (in vacuo at 50-55°C for 2 hours), a small amount of 8-hydroxyquinoline was lost from the complex (seen as a sublimate). More evidence is required to establish the 5:1 composition.

Since the two methods of analysis reported in this work give essentially the same result, it is concluded that the orange compound is deficient in 8-hydroxyquinoline, at least when prepared by the method (97) used in this work. The average composition determined from the several preparations is $Th(C_9H_6NO)_4 \cdot 0.9C_9H_6NOH.(xH_2O)$.

(b) Thermal preparation of pure tetrakis(8-hydroxyquinolinato)thorium(IV) and thermal ligand exchange

The data of Section (c), PART B, EXPERIMENTAL AND RESULTS, show that the yellow tetrakis compound can be readily prepared in reasonably pure form by heating the orange thorium(IV)—8-hydroxyquinoline compound at about 165°C in vacuo for 1 1/2 hours. Several workers have reported that the tetrakis compound can also be prepared by heating in air (43,44,46,47,49-51). The temperature conditions have ranged from 135 to 345°C, and the heating times from 2 1/2 to 5 hours. Takiyama et al. (50) have reported that in air, the tetrakis compound begins to decompose at about 190°C. The main advantage of preparing the tetrakis compound in vacuo is that oxidative decomposition of the 4:1 compound cannot occur as readily as in air.

The mechanism of the thermal reaction yielding the tetrakis compound is not known, although two proposals have been made (see PART B, INTRODUCTION). By analogy with the thermal reaction for the tris uranium(VI) complex (Section (b), PART A, DISCUSSION), the data of Table XX show that extensive intermolecular ligand exchange occurs ($\sim$ 60%) at the temperature of the thermal reaction, indicating extensive bond-breaking.

The larger extent of exchange found for the thorium adduct compared to that for the uranium(VI) reflects the greater overall lability of the thorium complex.

(c) Interaction of the orange thorium(IV)—8-hydroxyquinoline complex with solvents

The orange compound appears to be very unstable in organic solvents. Solvents with appreciable polarity replace the additional 8-hydroxyquinoline molecule in the complex (e.g., $Th(C_9H_6NO)_4 \cdot C_2H_5OH$ and $Th(C_9H_6NO)_4 \cdot 2OS(CH_3)_2$).

The more polar the solvent, the more readily the replacement occurs.

Adduct complexes of the thorium(IV) have also been reported by Muetterties (101), and Goldstein et al. (130) (e.g., $Th(C_7H_5O_2)_4 \cdot OS(CH_3)_2$, where $C_7H_5O_2^-$ is the tropolone anion, and the acetic acid adduct of tetrakis(thenoyltrifluoroacetylacetonato)thorium(IV)), who postulated nonacoordination for thorium in these complexes. The dimethylsulfoxide adduct reported above would require decacoordination, as is believed to exist in pentakis(tropolono)thorium(IV) (101).

With non-polar solvents such as dichloroethane, the additional molecule is removed without displacement, and the tetrakis compound is obtained as a precipitate. The energy of solvation of 8-hydroxyquinoline in dichloroethane is obviously sufficient to overcome the forces binding the extra molecule.

The dissociation of the 5:1 compound to the tetrakis compound and 8-hydroxyquinoline can be prevented by the presence of a large excess of 8-hydroxyquinoline in the dichloroethane. Indeed, the stoichiometry, within experimental error, is 5:1, no doubt due to the absence of competing ligands such as H_2O, OH^-, etc.

(d) Exchange reaction between the 5:1 thorium(IV)—8-hydroxyquinoline complex and C^{14}—8-hydroxyquinoline

The rationale of the exchange experiment has been stated previously in connection with the tris uranium(VI)—8-hydroxyquinoline compound (Section (e), PART A, DISCUSSION).

When a large excess of C^{14}—8-hydroxyquinoline was used in the exchange reaction(0.18 millimoles 5:1 compound vs 0.9 millimoles HQ; 0.03 millimoles of 5:1 vs 0.9 millimoles HQ), the specific activity found in the tetrakis and in the sublimed HQ was very low (< 0.1 mv/sec/mg), even after 6 hours. Therefore, little exchange occurred.

The same reasoning used for the tris uranium(VI)—8-hydroxyquinoline complex leads to the conclusion that the additional molecule of 8-hydroxyquinoline in the thorium(IV) complex must be coordinated to the central atom, and is not merely a lattice component held by van der Waals forces (as, for example, is $CHC\ell_3$ in $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH \cdot CHC\ell_3$ (20), pyridine in $AgC_9H_6NO \cdot C_9H_6NOH \cdot C_5H_5N$ (22), and $CHC\ell_3$ in the acetylacetone complexes of chromium, iron and aluminium (39)).

The lack of exchange cannot be due to a low solubility or to a slow rate of solubility in dichloroethane containing a large excess of 8-hydroxyquinoline, for these are each sufficient to allow most, if not all, of the solid present in the reaction mixture to participate in the relevant equilibria in 6 hours (see Section (e), PART A, DISCUSSION).

Nevertheless, the lack of activity in the reaction product is most surprising, since, unlike the tris uranium(VI) compound, the 5:1 thorium(IV) compound dissociates extensively in dichloroethane, according to the reaction:

$$Th(C_9H_6NO)_4 \cdot C_9H_6NOH \rightleftharpoons \underset{\text{(precipitates)}}{Th(C_9H_6NO)_4} + C_9H_6NOH$$

Thus, although a large excess of 8-hydroxyquinoline in solution can be expected to repress the dissociation, the equilibrium is dynamic, and in the presence of C^{14}—8-hydroxyquinoline, activity would be expected in the isolated product. In fact, when the amount of dissolved C^{14}—8-hydroxyquinoline was decreased by 60%, considerable activity was found in both the tetrakis compound and sublimed 8-hydroxyquinoline. Reduction by 80% led to an even greater level of activity in these species (essentially the level expected for complete exchange equilibrium).

It is apparent that in the presence of a large excess of 8-hydroxyquinoline, the equilibrium is not merely shifted towards the 5:1 compound, but that the dissociation is quantitatively prevented because of stabilization of the 5:1 compound through some interaction with the excess 8-hydroxyquinoline. This is best illustrated by the observation that when even a small amount of the 5:1 compound is placed in dichloroethane containing no 8-hydroxyquinoline, precipitation of the tetrakis compound (solubility = 0.7 mg/ml) occurs, but when the solution contains a large excess of 8-hydroxyquinoline, precipitation does not occur even when a relatively large amount of the 5:1 compound is dissolved.

A possible explanation of the role of 8-hydroxyquinoline in stabilizing the orange compound in solution is given in Section (f), below.

(e) Infrared spectra of solid thorium(IV) complexes of 8-hydroxyquinoline and derivatives

The infrared spectrum of the orange thorium(IV)—8-hydroxyquinoline complex has not been closely examined by other workers (52,53) and little direct evidence for the bonded nature of the additional 8-hydroxyquinoline molecule has been obtained. In one study (53), the samples were prepared as KBr discs, so that interpretation of the —OH stretching region with regard to the complex was complicated. In the present work, the samples for infrared examination were prepared as mulls in hexachloro—1,3-butadiene.

The infrared spectrum (D, Figure 8) of the carefully dried 5:1 thorium(IV)—8-hydroxyquinoline complex exhibits an unusually broad band centered at about 2650 cm^{-1} and a very weak band at about 2075 cm^{-1}. These bands are very similar to those obtained for the tris uranium(VI) complexes, and are characteristic of hydrogen-bonded $>\overset{+}{N}H$ (see Section (c), PART A, DISCUSSION). In the spectrum of the deuterated complex, these bands are shifted to 2050 ($\nu_H/\nu_D = 1.29$) and 1510 cm^{-1} ($\nu_H/\nu_D = 1.37$), respectively. The bands are absent in the spectrum of tetrakis(8-hydroxyquinolinato)-thorium(IV) (E, Figure 8). By analogy to the tris U(VI) complex, the additional molecule in the thorium(IV) adduct is likely coordinated to the central thorium atom, and through the phenolate oxygen only. The proton on the nitrogen atom could be hydrogen-bonded in one of several ways, e.g., to the oxygen of the same ligand, or to the oxygen of an intramolecular bidentate ligand, or intermolecularly to the oxygen of a ligand in a neighbouring molecule of the complex.

The infrared spectra of the carefully dried 5:1 complexes of 3-methyl— and 7-phenyl—8-hydroxyquinoline (B, E, Figure 9) also exhibit the characteristic bands at 2650 and 2075 cm^{-1}. These complexes likely have a structure similar to the pentakis 8-hydroxyquinoline complex. The bands are absnet in the spectra of the tetrakis compounds (F, Figure 9, and A, B, Figure 10).

In spectra A, B and C, Figure 8, the absorption band at 3350 cm^{-1} appears to be due solely to water in the 5:1 8-hydroxyquinoline complex. The data in Table XXII show that the intensity of the band gradually decreases and eventually disappears as the compound is dried with increasing care. Also, a corresponding increase in the resolution of the 2650 cm^{-1} band is obtained.

The resolution of the 2650 cm^{-1} band is also decreased when water is present in the 5:1 complexes of 3-methyl—, 7-methyl—, and 5-phenyl—8-hydroxyquinoline (A, C, D, Figure 9).

The infrared and carbon-14 exchange experiments developed for the U(VI) compound thus provide diagnostic tests for the Th(IV) adducts and, presumably, for the adducts of other ions.

The sensitivity of the formation of 5:1 complexes to substitution in the 2 and 7 positions of the quinoline ring (i.e., positions adjacent or close to donor atoms) seems best explained on the basis of steric hindrance to coordination of the extra molecule, just as in the uranium(VI) complexes. Thus, 2-methyl—8-hydroxyquinoline yields only a 4:1 complex (69, 97), 2-phenyl—8-hydroxyquinoline forms no complex (thorium hydroxide precipitates), and 7-t-butyl—8-hydroxyquinoline forms a 4:1 compound only. The 2-position seems to be more sensitive to substitution, since 7-methyl— and 7-phenyl—8-hydroxyquinoline yield pentakis complexes.

The thorium(IV)—8-hydroxyquinoline adduct appears to be less stable than the uranium(VI)—8-hydroxyquinoline adduct. In the thorium complex, the monodentate ligand is lost more easily on heating and is displaced more readily by solvents. This behaviour is probably the result of the greater crowding of ligands around the thorium atom compared to the uranium atom.

In the structures proposed above for the 5:1 complexes, the coordination number of thorium is 9. Nonacoordination for thorium has been proposed by Muetterties (101) in the dimethylsulfoxide adduct of tetrakis(tropolono)-thorium(IV), and by Goldstein et al. (130) in the acetic acid adduct of tetrakis(thenolytrifluoroacetylacetonato)thorium(IV). The idealized geometries for a 9-coordinate structure are the symmetrically tricapped trigonal prism and the monocapped square antiprism, which can be generated from the trigonal prism by relatively small distortions (23). Lattice distortions may prevent the thorium complexes from having either of these geometries, however.

(f) Stability of the orange thorium(IV)—8-hydroxyquinoline complex in dichloroethane containing free ligands

When the orange thorium(IV)—8-hydroxyquinoline complex was placed in dichloroethane and the mixture warmed, the yellow tetrakis compound precipitated immediately. When the solvent contained a large excess (e.g., 400%) of 8-hydroxyquinoline, 5-methyl— or 5-nitro—8-hydroxyquinoline, the solubility of the orange compound was greatly increased and precipitation of the tetrakis compound did not occur. The orange complex was recovered unchanged, although a slow exchange reaction probably occurred,as was observed when the solvent contained 5-methyl—8-hydroxyquinoline. (Little or no exchange was observed in the experiments with C^{14}—8-hydroxyquinoline (Section (d), above), but in the present case, the experimental temperature was 70°C.)

The infrared spectra of the solutions (A, C, D, Figure 11) exhibit the bands characteristic of $\overset{+}{N}$—H---O, as observed for the solid pentakis thorium(IV) and tris uranium(VI) complexes. In addition, all the spectra exhibit a relatively strong band at about 3350 cm^{-1}, which is due to the phenolic O—H group of the ligands present in excess.

It is proposed that the species present in the solution containing an excess of 8-hydroxyquinoline is the ion-pair species (III) formed between the 8-hydroxyquinolinium cation* and the pentakis(8-hydroxyquinolinato)thorium(IV) anion. Muetterties (101) has reported that the anion of pentakis(tropolono)-

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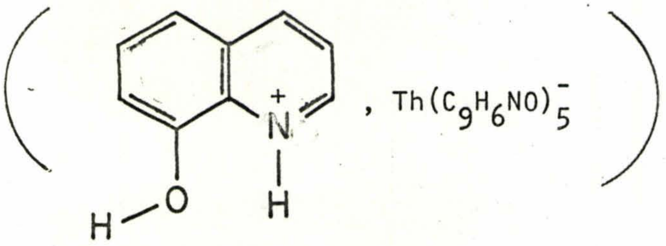
* The nitrogen of the monodentate ligand is expected to be at least slightly less basic than the nitrogen atom of the free 8-hydroxyquinoline present in solution.

thorium(IV) probably exists in chloroform solution in the form of ion aggregates. Also, in the solvent extraction of uranium(VI), Bullwinkel



III

et al. (89) have postulated the formation of an ion pair between the anion of the tris uranium(VI)—8-hydroxyquinoline complex and a quaternary ammonium cation.

The infrared bands at 2600 and 2075 cm^{-1} are attributed to the quinolinium $>\overset{+}{N}H$, in which the proton is likely hydrogen-bonded, either intramolecularly,or intermolecularly to the oxygen of a coordinated ligand.

The slow rate of exchange with C^{14}—8-hydroxyquinoline could now be explained on the basis that removal of the proton allows the monodentate ligand to become bidentate, thus causing a reduction in the rate of exchange.

In summary, it is proposed that in the neutral pentakis complex, the coordination number of thorium is nine, and in the anionic complex, it is ten. According to Muetterties (101), a large cation size and an f^0 electronic configuration appear to be two of the major conditions for formation of ten-coordinate molecular structures. Thorium(IV) satisfies both of these conditions.

In the orange solid, it appears that the coordination number of thorium is 9 rather than 10 only because the proton, which is present to give electroneutrality, must be accommodated in the molecular structure rather than in the crystal lattice.

It should be possible to prepare a solid salt (e.g., sodium salt, etc.) in which the coordination number of thorium would be 10. (In the ionic salts of the tris uranium(VI) complex, it is believed (64) that the coordination number of the central uranium atom is 8.) To date, attempts have failed, however. An attempt to obtain the 8-hydroxyquinolinium salt led to the crystallization of the neutral pentakis compound. This failure is probably related to the relative crystal stabilities of the two compounds. Other workers have failed in an effort to titrate the proton in an acetonitrile solution of the complex (38). It is likely that this failure was due to displacement of the monodentate ligand by acetonitrile. Finally, an attempt to prepare the sodium salt in alkaline solution led to hydrolysis of the thorium (97).

It is interesting that a compound with the formula, $[Th(C_9H_6NO)_4 \cdot C_9H_6NOH]_2 , C_2H_8N_2$, was obtained when the orange complex was dissolved in dichloroethane containing ethylenediammine. This compound is probably a salt involving diprotonated ethylenediammine, and would be better represented by

$$[C_2H_{10}N_2^{++}\{Th(C_9H_6NO)_5^-\}_2]$$

Ten-coordinate thorium structures have been proposed by Muetterties (101) for the pentakis(tropolono) derivatives, by Bohigian and Martell (131) for the thorium compound of triethylenetetraminehexaacetic acid, and by Goldstein, Menis and Manning (130) for the bis(acetic acid) complex of tetrakis(thenoyltrifluoroacetylacetonato)thorium(IV).

Possible idealized geometries for ten coordination are a symmetrically bicapped square antiprism, and a closely related one generated from the D_{2d} dodecahedral model, with the ninth and tenth positions on a C_2 axis. It has been pointed out by Muetterties (101) that the lifetime of the ground-state geometries in solution would be quite short, so that neither of the idealized structures could be detected.

Finally, the failure of pyridine and quinoline to prevent dissociation of the orange compound to the tetrakis compound is disconcerting, since the basicity of the nitrogen atoms in these compounds is comparable to that of the 8-hydroxyquinoline nitrogen.

(g) Addition of 8-hydroxyquinoline to tetrakis(8-hydroxyquinolinato)thorium(IV)

Unlike the addition of 8-hydroxyquinoline to bis(8-hydroxyquinolinato)-uranium(VI), the addition reaction between 8-hydroxyquinoline and the tetrakis thorium(IV) compound is slow and incomplete under the conditions studied (Table XXIII). Assuming the addition reaction to occur primarily via the equilibrium given in Section (h), PART A, DISCUSSION, the low rate must be due at least in part to the much lower solubility of the tetrakis compound (8.7×10^{-4} millimoles/ml) compared to the bis uranium(VI) compound (4.1×10^{-3} millimoles/ml). Given sufficient time, the addition reaction should be quantitative, since under similar conditions, it was previously demonstrated that the 5:1 compound does not dissociate. With the marked decrease in rate after one hour, a minimum of about 30 hours would be required for complete reaction. Using a more favourable temperature, a higher concentration of 8-hydroxyquinoline, and a nonpolar solvent in which the solubility of the tetrakis compound is higher than in dichloroethane, 100 percent addition could be expected in less time. It should be pointed out that because of the difference in solubility between 5:1 compound and the tetrakis compound, the experimentally determined percent addition is in error by small percentage points. Frere (43) has reported 100 percent addition, but very few experimental details were given. Furthermore, his calculations were in error. Using his data, 85% addition at best was obtained.

The data of Table XXIII indicate that there are several similarities between the addition reactions for the thorium(IV) and uranium(VI) systems. (i) There is more activity in the addition product than is expected from the amount of active 8-hydroxyquinoline added. This point is illustrated, for example, by the data corresponding to a 5-minute reaction time in Table XXIII. Under the conditions of the addition reaction, 145 mg of the tetrakis compound would add 9 mg (corresponding to 34% addition) of the active 8-hydroxyquinoline (original specific activity = 3.58 mv/sec/mg). Since 145 mg of the tetrakis compound contain 104 mg of 8-hydroxyquinoline, the specific activity of the addition product should be equal to $[9/104 + 9] \times 3.6 = 0.3$ mv/sec/mg, in the absence of complicating reactions. The measured specific activity, however, is 1.78 mv/sec/mg. The higher specific activity could only result if an exchange reaction involving the originally inactive ligands of the tetrakis compound and the active 8-hydroxyquinoline in solution is occurring together with the addition reaction. This exchange could only occur before or during the addition step (in which, presumably, a rearrangement of the existing ligands, and therefore bond-rupture, occurs), since the 5:1 compound, once formed, exchanges relatively slowly (Section (d), above).

(ii) For short reaction times, the specific activity of the tetrakis compound and of the sublimed 8-hydroxyquinoline are different, but become equal for longer reaction times. As explained earlier (Section (h), PART A, DISCUSSION), this observation could merely mean that after 5 minutes, a certain amount of the tetrakis compound had not undergone addition or ligand exchange, thereby diluting the activity of the tetrakis compound obtained in the thermal reaction. It could also mean that intramolecular exchange, given sufficient time to occur, randomized the activity of all five molecules of 8-hydroxyquinoline associated with a thorium ion.

(iii) When the exchange and addition reactions have reached equilibrium, the specific activity of the tetrakis compound and the sublimed 8-hydroxyquinoline should each be 2.0 mv/sec/mg. After reaction for 180 minutes, the specific activities of the two species are, indeed, equal to each other, but are higher than 2.0.

The data in Table XXIII must be accepted as being only qualitative, since, as discussed in Section (b), above, intermolecular (and hence intramolecular) exchange of ligands occurs during the thermal reaction. The effect of the thermal ligand exchange is to lower the specific activity of the sublimed 8-hydroxyquinoline and to raise that of tetrakis compound. However, since a difference in specific activity was obtained (for 5- and 60-minute reaction times), the thermal exchange could not have been complete.

Although the data of Table XXIII is of interest in relation to the addition reaction itself, they give no knowledge about the nature of extra 8-hydroxyquinoline molecule in the 5:1 complex. This is unlike the data for the uranium(VI) system which indicated that the additional ligand was either stereochemically different, or bonded differently (e.g., monodentate) from the other two ligands.

For the data at 5 and 60 minutes to be useful, 100 percent addition would have been required.

In this thesis, an attempt has been made to more fully understand the chemistry of the uranium(VI) and thorium(IV) addition complexes of 8-hydroxyquinoline, and to obtain structural information on these compounds.

Suggestions for further work

The findings of the present work suggest further research in the following areas:

(1) Further attempts should be made to determine the cause of non-stoichiometry in the addition complexes of 8-hydroxyquinoline, particularly in the thorium(IV)—8-hydroxyquinoline compound. The effect of pH, temperature of precipitation, the concentration of reagent and the concentration and rate of addition of base should be examined in detail.

(2) The mechanism by which the 5:1 thorium(IV)—8-hydroxyquinoline compound is stabilized in solutions containing an excess of 8-hydroxyquinoline, merits further study. Conductometric experiments might help to further characterize the species present in solution.

(3) Additional attempts should be made to prepare salts of the thorium(IV)—8-hydroxyquinoline addition compound.

(4) The proposed structure for the thorium(IV)—8-hydroxyquinoline addition complex and for the newly prepared U(VI) and Th(IV) compounds should be further confirmed by three dimensional X-ray analyses.

(5) The infrared and carbon-14 studies should be extended to determine the structural nature of the 8-hydroxyquinoline addition complexes with other metal-ions.

SUMMARY

1. The composition of the tris uranium(VI)—8-hydroxyquinoline compound and of the pentakis thorium(IV)—8-hydroxyquinoline compound have been precisely determined and shown to be slightly non-stoichiometric.

2. Because of oxidative decomposition, the pure bis(8-hydroxyquinolinato)-dioxouranium(VI) cannot be thermally prepared by the method of Moeller and Wilkins. This compound and tetrakis(8-hydroxyquinolinato)thorium(IV) can be prepared in pure form by thermal conversion of the addition complexes in vacuo. The thermal energies required cause considerable bond rupture in the complexes.

3. The additional ligand in the tris U(VI) compound is replaced by strongly coordinating solvents such as dimethylsulfoxide. The tris compound is stable, however, in more weakly coordinating solvents.

The additional ligand in the pentakis Th(IV) compound is replaced by coordinating solvents such as absolute ethanol and dimethylsulfoxide. In non-coordinating solvents, the pentakis compound is dissociated to the tetrakis compound and 8-hydroxyquinoline.

4. The pentakis Th(IV) compound is stable in solutions containing an excess of 8-hydroxyquinoline (or derivatives), and can be recovered unchanged. It is proposed that the species in solution is an ion-pair formed between the 8-hydroxyquinolinium cation and the pentakis(8-hydroxyquinolinato)thorium(IV) anion. Coordination number 10 is proposed for Th(IV) in the anion. The compound $[Th(C_9H_6NO)_4 \cdot C_9H_6NOH]_2 \cdot C_2H_8N_2$ is isolated from a solution of the pentakis compound in dichloroethane containing an excess of ethylenediammine, and is

probably the salt of diprotonated ethylenediammine.

5. In 50% V/V agueous dioxane, U(VI) and 8-hydroxyquinoline in low concentrations react to form the soluble complex $UO_2(C_9H_6NO)_2 \cdot H_2O$. At significantly higher concentrations, the tris compound can be precipitated. If the pH is raised by hydrolysis of urea, the complex $UO_2(C_9H_6NO)_2 \cdot CO(NH_2)_2$ is obtained.

6. Disproportionation of bis(8-hydroxyquinolinato)dioxouranium(VI) to the tris compound occurs in water-containing solvents. Solvolysis of the bis compound in coordinating solvents also occurs, yielding compounds such as $UO_2(C_9H_6NO)_2 \cdot CO(CH_3)_2$.

7. Carbon-14 studies showed that the extra 8-hydorxyquinoline molecule in the Th(IV) compound does not exchange quickly with free 8-hydroxyquinoline in solution. The result was interpreted to mean that additional molecule is coordinated to central thorium(IV) atom, and is not a lattice component.

8. An infrared investigation has shown that in the tris uranium(VI)—8-hydroxyquinoline compound, the acidic proton is located on the nitrogen atom of the additional ligand and is hydrogen-bonded, likely to the oxygen donor of an adjacent bidentate ligand. The newly prepared tris U(VI) complexes of 5-nitro— and 5-acetyl—8-hydroxyquinoline have identical infrared spectra, and are likely structurally similar to the tris 8-hydroxyquinoline complex.

Infrared analysis has also shown that in the pentakis Th(IV) compound, the acidic proton is located on the nitrogen atom of the extra ligand and is hydrogen-bonded. This result strongly suggests that the extra ligand is bonded to thorium only through the phenolate oxygen. The pentakis Th(IV) compounds of 7-phenyl—, 7-methyl—, 5-phenyl— and 3-methyl—8-hydroxyquinoline have similar spectra. The intensity of the infrared bands characteristic of hydrogen-bonded $\geqslant\overset{+}{N}H$ is decreased when water is present in these compounds.

9. Addition of 8-hydroxyquinoline to the bis U(VI) and tetrakis Th(IV) compounds has been investigated. Mechanisms for the addition reaction have been proposed. A study of the addition reaction with C^{14}—8-hydroxyquinoline showed that partial exchange of the bidentate ligands also occurs. Assuming no knowledge of known structure of the tris U(VI) compound, the data was interpreted to show that the additional 8-hydroxyquinoline molecule is not structurally equivalent to the two bidentate ligands. However, the data obtained for the Th(IV) compound was not useful in this respect.

10. The following new Th(IV) compounds have been synthesized and characterized: pentakis compounds of 7-phenyl—, 7-methyl— and 5-phenyl—8-hydroxyquinoline, and tetrakis compounds of 7-phenyl— and 7-t-butyl—8-hydroxyquinoline.

11. The experimental methods used to obtain the observations of 7, 8 and 9 should yield considerable information about the structural nature of the 8-hydroxyquinoline addition complexes with other metal-ions.

APPENDIX I

INFRARED SPECTRA OF COMPLEXES OF 8-HYDROXYQUINOLINE AND DERIVATIVES WITH URANIUM(VI) AND THORIUM(IV)

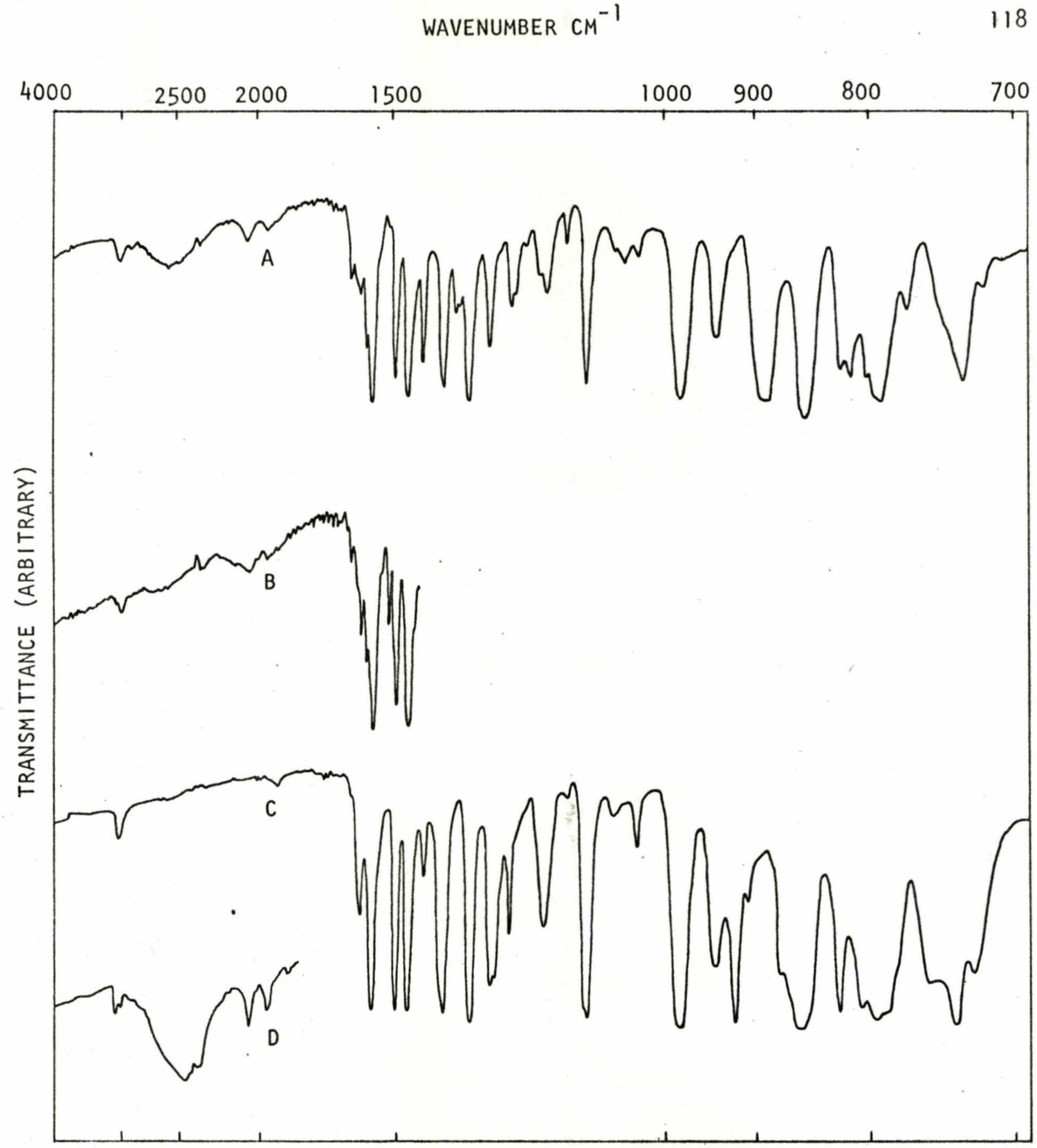


Figure 1. Infrared Spectra of Uranium(VI)—8-hydroxyquinoline Complexes and 8-Methoxyquinoline Hydrochloride. A - $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOH$, B - $UO_2(C_9H_6NO)_2 \cdot C_9H_6NOD$, C - $UO_2(C_9H_6NO)_2$, D - 8-Methoxyquinoline Hydrochloride.

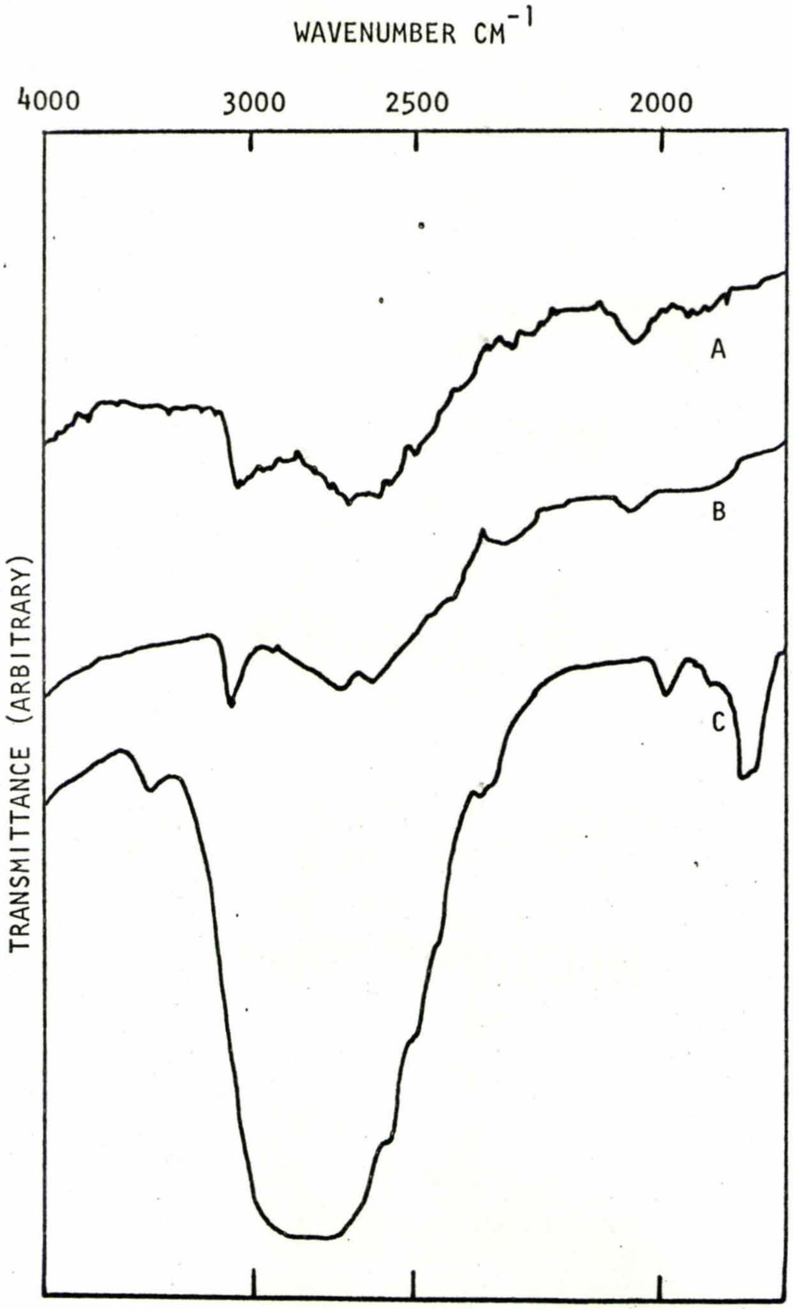


Figure 2. Infrared Spectra of Tris U(VI) Complexes of 8-Hydroxyquinoline Derivatives, and 2-Methyl—8-hydroxyquinoline Hydrochloride.
A - Tris Uranium(VI)—5-acetyl—8-hydroxyquinoline Complex,
B - Tris Uranium(VI)—5-nitro—8-hydroxyquinoline Complex,
C - 2-Methyl—8-hydroxyquinoline Hydrochloride.

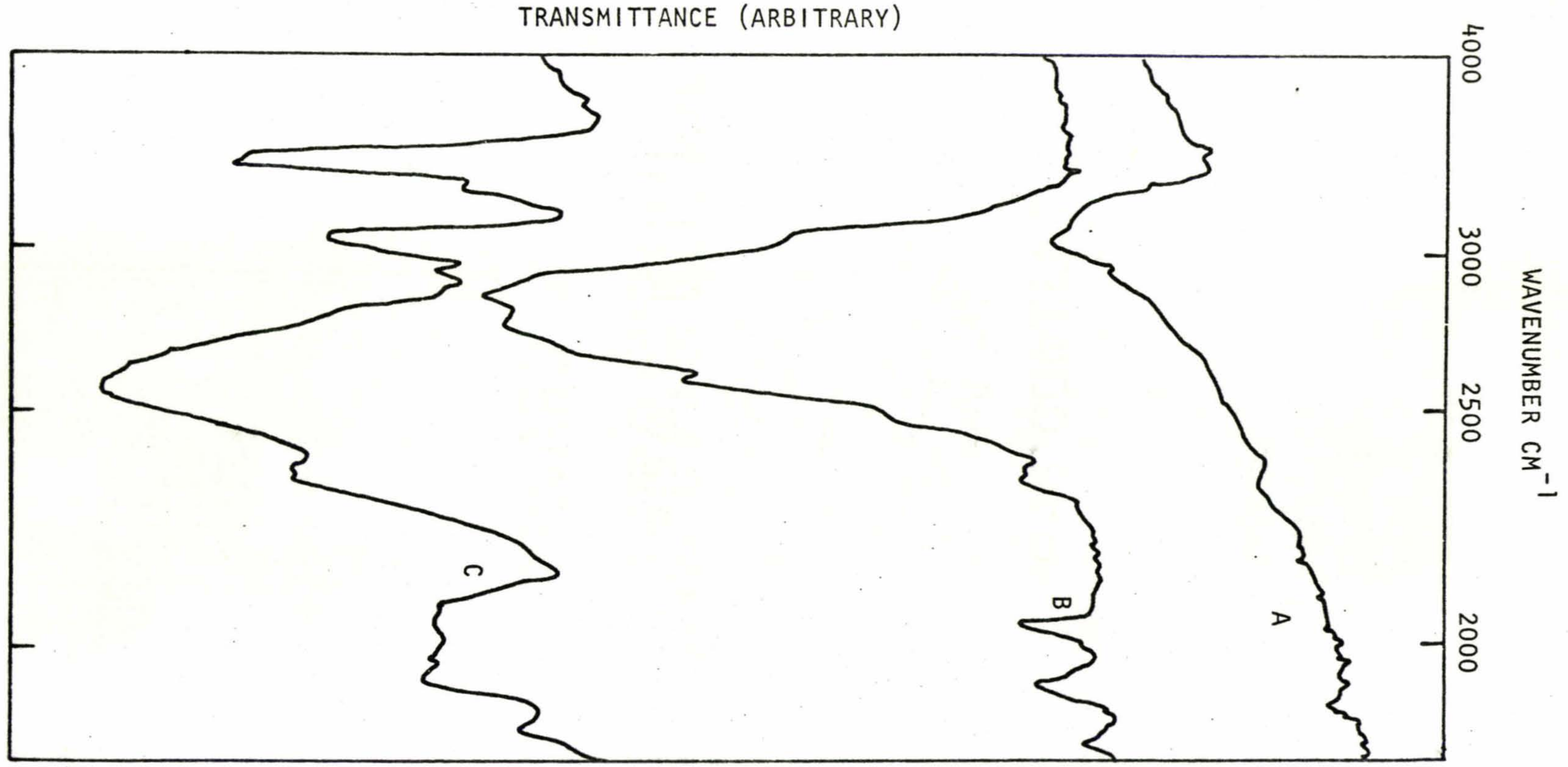


Figure 3. Infrared Spectra of 8-Hydroxyquinoline, and Hydrochloride Salts of 8-Hydroxyquinoline and Quinoline. A - 8-Hydroxyquinoline, B - 8-Hydroxyquinoline Hydrochloride, C - Quinoline Hydrochloride.

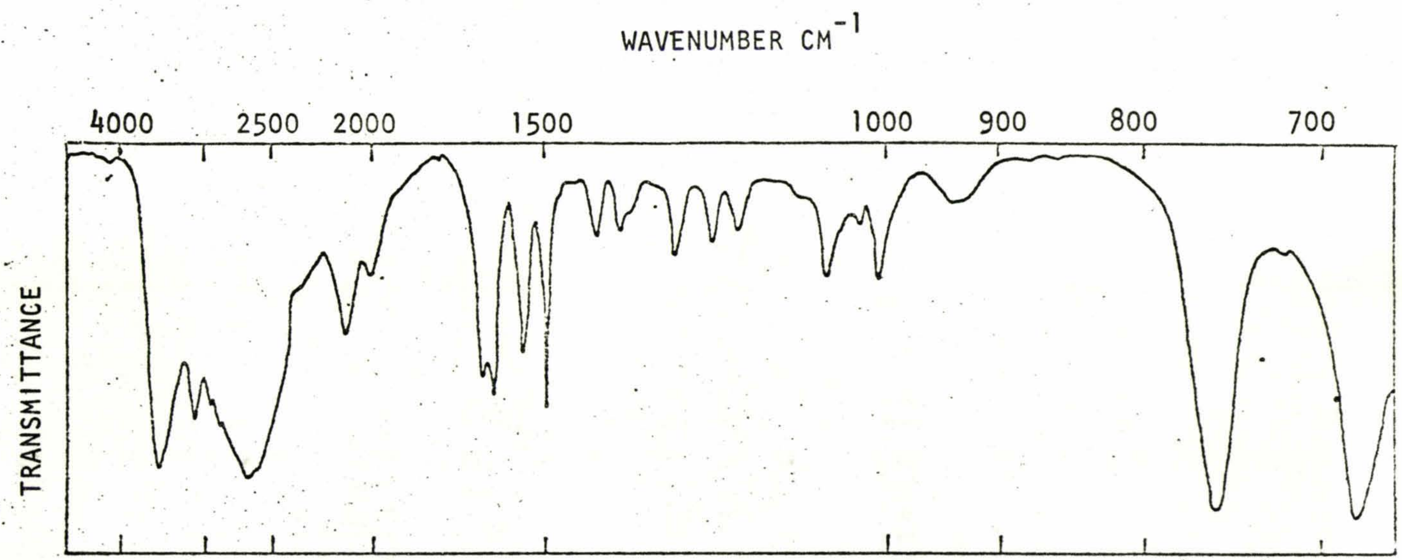


Figure 4. Infrared Spectra of Pyridine Hydrochloroide.

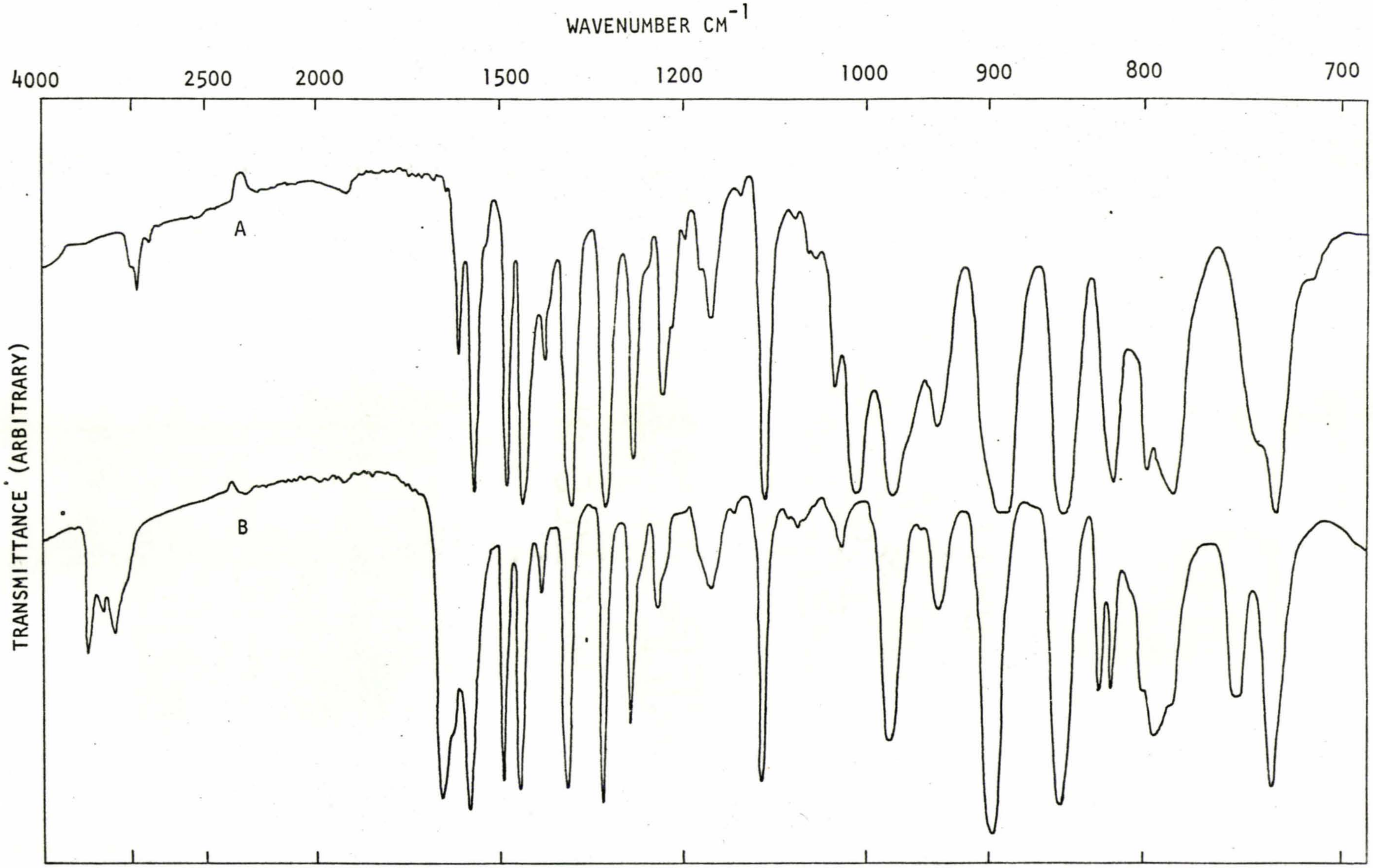


Figure 5. Infrared Spectra of U(VI) Adducts of Dimethylsulfoxide and Urea.

A - $UO_2(C_9H_6NO)_2 \cdot OS(CH_3)_2$, B - $UO_2(C_9H_6NO)_2 \cdot CO(NH_2)_2$.

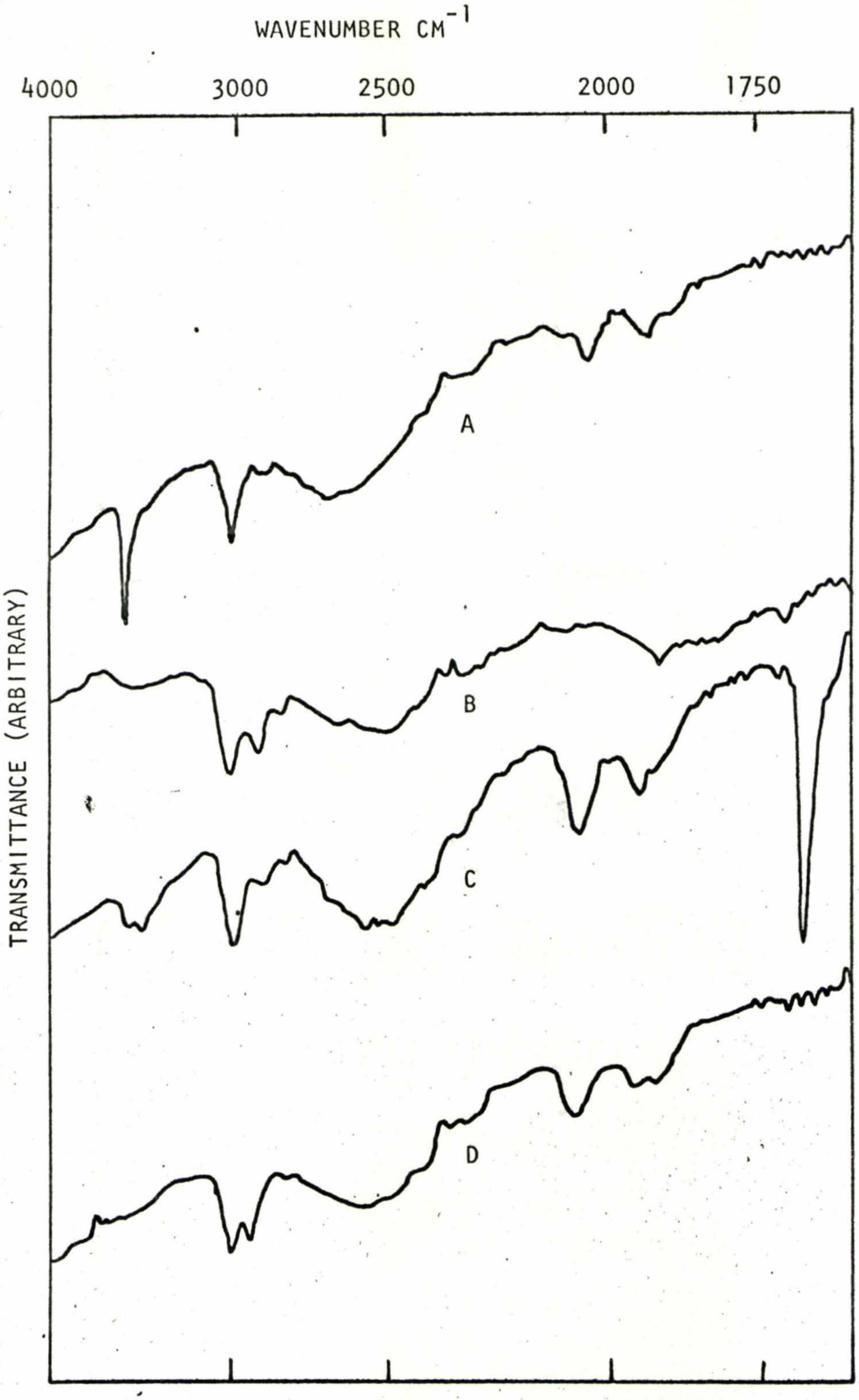


Figure 6. Infrared Spectra of Products from Interaction of Bis(8-hydroxyquinolinato)dioxouranium(VI) with Solvents. A - Ethanol, B - Methanol, C - Acetone, D - Chloroform.

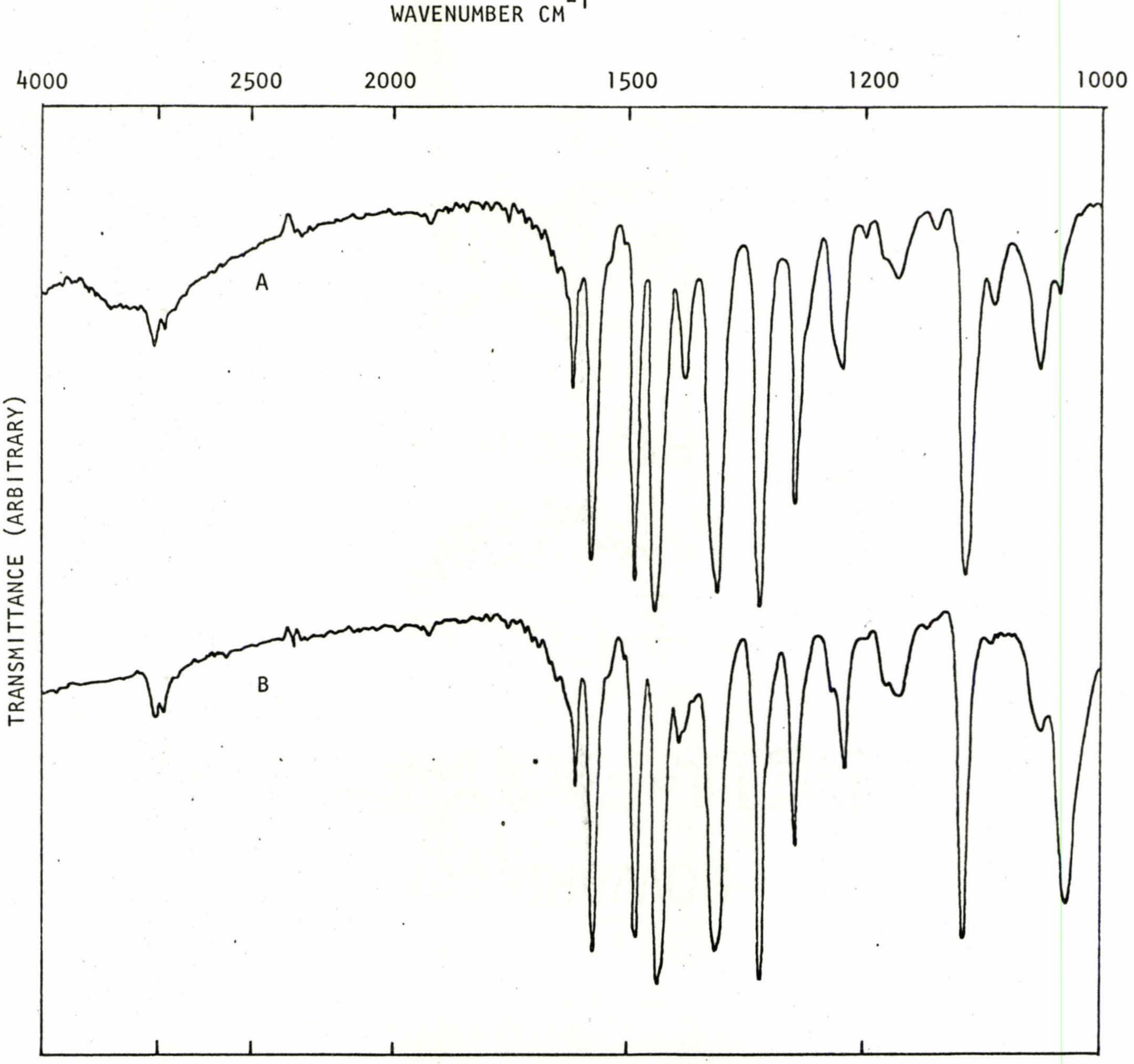


Figure 7. Infrared Spectra of Thorium(IV) Adducts of Ethanol And Dimethylsulfoxide. A - $Th(C_9H_6NO)_4 \cdot C_2H_5OH$, B - $Th(C_9H_6NO)_4 \cdot 2OS(CH_3)_2$.

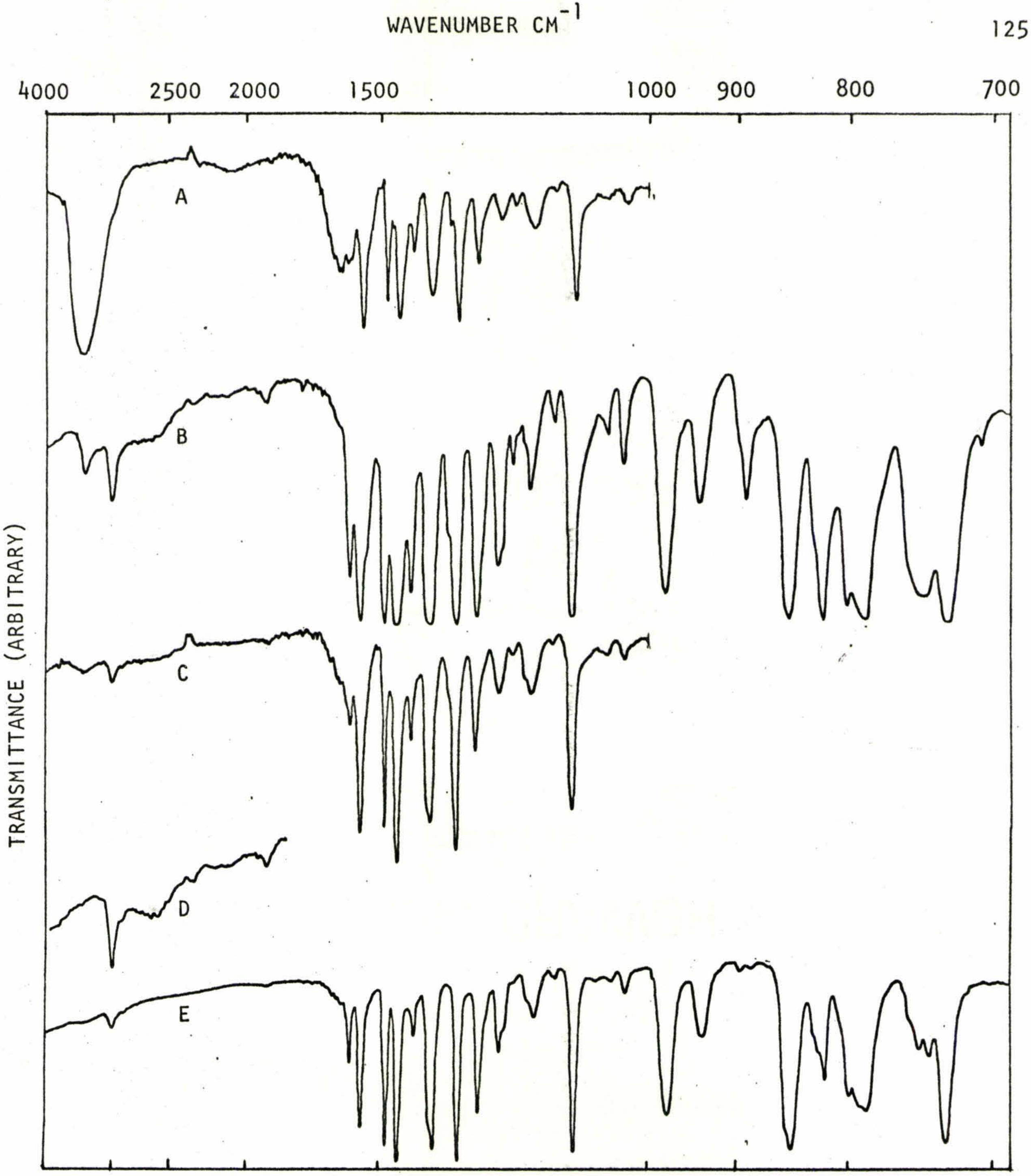


Figure 8. Effect of Drying on Infrared Spectra of the Pentakis Thorium(IV)—8-hydroxyquinoline Complex, and Spectrum of Tetrakis(8-hydroxyquinolinato)thorium(IV). A - Without Drying, B - Dried in Air, C - Dried in Vacuo for 53 Hours, D - Dried in Vacuo for 72 Hours, E - Th(C_9H_6NO)$_4$.

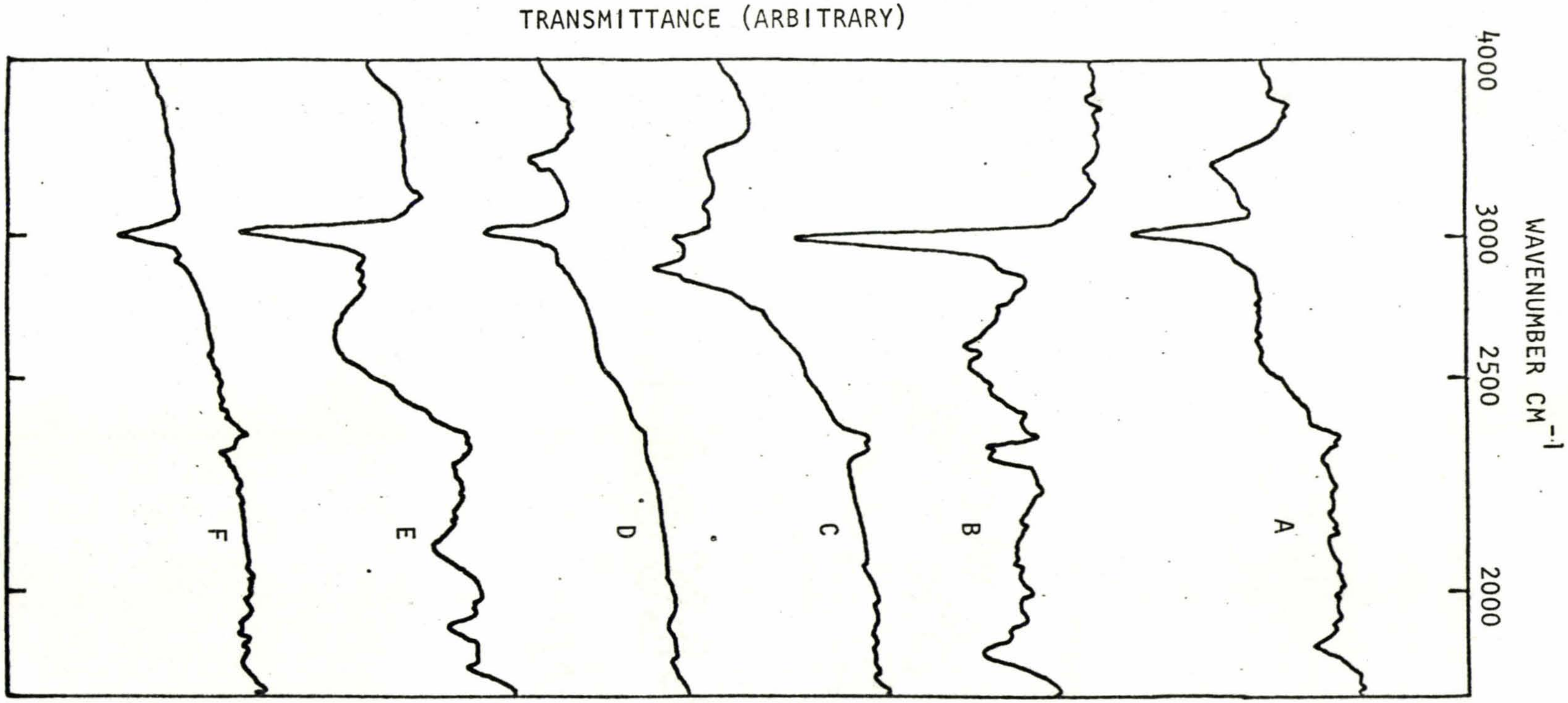


Figure 9. Infrared Spectra of Thorium(IV) Complexes of 8-Hydroxyquinoline Derivatives. A - Pentakis Complex of 3-Methyl Derivative (Dried in Air), B - Pentakis Complex of 3-Methyl Derivative (Dried in Vacuo), C - Pentakis Complex of 7-Methyl Derivative, D - Pentakis Complex of 5-Phenyl Derivative, E - Pentakis Complex of 7-Phenyl Derivative, F - Tetrakis Complex of 7-Phenyl Derivative.

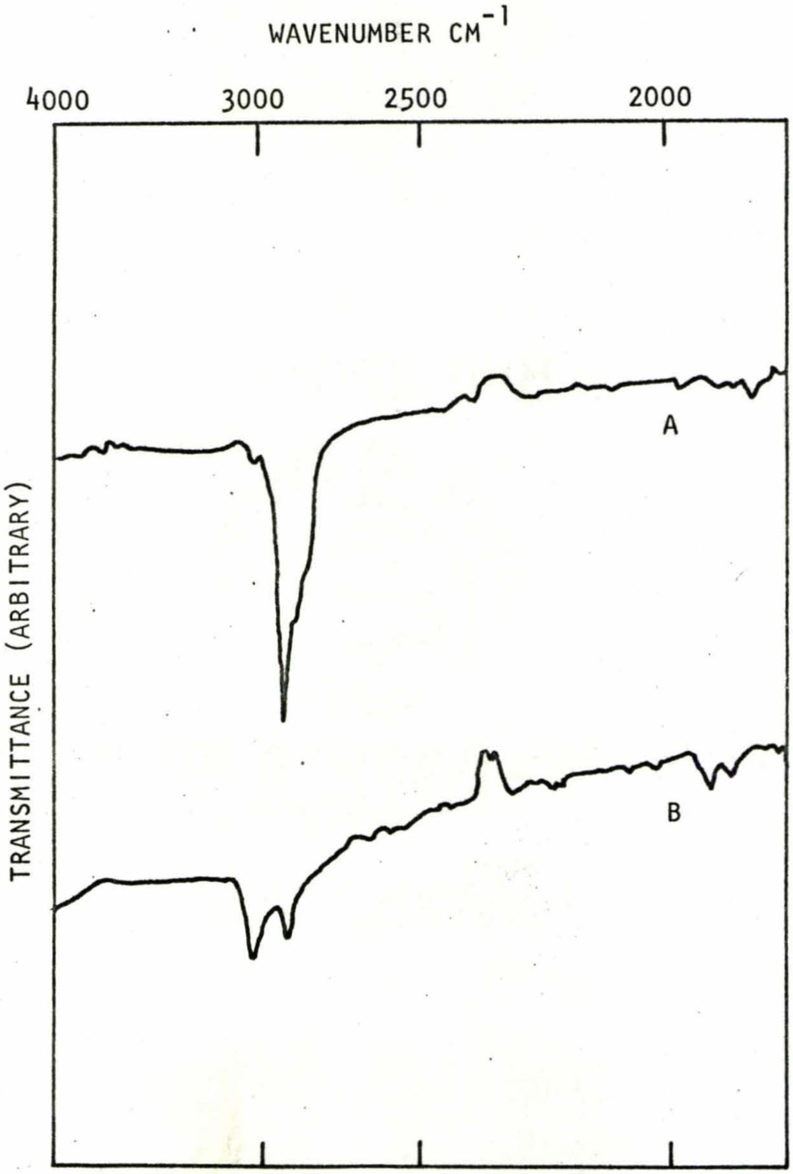


Figure 10. Infrared Spectra of Thorium(IV) Complexes of 8-Hydroxyquinoline Derivatives. A - Tetrakis Complex of 7-t-Butyl Derivative, B - Tetrakis Complex of 2-Methyl Derivative.

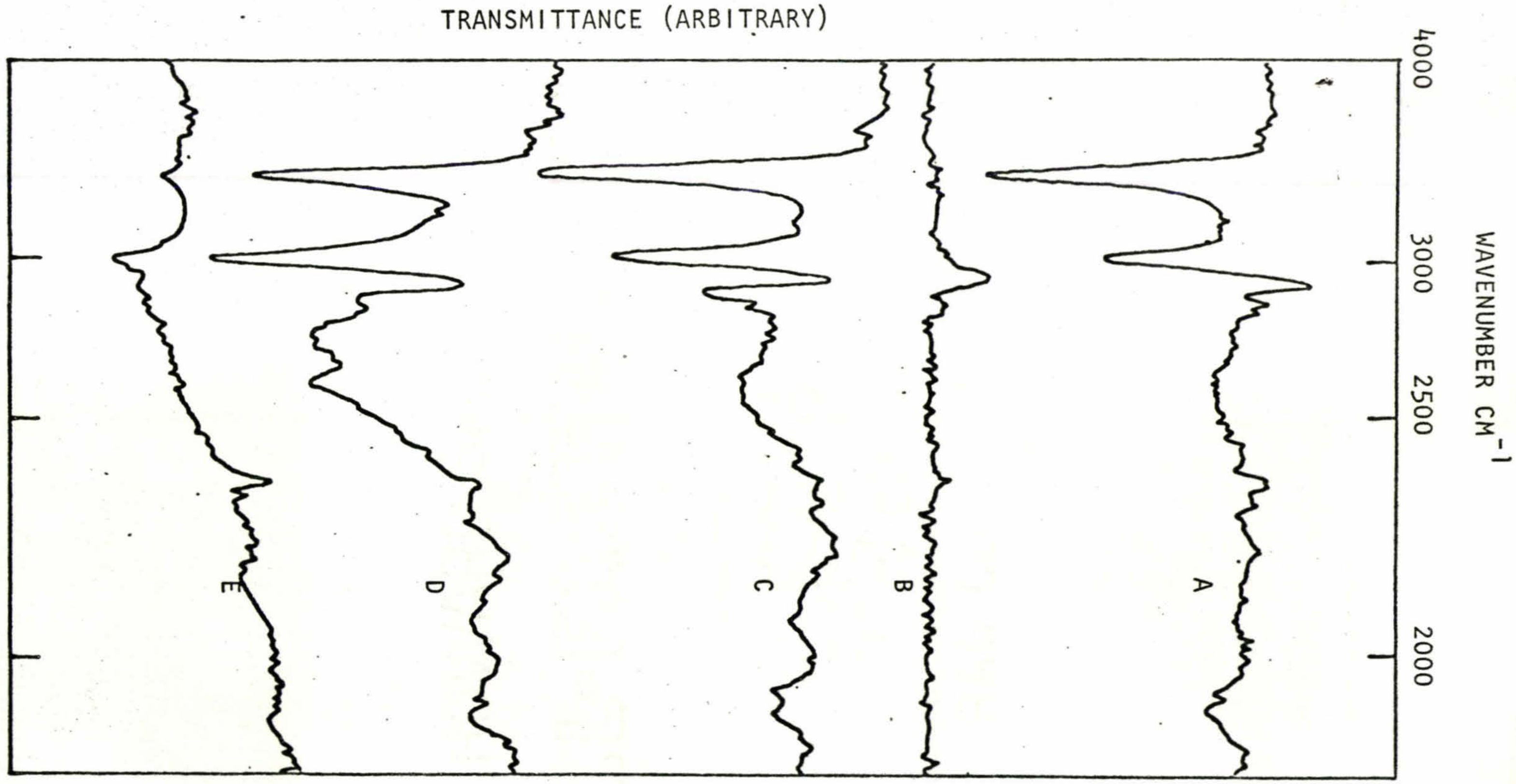


Figure 11. Infrared Spectra of Dichloroethane Solution Containing the Pentakis Thorium(IV)—8-hydroxyquinoline Complex and Excess HQ or Derivatives. A - HQ, B - Spectrum Using Matched Cells Containing Dichloroethane, C - 5-Methyl Derivative, D - 5-Nitro Derivative, E - Spectrum of the Salt of Diprotonated Ethylenediammine, $[C_2H_{10}N_2^{++}\{Th(C_9H_6NO)_5^-\}_2]$.

APPENDIX II

FIGURES 1, 2 AND 3

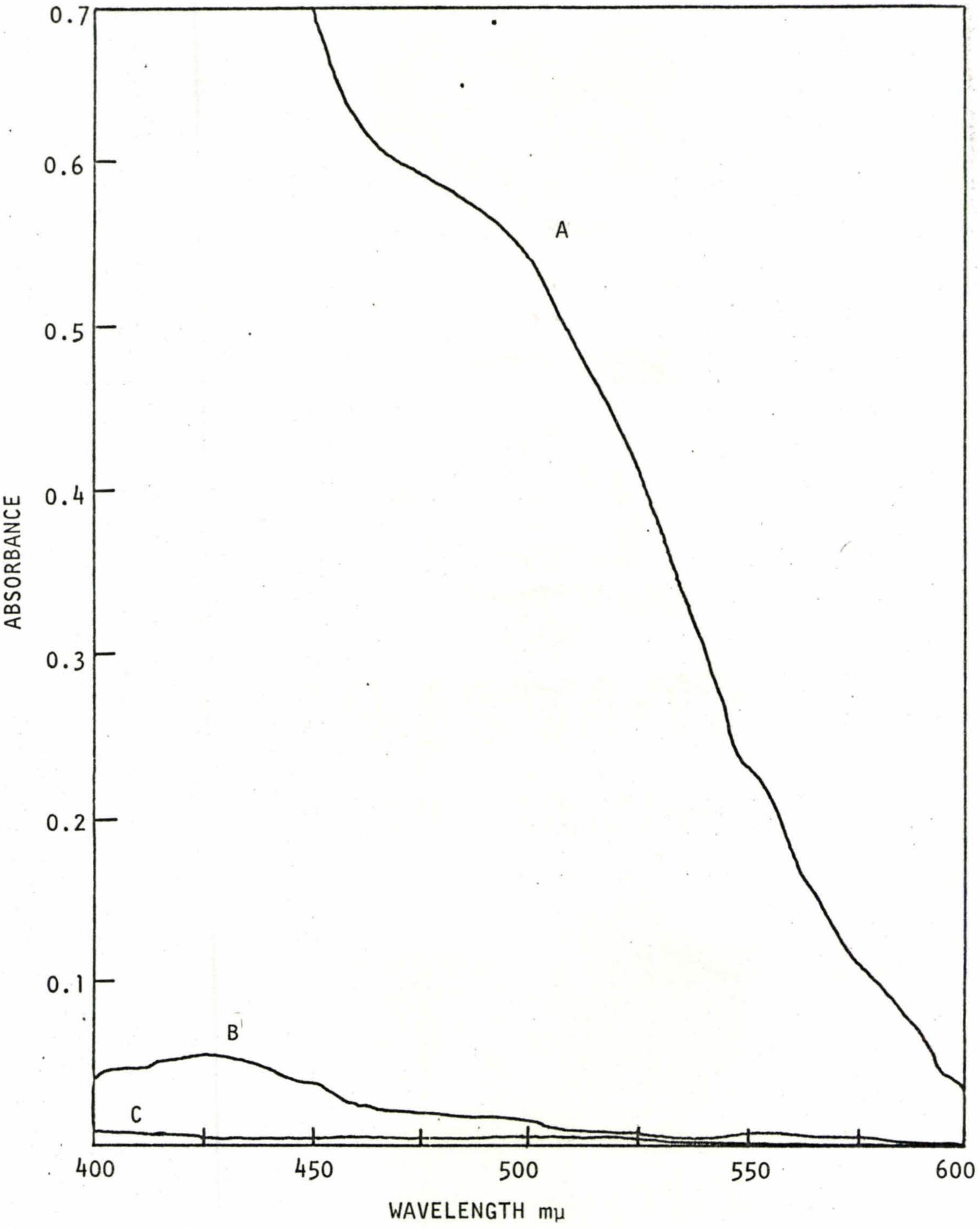


Figure 1. Absorption Spectra of U(VI) Complex of 8-Hydroxyquinoline in 50% V/V Aqueous Dioxane. A - Complex in 50% Dioxane, pH 6-7; B - Uranyl Nitrate (6.0×10^{-4} M) in 50% Dioxane; C - 8-Hydroxyquinoline (3.14×10^{-3} M) in 50% Dioxane, pH 6-7.

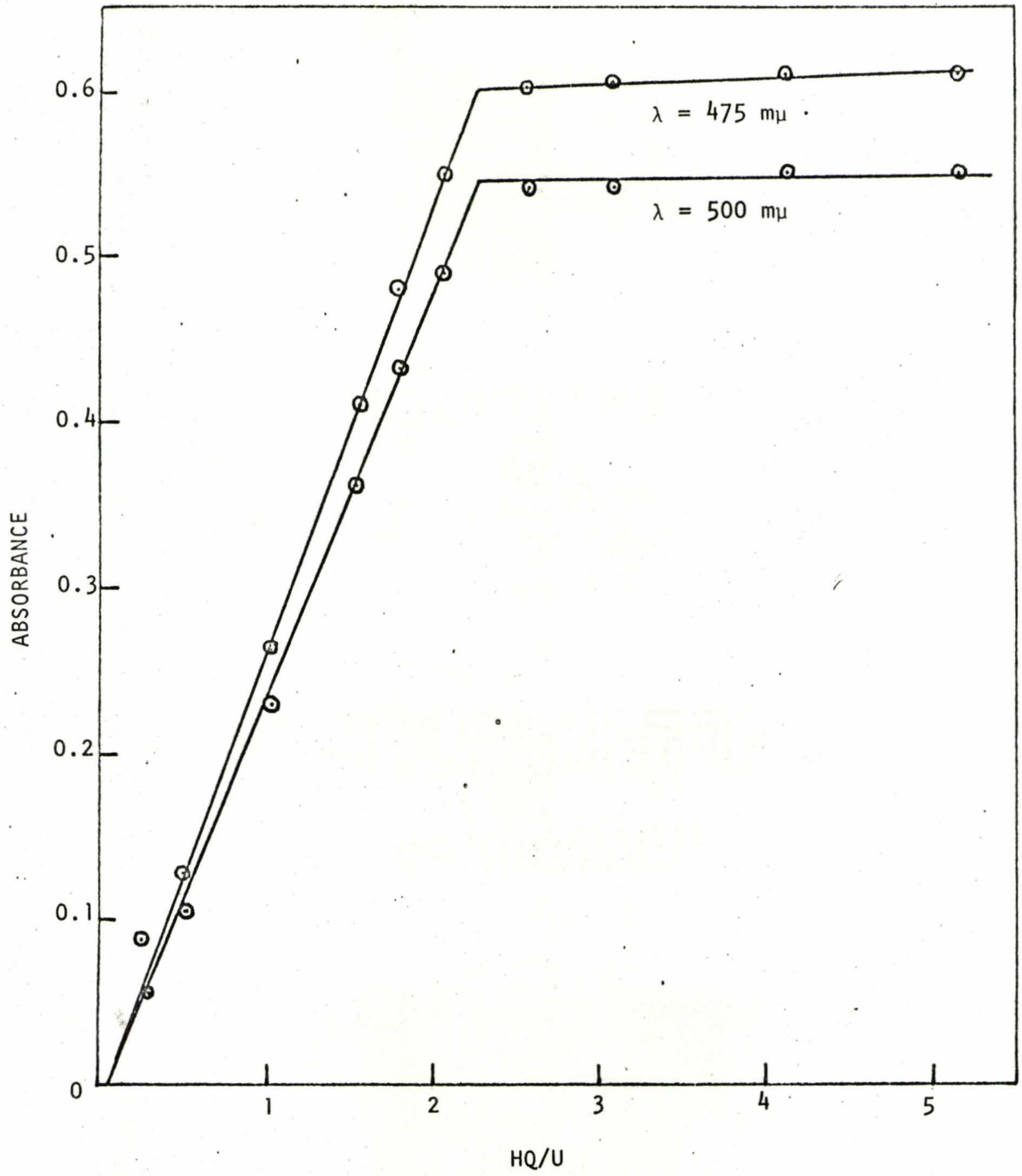


Figure 2. Mole-Ratio Diagram.

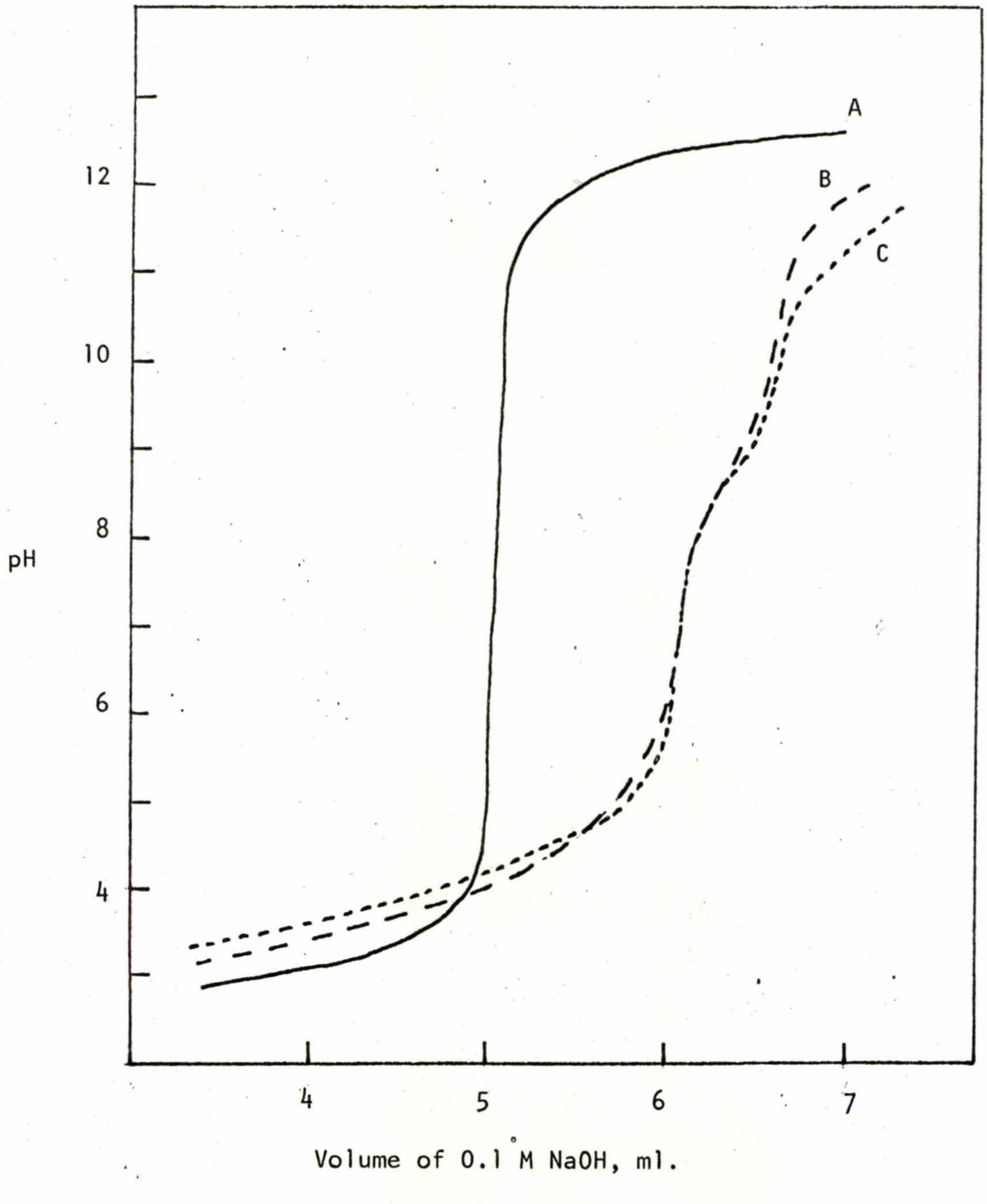


Figure 3. Titration Curve of the Uranium(VI) Chelate of 8-Hydroxyquinoline. A - Perchloric Acid, B - HQ:U = 2:1, C - HQ:U = 3:1.

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