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# URANIUM(VI), THORIUM(IV) AND SCANDIUM(III) COMPLEXES OF TROPOLONE

# URANIUM(VI), THORIUM(IV) AND SCANDIUM(III) COMPLEXES
# OF
# TROPOLONE

By

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A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Master of Science

McMaster University
August, 1975

MASTER OF SCIENCE (1975)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Uranium(VI), Thorium(IV) and Scandium(III) Complexes of Tropolone

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NUMBER OF PAGES: viii, 74

SCOPE AND CONTENTS:

New complexes formed between U(VI), Th(IV) and Sc(III) and tropolone have been prepared. These include the solvates $UO_2T_2.X$ and $ThT_4.X$ (T = the tropolone anion; X = $H_2O$ and $CH_3OH$), and the unsolvated chelate $ScT_3$. Some U(VI), Th(IV) and Sc(III) tropolonates reported in the literature have been re-examined and found to be incorrectly formulated.

The adduct chelates $UO_2T_2.HT$, $ScT_3.HT$ and the previously-unreported $ThT_4.HT$ have been prepared. Evidence has been presented for hydrogen-bonding in the additional monodentate tropolone ligand.

The thermal conversion of the above solvates and adducts to yield $UO_2T_2$, $ThT_4$ and $ScT_3$ has been described.

The ability of tropolone and other bidentate ligands to displace the water molecule in $UO_2T_2.H_2O$ and $ThT_4.H_2O$, and the addition of such ligands to $ScT_3$, has been studied.

# ACKNOWLEDGEMENTS

The author wishes to express his appreciation to Dr. A. Corsini for his advice and encouragement throughout the course of this work.

Also, he wishes to thank David Fowler for helpful discussion, Theresa MacFarlane for the typing of this thesis and Fadjar Ramelan for drawing the diagrams.

Financial assistance from the Department of Chemistry and the Province of Ontario is gratefully acknowledged.

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# CHAPTER I

## GENERAL INTRODUCTION

The importance of organic chelating agents in metal-ion analysis has been the subject of several books(1-3). Much of the research in this field has been devoted to the development of analytical procedures based on chelating agents, to the use of chelating agents as sequestering agents and to the study of structural factors and solution conditions which improve the selectivity of these reagents in the determination of metal ions.

The significance of organic chelating agents has been extended to the field of biochemistry and medicine. For example, great interest has been focused on the complexes of porphyrin and related ligands, particularly with respect to their relationship to hemoglobin and cobalamine (vitamin $B_{12}$)(4). Also, the cure or reduction of symptoms of poisoning by certain heavy-metal ions has been made possible through treatment using chelating agents(5).

This thesis is concerned with the ligand tropolone (2-hydroxy-2,4,6 cycloheptatrien-1-one) and its U(VI), Th(IV) and Sc(III) complexes. Tropolone is a bidentate ligand and was first synthesized and characterized by Dewar(6) in 1945. Early work(7-9) was concerned primarily with the organic reactions of tropolone, rather than with its use as an organic chelating agent and its application to metal-ion analysis. Dutt, Singh, and Katyal(10) were the first to review the analytical applications of tropolone extensively.

Tropolone is an aromatic, seven-membered ring compound (I)*,

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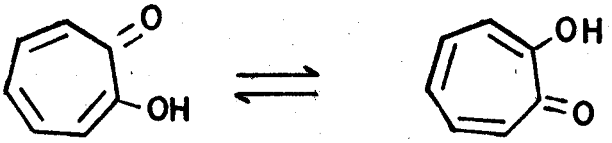
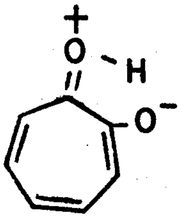
*Hereafter, this ligand will be referred to as HT.

which undergoes keto-enol tautomerism in solution:



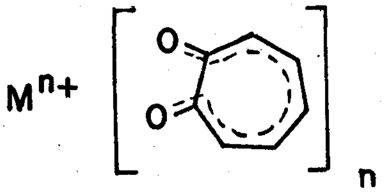
I

In solution the compound is further stabilized by its ability to exist as a zwitterion (II):



II

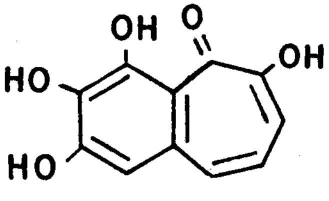
In complexation with a metal ion, the ketonic and enolic oxygen atoms become chemically equivalent through resonance:



The ligand has a short "bite" because of the close proximity of the two donor oxygen atoms on tropolone, which promotes high coordination numbers. Indeed, the highest coordination numbers reported to date for several metal ions are with the tropolone ligand(11). X-ray structural determinations have been reported for several of the solid chelates of high coordination number . Muetterties and Wright have prepared many metal complexes between bivalent(12), tervalent(11-14), quadrivalent(11-13) and quinquevalent(11-15) ions and tropolone or its derivatives, and have recently reviewed the field of high-coordination polyhedra and their structures(1

Many of the metal tropolonates are coloured, and the most thorough study of the analytical applications of tropolone and its derivatives has been with regard to spectrophotometric determinations. Most of these determinations involve metal ions in their highest oxidation state. Tropolone has been used in the spectrophotometric determination of Fe(III)(17), Nb(V)(18), Ti(IV)(19) and Zr(19). Actually, the spectrophotometric use of tropolone derivatives, rather than tropolone itself, has been more common. These derivatives include purpurogallin for the determination of Ge(20), Zr(21) and Mo(VI)(22); tropolone-5-sulphonic acid for Fe(III)(23), Th(24) and U(VI)(25); and β-isopropyltropolone for Th(19), Ti(IV)(26) and U(VI)(27). Advantage has been taken of the greater absorption-band shift to longer wavelengths when highly conjugated tropolones, eg., hydroxybenzotropolones, form complexes(22). The colours of the complexes have been explained in terms of charge transfer from ligand to metal.

Gravimetric determinations involving tropolone chelates have been thus far confined to high molecular-weight derivatives such as purpurogallin (III) and its derivatives. These ligands have the advantage



III

over tropolone as gravimetric reagents in that because they possess additional coordination sites, insoluble polynuclear complexes are formed. For example, Dutt and Singh(28) have used purpurogallin, its dibromo and carboxylic acid derivatives, and 3', 4'-dihydroxybenzotropolone for the gravimetric determination of ten elements. In the same study they separated by precipitation Th(IV) from U(VI), the lanthanide ions from one another, and Ti from Zr using the above chelating agents.

Solvent extraction of metal complexes with tropolone(29) and its β-isopropyl derivative(30), as well as the composition of various extracted species, have been investigated extensively by Dyrssen.

Stability constants of numerous metal ions with tropolone and its derivatives have been measured, mainly by spectrophotometric and potentiometric means(30-33).

Normally, the number of mono-protonated bidentate ligands (H bidentate) which react with a metal ion equals the charge on that particular metal ion, according to the reaction:

$$M^{n+} + n(\text{H bidentate}) = M(\text{bidentate})_n + nH^+$$

In some cases, however, the following reaction occurs:

$$M^{n+} + (n+m)\ \text{H bidentate} = M(\text{bidentate})_n \cdot m\ \text{H bidentate} + nH^+$$

in which the number of reacting ligands is one or more greater than the charge on the metal ion ($m \geq 1$), with the retention of the proton on the m additional molecules of reagent to preserve charge neutrality. These compounds have been termed "addition" compounds, "adducts" or "solvates", in contrast to the non-adduct or normal compound. For example, uranium (VI)(34), thorium (IV)(35) and scandium (III)(36) yield so-called adducts with 8-hydroxyquinoline; also, uranium (VI) forms adducts with acetylacetone(37), α-picolinic acid(38) and salicylic acid(39).

In view of the significance of metal tropolonates in analytical chemistry and in coordination chemistry, it was felt that additional clarification of the chemistry of the chelates (both non-adduct and adduct) formed by U(VI), Th(IV) and Sc(III) with tropolone was desirable. This thesis is concerned with this subject. In particular, study is given to: (i) the composition of the normal and adduct complexes, (ii) the thermal preparation of the normal compounds from the adducts, and (iii) the addition reaction between the normal compounds and tropolone and other bidentate ligands.

# CHAPTER II

# HISTORICAL INTRODUCTION

## II.A. Uranium(VI) Tropolonate Complexes

Considerable work has been done on the solution and solid complexes formed between uranium(VI) ion and tropolone. The early work was concerned with chelates formed in solution. Bryant, Fernelius and Douglas(31) attempted to obtain the formation constants of uranyl tropolonate chelates in a 50% v/v aqueous dioxane medium, but a flocculent orange precipitate formed, and they conducted no further investigations.

Dyrssen(29) showed that $UO_2^{2+}$ and $Th^{4+}$ ions can be separated readily from trivalent ions like $Y^{3+}$ and $La^{3+}$ by extraction into a chloroform solution of tropolone. In a later paper(30), he showed that the composition of the extracted complex is the "adduct" $UO_2T_2.HT$. Dyrssen and Ekberg(27) established a spectrophotometric method for the determination of uranium in which a potential coordinating solvent molecule, e.g., pyridine, replaces the extra β-isopropyltropolone molecule in the 1:3 complex formed between $UO_2^{2+}$ and β-isopropyltropolone.

In the preparation of solid complexes, Dutt and Singh(40) reported that $UO_2^{2+}$ combines with tropolone in the ratios 1:1, 1:2 and 1:3 in 50% aqueous ethanol. Plymale and Smith(41), however, could isolate only the 1:2 and 1:3 solid complexes from methanol medium. The compounds were characterized by elemental analysis, molecular-weight determination (DMSO solvent), density measurements, X-ray powder patterns, thermogravimetry, and by infrared spectra. The authors did not report the presence of coordinated solvent in the 1:2 chelate. Since coordinated solvent has been found in the bis (8-hydroxyquinolinato) dioxouranium(VI) solid chelate(42), it was felt that in the present study, the presence or absence of coordinated solvent in the bis (tropolonato) dioxouranium (VI) compound should be investigated more closely. Evidence is presented later for coordinated solvent in the bis compound prepared from both aqueous and methanol media.

In addition, work previous to this study did not indicate whether the extra ligand in the tris chelate is coordinated to the central $UO_2^{2+}$ ion or is merely a lattice component. This thesis presents infrared evidence which indicates that the extra tropolone molecule is probably a coordinated component of the complex.

The reaction of the bis chelate with tropolone and foreign bidentate ligands to yield tris adducts was also studied.

## II.B. Thorium(IV) Tropolonate Complexes

Early work was concerned with the solution complexes formed between Th(IV) and tropolone. Dyrssen and Rydberg(43,44) measured the stability constants for the 1:1 to 1:6 complexes using the distribution technique, and separated $Th^{4+}$ from trivalent ions by chloroform extraction of its β-isopropyltropolonate complex. Sekine and Dyrssen(45), in a further solvent-extraction study, proposed the formation of $ThA_4L$ and $ThA_4L_2$ adduct complexes (A = β-isopropyltropolone and L = tributylphosphate). Absorption of the 1:4 thorium tropolonate complex in the ultraviolet has been used for a spectrophotometric determination of thorium(19).

The solid tetrakis thorium tropolonate chelate was first prepared by Muetterties and Wright from a 50% chloroform-acetonitrile medium by reacting stoichiometric amounts of reagents under appropriate conditions(11). In a later paper, Muetterties reported a simpler method for the preparation of the tetrakis complex from an aqueous methanol medium(46). Selbin and Ortego(47) also prepared the same tetrakis compound by the method proposed by Muetterties.

The electron-accepting ability(i.e.,Lewis acidity) of Th(IV) in the tetrakis chelates is evident in the formation of apparent nine-coordinate complexes with strong donor molecules. For example, Muetterties(46) obtained the adduct, $ThT_4$.DMSO, on recrystallizing the tetrakis chelate from dimethylsulfoxide. An analogous dimethylsulfoxide adduct has been prepared for the tetrakis (8-hydroxyquinolinato) thorium(IV) solid chelate(48). Also, Hoard and Day(49) isolated the tetrakis (tropolonato)-N, N'-dimethylformamide thorium(IV) adduct, $ThT_4$.DMF. However, neither Muetterties(46) nor Selbin and Ortego(47) have reported the presence of coordinated solvent in their initial preparations of the tetrakis chelate. In the present study, evidence is presented for coordinated solvent in the tetrakis chelate prepared from aqueous and from 50% aqueous methanol media.

In an attempt to obtain a ten-coordinate chelate, Muetterties(46) prepared the pentakis (tropolonato) thorium(IV) and the pentakis (γ-isopropyltropolonato) thorium(IV) complexes as sodium salts by reacting the neutral tetrakis chelates with sodium tropolonate in a mixture of acetonitrile, water and ethanol. The compounds $NaThT_5$ and $NaThB_5$ (B = γ-isopropyltropolone) were isolated. The lithium and potassium salts were also prepared similarily. Muetterties reported that the infrared spectra of $NaThT_5$ and $NaThB_5$ in nujol mull indicated the possible presence of water in the lattice because of the very weak absorption band at 3430 $cm^{-1}$, although the analytical data corresponded closely to the anhydrous compound. Other principal infrared absorption bands were reported but not assigned. The preparation of the pentakis chelate $HThT_5$ has not been reported previously. Its formation from aqueous medium and its characterization are described in this thesis.

Considerable work has been done to determine whether the tropolone ligands in each of the tetrakis and pentakis chelates are chemically equivalent. Muetterties and Wright(11) have reported that the infrared and proton n.m.r. spectra of the $ThT_4$ compound gave no indication of distinctly different tropolone ligands. In an x-ray crystal structure determination of the adduct, $ThT_4.DMF$, Hoard and Day(49) showed Th(IV) to be nine-coordinate in a monocapped square antiprism coordination polyhedron. They found all four tropolone ligands to be bidentate, but the length of the Th-O bond to the apical oxygen from the one tropolonato ligand spanning a slant edge of the pyramidal cap is significantly greater than the average for the other seven Th-O bonds.

An investigation of the pentakis anionic thorium tropolonates by Muetterties(46) showed the infrared spectra to be "significantly less complex" than those of the parent tetrakis compounds, and the proton n.m.r. spectra in $(CD_3)_2SO$ to be quite similar to those for tetrakis chelates. This led Muetterties to propose that in solution the ligands are bonded equivalently in the pentakis anion. On the basis of the solution chemistry, Muetterties speculated that the solid is not merely a solid solution of the 1:4 complex and tropolone.

In a further study, Selbin and Ortego(47) prepared $ThT_4$ and $LiThT_5$ and examined their vibrational and electronic spectra in the 4000 - 650 $cm^{-1}$ and 4500 - 2200 $A^o$ regions respectively. Contrary to the statement by Muetterties that the i.r. spectrum of the pentakis compound is "significantly less complex" than that of the tetrakis compound, these authors found that the number of bands for each compound was about the same. They suggested that the greater steric effects expected in the pentakis compound might account for the differences in the 1220-1270 $cm^{-1}$ region, tentatively assigned to the C-H in-plane deformation. In the present study, infrared and thermogravimetric studies of the previously unprepared pentakis acid chelate, $HThT_5$, are reported. Also, the direct addition of tropolone (and other bidentate ligands) to the tetrakis Th(IV) tropolonate is reported.

## II.C. Scandium (III) Tropolonate Complexes

On reacting scandium nitrate with slightly substoichiometric amounts of tropolone in an aqueous methanol medium, Muetterties and Wright(11) obtained yellow crystals of hydrogen tetrakis (tropolonato) scandium(III), $HScT_4$. The authors reported little analytical data for the compound. The coordination environment of the scandium(III) ion was unresolved until Olszanski et al.(50) determined the crystal and molecular structure of the acid. They found that the compound exists as a hydrogen-bonded dimer with each scandium atom coordinated to eight oxygen atoms from four tropolonate ligands. The coordination environment about the $Sc^{3+}$ ion is a $D_{2d}$ dodecahedron, the two dodecahedra being held together in the crystal about the center of symmetry by almost linear hydrogen bonds. This hydrogen bonding may account for some of the slight distortions from an ideal dodecahedron.

The same authors presented infrared data associated with $\nu_{C=O}$ and $\nu_{O-H}$ to show the absence of uncoordinated ligand. The ESCA spectrum of $HScT_4$ was symmetrical in the oxygen (1S) region, suggesting that the eight oxygen atoms are equivalent.

In the present study, the preparation of $HScT_4$ from an aqueous rather than an aqueous-organic medium is outlined. Also, data from thermogravimetric analysis and a re-examination of the infrared spectrum in the O-H absorption region of the tetrakis chelate are given to provide additional information on the chemical equivalence of the four ligand molecules.

Muetterties and Wright(11) reported the indirect preparation of the tris compound $ScT_3$ by dissolution of the tetrakis compound in a hot methanol-chloroform mixture and subsequent concentration of the solution.

Anderson, Neuman and Melson(51) obtained a mixture of pale yellow $HScT_4$ and red-brown $ScT_3$ crystals on reacting scandium nitrate and tropolone in aqueous methanol medium. In addition, they determined the crystal and molecular structure of $ScT_3$ by a single-crystal x-ray diffraction technique. The coordination environment was found to be intermediate between trigonal antiprismatic and trigonal prismatic.

Olszanski et al(50) have assigned the C=O absorption band in the infrared spectrum of $ScT_3$, but no other assignments were made. Their ESCA data showed all six oxygen atoms to be equivalent.

The direct precipitation of the tris chelate in aqueous medium is described in this thesis, and infrared and thermogravimetric studies are reported.

Muetterties and Wright(11) have prepared the sodium salt $NaScT_4$ by reacting $ScT_3$ with sodium tropolonate in an acetonitrite-water-methanol medium.

# CHAPTER III

# EXPERIMENTAL AND RESULTS

## III.A. Apparatus

Certified volumetric ware was used when appropriate.

Weighings were made on a conventional double-beam trip balance and, when necessary, on a semimicro analytical balance (Type B-6, Mettler).

Measurements of pH were made with a Coleman Model Metrion IV pH Meter, equipped with suitable electrodes.

Infrared spectra were recorded with a Beckman IR-5 spectrophotometer. Samples of the compounds were prepared as mulls in anhydrous hexachloro-1,3-butadiene (Figure Ia, Appendix). All spectra were recorded over the range 5000-650 $cm^{-1}$ using sodium chloride windows (6mm). A polystyrene film was used as a calibrant for the spectra.

Thermograms were recorded on a Stanton HT-D automatic thermo-recording balance.

A heated vacuum dessicator (P5, Precision Scientific Company) was used when appropriate for drying prepared compounds.

The apparatus for the thermal reaction experiments consisted of a flat-bottomed 40-ml flask connected to one arm of a U-tube by a clamped ground-glass ball joint. The other arm of the U-tube was connected to a vacuum pump. In use, the apparatus was evacuated, a dry-ice bath was placed around the U-tube, and the flask immersed in an oil bath and heated under vacuum (0.1 mm Hg). Any sublimed material was found condensed in the initial portion of the U-tube.

## III.B. Reagents

All common laboratory chemicals were either reagent-grade or of sufficient purity for the purpose intended.

Uranyl nitrate hexahydrate (Fisher Scientific Company), thorium nitrate hexahydrate (Analar grade, British Drug Houses) and scandium chloride hexahydrate (Alfa Inorganics) were used without further purification. Stock solutions of these salts were prepared in aqueous media and standardized by established procedures: $4.00 \times 10^{-2}$ M $UO_2(NO_3)_2.6H_2O$, acidified with $HNO_3$ to pH 1.5, was prepared and standardized by precipitation of ammonium uranate and ignition to $U_3O_8$(52); $3.56 \times 10^{-2}$ M $ScCl_3 \cdot 6H_2O$ (1.60 mg Sc/ml), acidified as above, was prepared and standardized with EDTA(53); $5.81 \times 10^{-3}$ M $Th(NO_3)_4 \cdot 6H_2O$ (1.35 mg Th/ml), acidified as above, was prepared and standardized with EDTA(54). Tropolone (Aldrich Chemical Company) was used without further purification.

The deuterium oxide and methanol-$d_1$ were supplied by Stohler Isotope Chemicals and were 99.8% and 99% pure, respectively.

Hexachloro-1,3-butadiene (Eastern Chemical Corporation), used in preparing mulls for infrared samples, was vacuum distilled over barium oxide and then stored over molecular sieves (Type 4A, Fisher Scientific Company).

## III.C. Elemental Analyses

The elemental analyses for %C and %H in this thesis were performed by A.B. Gygli, Microanalysis Laboratories Limited, Toronto, with the exception of the uranyl tropolonates precipitated from methanol solution. The elemental analyses for these were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Max Planck Institut fur Kohlenforschung, Mulheim (Ruhr), Germany. The metal content of the compounds was determined by ignition to the oxide in this laboratory.

## III.D. Uranium (VI) Complexes of Tropolone

### III.D.1. Synthesis

### III.D.1.a. Precipitation of the bis (tropolonato) dioxouranium (VI) aquo complex from aqueous solution

Fifteen ml of the U(VI) stock solution (0.60 millimoles) were pipetted into a 100-ml beaker, to which a solution of tropolone (1.18 millimoles in 30 ml of water) was added dropwise with continuous stirring. An orange precipitate was formed immediately. The precipitate was allowed to digest at 40-50°C for 6 hours, filtered through a sintered-glass crucible (porosity M)*, washed with two 10-ml portions of 50% aqueous methanol, and dried at 55°C and 6-7 mm Hg for 24 hours. The pH of the gold-coloured filtrate was 1.60. The dried product was reddish-orange in colour.

Calculated for $UO_2(C_7H_5O_2)_2 \cdot H_2O$: %C, 31.71; H, 2.28; U, 44.89.

Found: %C, 31.38; H, 2.39; U, 44.49.

The thermogram and thermogravimetric data for the compound are presented in RESULTS AND DISCUSSION, Figure IA and Table II,respectively. The i.r. spectrum is shown in Figure IIa, APPENDIX.

### III.D.1.b. Precipitation of the bis (tropolonato) dioxouranium (VI) deuterium oxide complex from $D_2O$ medium

A solution of tropolone (0.147 g or 1.21 millimoles in 30 ml $D_2O$) was added dropwise, with stirring, to a solution of uranyl nitrate hexahydrate (0.303 g or 0.60 millimoles in 15 ml $D_2O$). The mixture was allowed to digest at 50°C for 2 hours, then filtered, washed with two 10-ml portions of $D_2O$ and dried as described above.

The i.r. spectrum of the reddish-orange product is given in Figure IIb, APPENDIX.

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*Unless otherwise stated, sintered-glass crucibles of porosity M were used for all filtrations.

### III.D.1.c. Precipitation of the bis (tropolonato) dioxouranium (VI) methanol complex from methanol medium

The reddish-orange 1:2 chelate was precipitated on dropwise addition (with stirring) of a solution of tropolone (0.565 g or 4.92 millimoles in about 5 ml of methanol) to a solution of uranyl nitrate hexahydrate (1.24 g or 2.46 millimoles in about 5 ml of methanol). The mixture was allowed to stand for 3 hours before filtration. The precipitate was washed with 10 ml of methanol and dried at 50°C and 6-7 mm Hg for 14 hours.

Calculated for $UO_2(C_7H_5O_2).CH_3OH$: %C, 33.10; H, 2.59; U, 43.74.

Found: %C, 33.49; H, 2.75; U, 43.58.

The thermogram and thermogravimetric data for the chelate are shown in RESULTS AND DISCUSSION, Figure IB and Table II, respectively. The i.r. spectrum is given in Figure IIIa, APPENDIX. Data for precipitations presented in sections a and c are summarized in Table I, RESULTS AND DISCUSSION.

### III.D.1.d. Precipitation of the bis (tropolonato) dioxouranium (VI) methanol-$d_1$ complex from $CH_3OD$ medium

The procedure for the precipitation of the deuterated complex was identical to that for precipitation of $UO_2T_2.CH_3OH$ described above, except that $CH_3OD$ was used as the solvent and wash liquid.

The i.r. spectrum of the reddish-orange product is presented in Figure IIIb, APPENDIX.

### III.D.1.e. Precipitation of the tris (tropolonato) dioxouranium (VI) complex from aqueous solution

Fifteen ml of the stock U(VI) solution (0.60 millimoles) were pipetted into a 100-ml beaker, to which was added a solution of tropolone (309 mg or 2.53 millimoles in about 30 ml of water), dropwise with continuous stirring. A yellow precipitate formed and was allowed to digest at 40-50°C for 6 hours. The yellowish-orange product was filtered, washed, and dried as previously described. The pH of the very pale yellow filtrate was 1.58.

Calculated for $UO_2(C_7H_5O_2).C_7H_6O_2$: %C, 39.76; H, 2.54; U, 37.52.

Found: %C, 39.87; H, 2.98; U, 36.79.

The thermogram and thermogravimetric data for the compound are given in RESULTS AND DISCUSSION, Figure IC and Table II, respectively. The i.r. spectrum is shown in Figure IV, APPENDIX.

### III.D.1.f. Precipitation of the tris (tropolonato) dioxouranium (VI) complex from methanol medium

The yellow-orange 1:3 chelate was formed upon addition of the first increments of tropolone solution (1.004 g or 8.22 millimoles in about 5 ml of methanol), dropwise with stirring, to a solution of uranyl nitrate (0.994 g or 1.98 millimoles in 5 ml of methanol). After standing for 3 hours, the mixture was filtered, washed with 10 ml of methanol and dried for 14 hours at 50°C and 6-7 mm Hg.

Calculated for $UO_2(C_7H_5O_2).C_7H_6O_2$: %C, 39.76; H, 2.54; U, 37.52.

Found: %C, 39.51; H, 2.56; U, 37.31.

The thermogram and i.r. spectrum of the compound were essentially identical to those obtained for the tris chelate prepared from aqueous medium.

## III.D.2. Thermal Studies

### III.D.2.a. Thermogravimetry

About 50-60 mg of the uranyl tropolonate complexes prepared as described in Section III.D.1. were placed in a small silica crucible and heated in thermobalance at an average initial heating rate of 1°C/minute to approximately 130°C, and thereafter, at 6°C/minute. The compounds were heated in air at atmospheric pressure until the constant-weight level corresponding to $U_3O_8$ (about 450-500°C) was obtained.

The thermograms of the various uranyl tropolonate complexes are given in Figure I, RESULTS AND DISCUSSION.

Thermogravimetric data for the uranyl tropolonate chelates are given in Table II, RESULTS AND DISCUSSION. All data were corrected for the buoyancy of the sample holders.

### III.D.2.b. Thermal reactions

Selected uranyl tropolonate complexes prepared in Section III.D.1 were heated in the thermal reaction apparatus described earlier (Section III.A.). The thermograms were used for the selection of conditions. The residues remaining in the bottom of the flask and the sublimed compounds condensed in the U-tube were examined by infrared analysis and, in some cases, by elemental analysis.

The reddish orange aquo complex, $UO_2T_2.H_2O$ (112 mg), was heated slowly to 100°C and maintained at that temperature for 5 hours. A droplet of clear, colorless liquid appeared in the bottom of the U-tube and the residue in the flask was a less intense red colour. Both products were characterized by i.r.

Thermal conversion of the methanol complex, $UO_2T_2.CH_3OH$ (106 mg), at 100°C for 8 hours resulted in the trapping of a small drop of clear, colorless liquid in the U-tube. The i.r. spectra of the solid residue and liquid droplet were taken. Analytical data were determined for the residue.

Calculated for $UO_2(C_7H_5O_2)_2$: %C, 32.83; H, 1.97; U, 46.47.

Found: %C, 33.37; H, 2.01; U, 46.10.

The yellow-orange adduct complex prepared from methanol medium, $UO_2T_2.HT$ (181 mg), was heated slowly to 200°C, and maintained at this temperature for 6 hours. The white, solid deposit in the U-tube and the residue were characterized by i.r., and the i.r. spectrum of the residue is shown in Figure V, APPENDIX.

Calculated for $UO_2(C_7H_5O_2)$: %C, 32.83; H, 1.97; U, 46.47.

Found: %C, 32.23; H, 1.89; U, 46.03.

### III.D.3. Interaction of the Bis (Tropolonato) Dioxouranium (VI) Aquo Complex With Bidentate Ligands

The purpose of this study was to see whether certain bidentate ligands were capable of displacing the water molecule from the bis complex to form an adduct complex.

#### III.D.3.a Interaction with tropolone

An amount of $UO_2T_2.H_2O$ (107 mg, 0.2 millimoles) was added to a solution of tropolone (99 mg or 0.8 millimoles in about 5 ml of water). The mixture was stirred magnetically and the solid became reddish-orange in colour within a few minutes. The beaker was left on a hotplate for 2 hours at 40°C, then filtered, washed with two 10-ml portions of water, and dried for 17 hours at 55°C and 6-7 mm Hg. The i.r. spectrum of the product was identical to that of the adduct chelate shown in Figure IV, APPENDIX.

#### III.D.3.b. Interaction with 8-hydroxyquinoline

$UO_2T_2.H_2O$ (106 mg, 0.2 millimoles) were added with stirring to an ethanol solution of 8-hydroxyquinoline (174 mg or 1.2 millimoles in 30 ml of ethanol). The heterogeneous mixture was allowed to stand for two days; then, it was filtered, washed with two 10-ml portions of 50% ethanol/water, and air-dried.

The i.r. spectrum of the product is presented in Figure VI, APPENDIX.

#### III.D.3.c. Interaction with α-picolinic acid

Twelve ml of 0.100 M aqueous α-picolinic acid solution (1.2 millimoles) were pipetted into a 30-ml beaker and 107 mg (0.2 millimoles) of $UO_2T_2.H_2O$ were added. The mixture was allowed to stand for 24 hours, then filtered and washed with two 10-ml portions of water. After drying for 16 hours at 50°C and 0.1 mm Hg, the i.r. spectrum of the compound was taken.

Table III, RESULTS AND DISCUSSION, summarizes the data of these "addition" reactions involving $UO_2T_2.H_2O$.

## III.E. Thorium (IV) Complexes of Tropolone

### III.E.1. Synthesis

#### III.E.1.a. Precipitation of the tetrakis (tropolonato) thorium (IV) aquo complex from aqueous solution

A solution of tropolone (0.49 g or 4 millimoles in 5 ml of methanol) was added dropwise, with stirring, to 167 ml (1 millimole Th(IV)) of the standard Th(IV) solution, previously adjusted to pH 2.40 with 2M aqueous ammonia. A pale yellow precipitate formed during addition of the tropolone solution; after 0.5 hours, the mixture was placed on a steam bath for about 3 hours. The fine, pale creamy-yellow precipitate was filtered, washed with three 10-ml portions of 50% aqueous methanol, and dried for 12 hours at 50-55°C and 6-7 mm Hg. The pH of the filtrate was 1.80. The compound was found to be slightly hygroscopic.

Calculated for $Th(C_7H_5O_2).H_2O$: %C, 45.79; H, 3.02; Th, 31.59.
Found: %C, 45.84; H, 2.99; Th, 31.96.

The thermogram and thermogravimetric data for the chelate are found in RESULTS AND DISCUSSION, Figure IIA and Table V,respectively. The i.r. spectrum is shown in Figure VIIa, APPENDIX.

#### III.E.1.b. Precipitation of the tetrakis (tropolonato) thorium (IV) deuterium oxide complex from $D_2O$ medium

A solution of tropolone (0.499 g or 4.09 millimoles in about 30 ml $D_2O$) was added dropwise, with stirring, to a solution of thorium nitrate (0.612 g or 1.00 millimoles in about 20 ml $D_2O$). The mixture was placed on a steam bath for 3 hours, then filtered, washed with two 10-ml portions of $D_2O$ and dried as described above.

The i.r. spectrum of the compound is presented in Figure VIIb, APPENDIX.

### III.E.1.c. Precipitation of the tetrakis (tropolonato) thorium (IV) methanol complex from 50% aqueous methanol medium

The method employed by Muetterties(46) was followed, using the same molar ratios and concentrations of reagents, but on a smaller scale. One millimole (0.48g) of thorium nitrate was dissolved in 10 ml of water and 5 ml of methanol. A solution of tropolone (0.52 g or 4.3 millimoles in 5 ml of methanol) was added dropwise, with constant stirring, to the Th(IV) solution. The solution turned yellow upon addition of initial amounts of tropolone, and a pale yellow precipitate appeared towards the end of addition. The mixture was allowed to stand at room temperature for 0.5 hours, digested for 2 hours at 40°C, and washed with two 10-ml portions of 50% methanol-water. The pale yellow product was dried at 50°C and 6-7 mm Hg for 14 hours. The pH of the pale yellow filtrate was 1.06.

Calculated for $Th(C_7H_5O_2)_4.CH_3OH$: %C, 46.41; H, 3.22; Th, 30.92.
Found: %C, 45.90; H, 3.23, Th, 31.20.

The thermogram and thermogravimetric data for the chelate are given in RESULTS AND DISCUSSION, Figure IIB and Table V,respectively. The i.r. spectrum is shown in Figure VIIIa, APPENDIX.

Data for precipitations presented in sections a and c are summarized in Table IV, RESULTS AND DISCUSSION.

### III.E.1.d Precipitation of the tetrakis (tropolonato) thorium (IV) methanol-$d_1$ complex from 50% $D_2O$-$CH_3OD$ medium.

The procedure for the precipitation of $ThT_4.CH_3OD$ was identical to that described above, except that 10 ml of $D_2O$ and 5 ml of $CH_3OD$ were used as the solvent for thorium nitrate, and 5 ml of $CH_3OD$ as the solvent for tropolone. A fine, bright yellow precipitate appeared upon mixing the reagents.

The i.r. spectrum of the compound is shown in Figure VIIIb APPENDIX.

### III.E.1.e. Precipitation of the pentakis (tropolonato) thorium (IV) complex from aqueous solution.

A solution of tropolone (0.52 g or 4.25 millimoles in 25 ml of methanol) was added dropwise (with stirring) over a period of 0.5 hours to 112.5 ml (0.65 millimoles) of the Th(IV) stock solution maintained at 50°C. A pale yellow precipitate resembling $ThT_4.H_2O$ in appearance was produced after addition of half of the tropolone. The mixture was allowed to digest on a hotplate at 40-50°C overnight (12 hours). After this time, the volume of the solution was reduced to about 25 ml and a fine, bright yellow precipitate was present. The compound was filtered, washed with three 10-ml portions of water, and dried for 16 hours at 50-55°C and 6-7 mm of Hg. The pH of the filtrate was 2.72.

Calculated for $Th(C_7H_5O_2)_4.C_7H_6O_2$: %C, 50.13; H, 3.13; Th, 27.67.
Found: %C, 49.99; H, 3.19; Th, 27.68.

The thermogram and thermogravimetric data are presented in RESULTS AND DISCUSSION, Figure IIC and Table V, respectively. The i.r. spectrum is shown in Figure IX, APPENDIX.

### III.E.2. Thermal Studies

### III.E.2.a. Thermogravimetry

Samples of three thorium-tropolone chelates described in the previous section were studied by thermogravimetric analysis. The thermogravimetric curves are given in Figure II, RESULTS AND DISCUSSION.

Thermogravimetric data for these complexes are given in Table V, RESULTS AND DISCUSSION.

### III.E.2.b. Thermal reactions

Selected thorium tropolonate complexes prepared in Section III.E.1. were heated in the thermal reaction apparatus described earlier (Section III.A.).

The pale yellow $ThT_4.H_2O$ complex (260 mg) was heated for 20 hours at 100°C. The clear, colorless liquid droplet in the bottom of the U-tube and the residue were characterized by i.r. analysis.

The pale yellow $ThT_4.CH_3OH$ complex (135 mg) was heated for 5 hours at 100°C, yielding a clear, colorless droplet in the U-tube and a pale yellow solid residue. The i.r. spectra of the products were taken.

Thermal conversion of the bright yellow adduct complex $ThT_4.HT$ (102 mg) for 18 hours at 165-170°C resulted in a pale yellow residue in the flask and a compact, white solid in the U-tube. Analytical data were obtained for the residue.

Calculated for $Th(C_7H_5O_2)_4$: %C, 46.94; H, 2.81; Th, 32.39.

Found: %C, 47.06; H, 3.01; Th, 32.09.

The i.r. spectra of the residue and sublimed product were taken, and the spectrum of the residue is shown in Figure X, APPENDIX.

### III.E.3. Interaction of the Tetrakis (Tropolonato) Thorium (IV) Aquo Complex With Bidentate Ligands

### III.E.3.a. Interaction with tropolone

The procedure and molar ratio of $ThT_4.H_2O$ to tropolone was as described earlier for the interaction of tropolone with $UO_2T_2.H_2O$ (Section III.D.3.a.). The i.r. spectrum of the product was identical to that of $ThT_4.HT$ (Figure IX, APPENDIX).

### III.E.3.b. Interaction with 8-hydroxyquinoline

Attempts to prepare the $ThT_4.HQ$ (HQ = 8-hydroxyquinoline) adduct chelate using the same procedure as for the $UO_2T_2.HQ$ chelate (Section III.D.3.b.) proved unsuccessful. Only the starting compound was isolated.

### III.E.3.c. Interaction with α-picolinic acid

Following the same procedure as outlined earlier (Section III.D.3.c.), attempts to prepare the adduct chelate $ThT_4.HPic$ (HPic = α-picolinic acid) resulted only in the isolation of the starting compound $ThT_4.H_2O$.

## III.F. Scandium (III) Complexes of Tropolone

### III.F.1. Synthesis

### III.F.1.a. Precipitation of the tris (tropolonato) scandium (III) complex by the method of Muetterties and Wright

The following procedure is essentially the same as the indirect preparation proposed by Muetterties and Wright(11): ten ml (0.36 millimoles) of Sc(III) stock solution were pipetted into a 150-ml beaker and diluted to 60 ml. The Sc(III) solution was constantly stirred as a solution of tropolone (0.217 g or 1.78 millimoles in about 5 ml methanol) was slowly added dropwise. Upon standing, shiny yellow crystals of $H[ScT_4]$ appeared. The mixture was filtered and the crystals were dried at 50°C and 6-7 mm Hg for 3.5 hours.

The yellow crystals were dissolved in 30 ml of hot 50% chloroform-methanol and the solution was allowed to evaporate overnight. A heterogeneous mixture of orange and yellow crystals separated from solution.

The product was filtered and dried at 80°C and 6-7 mm Hg for 2 hours.

The i.r. spectrum of the tris chelate is shown in Figure XIa, APPENDIX.

Subsequent attempts to prepare the tris chelate by changing the tropolone:Sc ratio from 5:1 to 4:1 and, finally, to 3:1 resulted in the same product as above.

### III.F.1.b. Precipitation of the tris (tropolonato) scandium (III) complex from aqueous solution

Fifteen ml (0.44 millimoles) of the Sc(III) stock solution were pipetted into a 100-ml beaker. A solution of tropolone (163 mg or 1.34 millimoles in about 5 ml of methanol) was added dropwise with continuous stirring. The pH of the greenish-yellow solution was raised from 1.12 to 2.25 using 2M aqueous ammonia and the resulting mixture was left to stand for 16 hours. The shiny, green platlets which crystallized were filtered, washed with three 10-ml portions of water, and dried for 20 hours at 55°C and 6-7 mm Hg. The pH of the pale yellow filtrate was 2.76.

Calculated for $Sc(C_7H_5O_2)_3$: %C, 61.78; H, 3.70; Sc, 11.01.

Found: %C, 60.45; H, 3.66; Sc, 10.46.

Table VI, RESULTS AND DISCUSSION, provides the percentage composition for possible solvates of $ScT_3$.

The thermogram and thermogravimetric data are given in RESULTS AND DISCUSSION, Figure IIIA and Table VII,respectively. The i.r. spectrum is shown in Figure XIb, APPENDIX.

### III.F.1.c. Precipitation of the tetrakis (tropolonato) scandium (III) complex from aqueous methanol medium

Ten ml (0.36 millimoles) of the Sc(III) stock solution were pipetted into a 150 ml beaker, diluted to 60 ml with deionized water, and warmed on a hotplate to 50°C. A solution of tropolone (434 mg or 3.56 millimoles in about 5 ml of methanol) was added dropwise with continuous stirring for 15 minutes. After stirring for several minutes longer, a fine, bright yellow solid precipitated from the clear, yellow solution. The mixture was allowed to digest for 12 hours at 40°C and then filtered, washed with three 10-ml portions of deionized water, and dried for 24 hours at 50°C and 6-7 mm Hg. The pH of the pale yellow filtrate was 1.65.

Calculated for $Sc(C_7H_5O_2).C_7H_6O_2$: %C, 63.40; H, 3.99; Sc, 8.48.
Found: %C, 63.20; H, 3.97; Sc, 8.46.

The thermogram and thermogravimetric data for the compound are presented in RESULTS AND DISCUSSION, Figure IIIB and Table VII,respectively. The i.r. spectrum is shown in Figure XII, APPENDIX.

### III.F.2. Thermal Studies

### III.F.2.a. Thermogravimetry

The thermogravimetric analysis of $ScT_3$ and $ScT_3$.HT was performed as described previously (Section III.D.2.a.).

The thermogravimetric curves for these two compounds are shown in Figure III, RESULTS AND DISCUSSION, and thermogravimetric data is presented in Table VII, RESULTS AND DISCUSSION.

### III.F.2.b. Thermal reactions

By the same procedure outlined earlier (Section III.A.), 115 mg of the lemon-yellow adduct complex, $ScT_3$.HT, were heated for 24 hours at 160-165°C. The i.r. spectra of the white solid in the U-tube and the pale yellow solid residue were recorded. The spectrum of the residue is shown in Figure XIII, APPENDIX.

### III.F.3. Interaction of the Tris (Tropolonato) Scandium (III) Complex With Bidentate Ligands

Attempts to prepare $ScT_3$.X where X = tropolone, 8-hydroxyquinoline, and α-picolinic acid, by procedures outlined earlier (Section III.D.3.), yielded the adduct with tropolone, but only the starting compound $ScT_3$ with 8-hydroxyquinoline and α-picolinic acid. The i.r. spectrum of the product isolated in the tropolone reaction was identical to that of $ScT_3$.HT (Figure XII, APPENDIX).

# CHAPTER IV

# RESULTS AND DISCUSSION

## IV.A. Uranium (VI) Tropolonate Complexes

### IV.A.a. Composition of the bis uranium (VI)-tropolone chelate.

The coordination of polar solvents in the bis chelates formed between $UO_2^{2+}$ and bidentate ligands has been reported previously. For example, in the bis (8-hydroxyquinolinato) dioxouranium (VI) chelate, solvates with coordinated water, methanol and acetone have been described(42). Similar solvates of the bis (acetylacetone) U(VI) complex have been reported(55). Since the analytical data of Plymale and Smith(41) did not indicate the presence of coordinated solvent in the $UO_2T_2$ chelate prepared in methanol solution, an investigation of the composition was made.

The procedure followed for the formation of the solid bis chelate from methanol was identical to that reported by Plymale and Smith, except that the product was dried at 50°C and 6-7 mm Hg rather than at 80°C "under vacuum" as reported by the above authors. These same workers observed that their unsolvated bis chelate was hygroscopic, which prompted the preparation and subsequent determination of the composition of the solid bis chelate from aqueous medium in the present work.

Analytical data for the bis chelate prepared from aqueous solution are in good agreement with the formula $UO_2T_2 \cdot H_2O$ (Table Ia).

The i.r. spectrum of the same compound (Figure IIa, APPENDIX) shows the definite presence of coordinated or lattice water through the broad band of medium intensity at 3300 $cm^{-1}$ ($\nu_{O-H}$ symmetric), the sharp,

## TABLE I

## ANALYTICAL DATA FOR POSSIBLE SOLVATES OF BIS (TROPOLONATO) DIOXOURANIUM (VI)

a. PRECIPITATION FROM AQUEOUS MEDIUM

| COMPOUND | C(%) | H(%) | U(%) |
|---|---|---|---|
| $UO_2T_2$ | 32.82 | 1.97 | 46.47 |
| $UO_2T_2.H_2O$ | 31.71 | 2.28 | 44.89 |
| $UO_2T_2.2H_2O$ | 30.67 | 2.57 | 43.42 |
| FOUND | 31.38 | 2.39 | 44.49 |

b. PRECIPITATION FROM METHANOL MEDIUM

| COMPOUND | C(%) | H(%) | U(%) |
|---|---|---|---|
| $UO_2T_2.CH_3OH$ | 33.10 | 2.59 | 43.74 |
| $UO_2T_2.2CH_3OH$ | 33.34 | 3.15 | 41.31 |
| FOUND | 33.49 | 2.75 | 43.58 |

medium-intensity shoulder at 3350 $cm^{-1}$ ($\nu_{O-H}$ antisymmetric), and the sharp band of medium-weak intensity at 1650 $cm^{-1}$ (H-O-H bending mode)(56). In addition, the strong band centered at 728 $cm^{-1}$ (attributed to O-H and C-H out-of-plane deformation modes and C-C stretch(57)) in the spectrum of $UO_2T_2.HT$ (Figure IV, APPENDIX) now appears in the $UO_2T_2.H_2O$ spectrum as a shoulder of a much broader peak centered at 742 $cm^{-1}$. This is the region in which wagging, twisting and rocking modes of the water molecule are activated upon coordination to the metal-ion(58,59). The i.r. spectrum (Figure IIb, APPENDIX) of the bis chelate prepared from deuterium oxide solution shows the $\nu_{O-H}$ symmetric band reduced in intensity and the appearance of a broad band of weak intensity centered at 2450$cm^{-1}$ ($^{\nu_H}/_{\nu_D}$ = 1.35). Also, the disappearance of the $\nu_{O-H}$ antisymmetric band at 3550 $cm^{-1}$, the reduction in the H-O-H bending mode at 1650 $cm^{-1}$, and changes in the 750 $cm^{-1}$ region are evident.

The thermogram of $UO_2T_2.H_2O$ (Figure IA) shows the loss of the water over the temperature range 100-130°C, followed by the decomposition to $U_3O_8$ above 350°C. Thermogravimetric date (Table II) indicate close correspondence between the calculated weight loss based on the formula $UO_2T_2.H_2O$ and that found experimentally.

Based on the analytical data given in Table Ib, the empirical formula for the bis chelate prepared form methanol medium (EXPERIMENTAL, Section D.1.c.) fits the composition $UO_2T_2.CH_3OH$ satisfactorily, and appears to be within or close to the usual experimental errors associated with these determinations. The slightly high values for %C and %H may be caused by a small amount of coprecipitated tropolone. Two weak bands at 1265 and 1240 $cm^{-1}$, assigned to C-O-H absorption modes of uncomplexed solid tropolone(57) are present in the i.r. spectrum of the $UO_2T_2.CH_3OH$

chelate (Figure IIIa, APPENDIX). These bands are absent in the spectrum of $UO_2T_2$ (Figure V, APPENDIX). The $\nu_{O-H}$ stretching frequency of uncomplexed solid tropolone occurs at 3208 $cm^{-1}$(57,60), but masking by the broad 3030 $cm^{-1}$ band of the methanol excludes the use of this band in detecting small amounts of coprecipitated reagent.

In addition to analytical data, further evidence for coordinated or lattice methanol in the bis chelate is provided by the i.r. spectrum (Figure IIIa, APPENDIX). The absorption bands at 3320 $cm^{-1}$ ($\nu_{O-H}$), about 2900 $cm^{-1}$ ($\nu_{C-H}$), and about 1035 $cm^{-1}$ ($\nu_{C-O}$) in the spectrum of reagent-grade methanol(61) now appear at 3030 $cm^{-1}$ (broad, medium intensity), 2770 $cm^{-1}$ (broad, weak intensity), and 1030 $cm^{-1}$ (sharp, medium intensity), respectively, in the spectrum of the bis complex. The absorption bands due to stretching vibrations in a proton donor group A-H have been found to shift to lower frequencies as a result of a hydrogen-bonded complex, A-H---B, with an acceptor group B(62,63).

The i.r. spectrum of $UO_2T_2.CH_3OD$ prepared from $CH_3OD$ (EXPERIMENTAL, Section D.1.d.) is shown in Figure IIIb, APPENDIX. The band due to $\nu_{C-H}$ is still at about 2770 $cm^{-1}$, but the 3030 $cm^{-1}$ band due to $\nu_{O-H}$ is greatly reduced in intensity, and a small band at 2150 $cm^{-1}$($^{\nu}H/\nu_D$ = 1.41) arising from the methanol O-D stretching frequency is observed. The splitting of the 1030 $cm^{-1}$ peak ($\nu_{C-O}$) into two smaller bands at 1035 $cm^{-1}$ and 1025 $cm^{-1}$ is probably caused by some hydrogen-deuterium exchange in the "adduct" $CH_3OD$ molecule when the solid was exposed to the atmosphere. For the same reason, the low-intensity band at 3030 $cm^{-1}$ is present.

The thermogram of $UO_2T_2.CH_3OH$ (Figure IB) shows the loss of methanol over the temperature range 70-140°C.*

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* In a recent publication(64), the methanol is reported to be removed at 142-172°C.

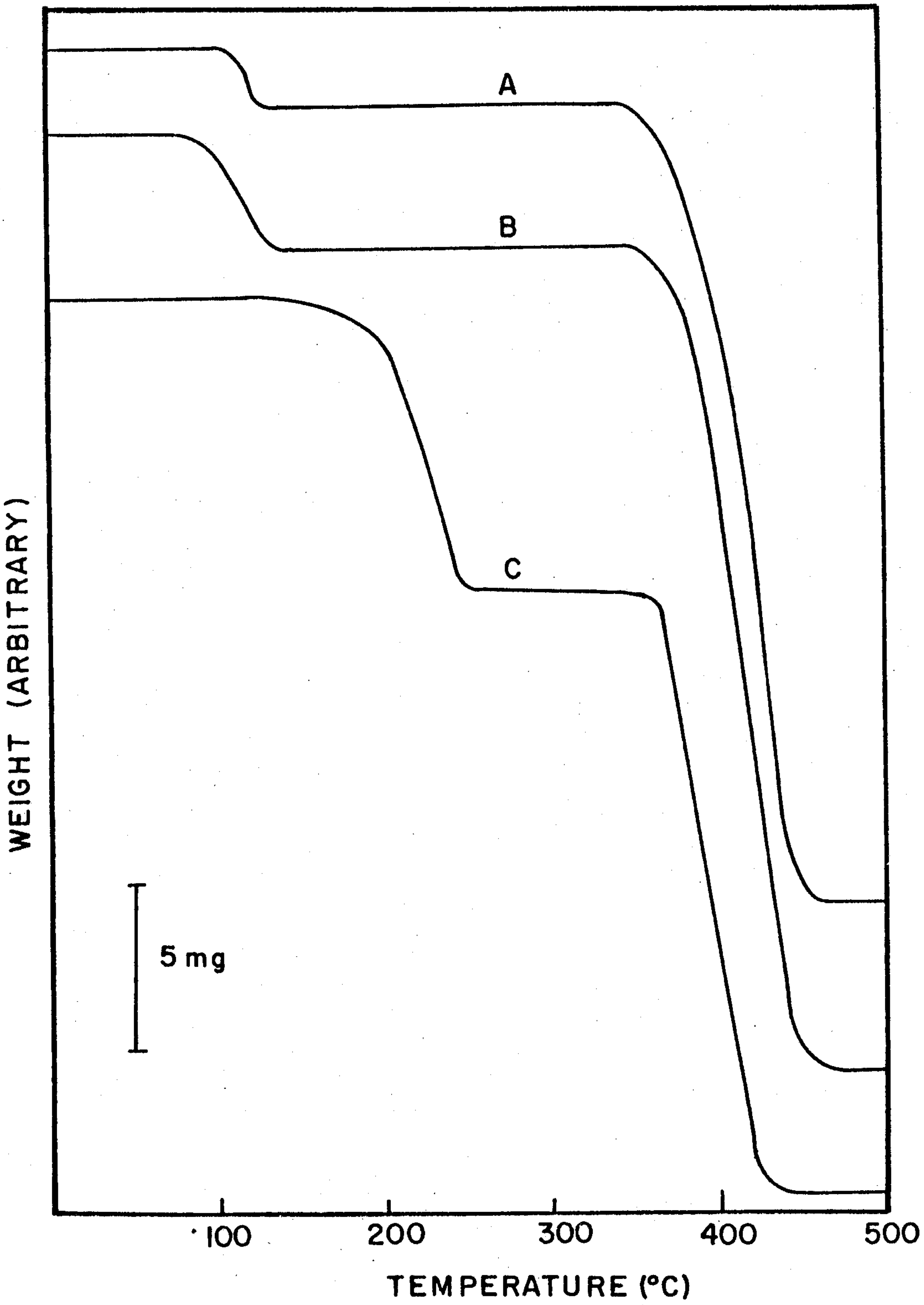

Figure I THERMOGRAMS OF U(VI) COMPLEXES OF TROPOLONE

A. $UO_2T_2.H_2O$ (initial weight 56.3 mg)
B. $UO_2T_2.CH_3OH$ (initial weight 58.7 mg)
C. $UO_2T_2.HT$ (initial weight 48.8 mg)

## TABLE II

## THERMOGRAVIMETRIC DATA FOR URANIUM (VI) TROPOLONATE COMPLEXES

| COMPOUND | SAMPLE WEIGHT (mg) | WEIGHT LOSS REGIONS | | | |
|---|---|---|---|---|---|
| | | Temp. Range (°C) | Reaction | Weight Loss (mgs) | % Weight Loss |
| $UO_2T_2 \cdot H_2O$ | 56.3 | 100 - 130 | $UO_2T_2 \cdot H_2O \rightarrow UO_2T_2$ | Calc.: 1.9<br>Found: 1.8 | Calc.: 3.4<br>Found: 3.2 |
| | | 350 - 475 | $UO_2T_2 \rightarrow U_3O_8$ | Calc.: 24.6<br>Found: 24.2 | Calc.: 45.2<br>Found: 44.4 |
| $UO_2T_2 \cdot CH_3OH$ | 58.7 | 70 - 140 | $UO_2T_2 \cdot CH_3OH \rightarrow UO_2T_2$ | Calc.: 3.5<br>Found: 3.5 | Calc.: 5.9<br>Found: 6.0 |
| | | 350 - 475 | $UO_2T_2 \rightarrow U_3O_8$ | Calc.: 24.9<br>Found: 24.8 | Calc.: 45.2<br>Found: 44.9 |
| $UO_2T_2 \cdot HT$ (prepared from aqueous medium) | 48.8 | 150 - 250 | $UO_2T_2 \cdot HT \rightarrow UO_2T_2$ | Calc.: 9.4<br>Found: 8.7 | Calc.: 19.2<br>Found: 17.8 |
| | | 350 - 475 | $UO_2T_2 \rightarrow U_3O_8$ | Calc.: 18.1<br>Found: 18.2 | Calc.: 45.2<br>Found: 45.4 |
| $UO_2T_2 \cdot HT$ (prepared from methanol medium) | 60.5 | 150 - 250 | $UO_2T_2 \cdot HT \rightarrow UO_2T_2$ | Calc.: 11.6<br>Found: 11.6 | Calc.: 19.2<br>Found: 19.2 |
| | | 350 - 450 | $UO_2T_2 \rightarrow U_3O_8$ | Calc.: 22.1<br>Found: 22.3 | Calc.: 45.2<br>Found: 45.6 |

The calculated weight loss of methanol, based on the stoichiometric formula $UO_2T_2.CH_3OH$, is identical to that found from thermogravimetric data (Table II). It is quite evident then, that the drying conditions used by Plymale and Smith (80°C, under vacuum) were sufficient to remove the solvent. The constant-weight level associated with the formation of $U_3O_8$ occurs above 475°C, just as for the $UO_2T_2.H_2O$ solvate.

The evidence presented in this thesis for the aquo and methanol solvates of $UO_2T_2$, together with the observations made by Plymale and Smith(41) that their $UO_2T_2$ compound is hygroscopic and soluble in strongly coordinating solvents such as dimethylsulfoxide and N,N'-dimethylformamide, shows the strong affinity of $UO_2T_2$ for polar unidentate ligands. It appears almost certain that the DMSO and DMF solvates, in addition to others, can be formed, especially in view of the fact that the DMSO(46) and DMF(49) solid solvate compounds have been isolated for tetrakis (tropolonato) thorium (IV).*

The affinity of $UO_2T_2$ for the polar unidentate solvent ligands is in common, as mentioned, with the nature of the bis $UO_2^{2+}$ chelates of the bidentate acetylacetone and 8-hydroxyquinoline ligands. This reflects the strong tendency of U(VI) to achieve molecular seven-coordination(65). For example, the x-ray molecular structure of $UO_2Q_2.HQ$(66) (where Q = the 8-hydroxyquinoline anion) shows that the additional HQ molecule is coordinated only as a unidentate ligand (through the donor oxygen of HQ), resulting in a 7-coordinated, distorted pentagonal bipyramid configuration about the central U atom. Based

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* Degetto et al(64) have recently reported the preparation of a series of adducts, $UO_2T_2.L$, where L = methanol, water, dimethylsulfoxide, pyridine N-oxide, triphenylphosphine oxide, cyclohexanone, pyridine, and aniline.

on this evidence, it is likely that in $UO_2T_2.CH_3OH$ and $UO_2T_2.H_2O$ (and in the corresponding complexes of acetylacetone and 8-hydroxyquinoline), the solvent molecule is coordinated to the central atom, rather than being merely lattice solvent or solvent of constitution. In fact, the molecular structure of the pyridine adduct, $UO_2T_2.py$(64), has recently been shown to have a 7-coordinated, slightly distorted pentagonal bipyramidal configuration about the central U atom.

In $UO_2Q_2$, it has been proposed that the central U atom achieves coordination seven through polymerization of the $UO_2Q_2$ units(42,67), although this has not been proven experimentally. In $UO_2T_2$, the same proposal has been made by Degetto et al(64), supported by physicochemical and infrared data. In particular, the presence of a weak sharp band at ca. 1575 $cm^{-1}$ has been diagnosed as a common feature of "polymeric" metal tropolonates in which chelate oxygen atoms are shared between metal atoms (11,63).

It is of interest that the bis chelate of 8-hydroxyquinoline, $UO_2Q_2$, cannot be prepared by direct precipitation from solution, (which yields only $UO_2Q_2.HQ$), but rather only by careful thermal treatment of $UO_2Q_2.HQ$(42). Indeed, solvates of the bis chelate, e.g., $UO_2Q_2.CH_3OH$, $UO_2Q_2.OC(CH_3)_2$ and $UO_2Q_2.CHCl_3$, have been prepared by treating the thermally-produced $UO_2Q_2$ with appropriate coordinating solvents(42). With tropolone and acetylacetone, the bis chelates can be prepared directly from solution but in solvated form. The unsolvated complex can then be made by suitable thermal treatment of the solvate. There is one report(38) in the literature of an unsolvated bis U(VI) compound with a bidentate ligand, i.e. α-picolinic acid.* It may well be that

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* This work has been confirmed in this laboratory

the compound precipitates directly as a polymer which is more stable than the solvated bis chelate. This could perhaps occur through intermolecular interaction of bis units with the carbonyl group of the carboxylic acid.

## IV.A.b. Composition of the tris uranium (VI) - tropolone complex.

So-called solid "adduct" chelates involving $UO_2^{2+}$ and several acidic bidentate ligands (H bidentate) have been reported. For example, uranium(VI) yields adducts with α-picolinic acid(38), tropolone(41), acetylacetone(37), and 8-hydroxyquinoline and its derivatives(68). These adducts have been assigned the general formula $UO_2(\text{bidentate})_2$.Hbidentate. This formula, as well as the term "adduct" itself, are inaccurate descriptions of the compounds,* because firstly, they imply that the compounds are formed by an addition reaction to the precipitated non-adduct chelate; secondly, they imply that the extra molecule may not be coordinated to the central ion; and thirdly, they suggest that if the extra molecule is coordinated, it remains essentially intact in that the proton is in the same location in the "adduct" ligand as in the free ligand. In fact, these adducts are prepared directly without having to make the solid bis complex first, followed by an addition reaction. Furthermore, the extra ligand is most probably coordinated (as in the analogous adducts of 8-hydroxyquinoline(66) and acetylacetone(69)), and the proton is not situated exactly as in the free ligand.

Plymale and Smith(41) first reported the preparation of the solid adduct $UO_2T_2$.HT from methanol medium. By use of the same medium

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*To comply with the terminology used in the current literature, the word "adduct" is used throughout this thesis.

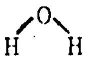
and slightly different conditions (EXPERIMENTAL, Section D.1.f.), the tris compound with improved analytical data was obtained in the present study. The hygroscopic behaviour of the tris chelate, as described by Plymale and Smith, was not evident. The tris chelate was also prepared from aqueous solution (EXPERIMENTAL AND RESULTS, Section D.1.e.), although the analytical data was not as satisfactory as for the tris chelate prepared from methanol medium.

A comparison of the i.r. spectra of the tris chelates prepared from both aqueous and methanol media showed them to be identical (Figure IV, APPENDIX). More significant is a comparison of the spectra of the tris and bis chelates. (Figures IIa, IIIa, IV, APPENDIX). The strong bands at 1613 $cm^{-1}$ (C=O stretch) and at 1548 $cm^{-1}$ (C=C stretch) found in the spectrum of solid tropolone(57) have now shifted to 1593 $cm^{-1}$ and 1517 $cm^{-1}$ respectively, on complexation, for both the bis and tris chelates(41,70). Plymale and Smith stated that the major difference in the spectra of the two chelates is the presence of C-O-H frequencies (the proton is still attached to the phenolic oxygen) in the $UO_2T_2$.HT spectrum, which occur at 1480 $cm^{-1}$ (sharp, weak intensity), 1283 $cm^{-1}$ (sharp, medium intensity), and 752 $cm^{-1}$ (shoulder, weak intensity). Surprisingly, no study had previously been made on the effect of complexation on the position of the O-H stretch absorption band located at 3208 $cm^{-1}$ in solid tropolone in which the proton is intermolecularly hydrogen-bonded(60). Such an investigation has been made in various $UO_2^{2+}$ tris chelates of 8-hydroxyquinoline and derivatives(42,71), and has provided insight on the manner in which the extra molecule is coordinated to the central metal ion. Also, the study provides a valid diagnostic test for the presence of the additional ligand. On complexation, the O-H stretching frequency of the additional HT ligand shifts from 3208 $cm^{-1}$ to ca. 3025 $cm^{-1}$ (Figure IV, APPENDIX). A shift to lower frequency (i.e., to about 3140 $cm^{-1}$) has also been found for tropolone in the solution and gaseous states, as compared to 3208 $cm^{-1}$ in the solid, and has been explained on the basis of the formation of a stable chelate system through intermolecular hydrogen-bonding of the type $-O---H---O = C<$. By contrast, the O-H stretching mode occurs at 3518 $cm^{-1}$ for solid tropolone in the absence of hydrogen-bonding(60). Although the shift to lower frequency may merely indicate the presence of hydrogen-bonded rather than coordinated tropolone, by analogy with the x-ray crystal structures of $UO_2.(acac)_2.H_2O$ (69), $UO_2.Q_2.HQ$(66) and, more significantly, $ThT_4.DMF$(49), the extra HT molecule in $UO_2T_2.HT$ is likely coordinated to the central U(VI) ion. The absence of the O-H stretching frequency in the bis chelate permits the use of this band as a diagnostic test for the presence of the extra HT molecule.

Thermogravimetric analysis of the $UO_2T_2.HT$ compound by Plymale and Smith(41) indicated the sudden loss of one molecule of tropolone on heating to 155°C, followed by decomposition to $U_3O_8$ at 400°C. The thermogravimetric curve for the adduct in the present work (Figure IC) shows that initial decomposition does indeed occur at 150°C, but the weight loss is gradual up to 250°C. The constant weight level associated with $UO_2T_2$ occurs in the 250-350°C range, followed by decomposition to $U_3O_8$. In comparing the thermogravimetric data for $UO_2T_2.HT$ prepared from both aqueous and methanol media (Table II), it appears that the tris chelate prepared from aqueous solution is slightly deficient in the additional molecule of tropolone. Analytical data (EXPERIMENTAL, Section D.1.e.) show that the %H is quite high and the %U is low, but the %C is in very good agreement. Based on thermogravimetric data, the formula of the tris compound prepared from aqueous medium can be written as $UO_2T_2.0.93$ HT, although the corresponding compound prepared from methanol appears to be stoichiometric and can be assigned the formula $UO_2T_2.HT$. It is noteworthy that the tris (8-hydroxyquinolinato) dioxouranium(VI) solid chelate prepared in aqueous solution has also been found to be slightly deficient in 8-hydroxyquinoline, and competition with other ligands such as water has been proposed(72).

### IV.A.c. Thermal reactions.

The thermal treatment of $UO_2T_2.CH_3OH$ and $UO_2T_2.HT$ under appropriate conditions (EXPERIMENTAL, Section D.2.b.) leads to $UO_2T_2$. The i.r. spectrum of the residue (Figure V, APPENDIX) shows the absence of absorption bands characteristic of the additional $CH_3OH$ and HT molecules. The i.r. spectra (not shown) of the products trapped in U-tube from thermal conversion of $UO_2T_2.CH_3OH$ and $UO_2T_2.HT$ were characteristic of $CH_3OH$ and HT,respectively. Analytical data show the conversion to $UO_2T_2$ to be essentially complete under the conditions described, and the product was non-hygroscopic.

Thermal conversion of $UO_2T_2.H_2O$, however, is incomplete under the conditions used. The absorption bands for O-H stretch and  bend are still apparent in the i.r. spectrum (not shown), but are reduced in intensity. A higher temperature and/or a longer heating period would likely have resulted in pure $UO_2T_2$.

### IV.A.d. Ligand addition reactions.

Previous addition reactions by others have involved the unsolvated $UO_2$(bidentate)$_2$ chelate. For example, the formation of the adduct $UO_2Q_2.HQ$ by reaction of $UO_2.Q_2$ with a solution of HQ has been noted(42). The tris chelate $UO_2Pic_2.HPic$ has also been prepared by ligand addition to the bis chelate in solution(38).

There have also been reports on the addition of foreign ligands to the $UO_2$(bidentate)$_2$ chelates to yield "mixed" ligand adducts. The compounds $UO_2Pic_2.HA$ (HA = 8-hydroxyquinoline, 2-methyl-8-hydroxyquinoline, and 8-hydroxyquinoline)(38) and $UO_2(acac)_2.X$ (acac = acetylacetone anion; X = acetophenone, dioxane, pyridine, ammonia and acetone)(55) are examples.

The heterogeneous reaction between $UO_2T_2.H_2O$ and tropolone ligand in aqueous solution to form $UO_2T_2.HT$ was described earlier (EXPERIMENTAL, Section D.3.a.). The O-H and C-O-H absorption bands characteristic of the additional tropolone molecule (RESULTS AND DISCUSSION, Section A.b.) were present in the i.r. spectrum of the product (not shown). The experimental conditions reported gave reasonably good yields for the addition reaction (Table III).

The water molecule in $UO_2T_2.H_2O$ can be displaced by 8-hydroxyquinoline also (EXPERIMENTAL, Section D.3.b.). The i.r. spectrum of the product (Figure VI, APPENDIX) exhibits a broad band of moderate intensity centered at about 2700 $cm^{-1}$, along with a very weak band at 2060 $cm^{-1}$. These frequencies correspond closely to the broad 2650 $cm^{-1}$ and weak 2050 $cm^{-1}$ bands in the spectra of tris uranyl chelates of 8-hydroxyquinoline and derivatives(71), and are indicative of the hydrogen-bonded $^+N-H---O$ system. Based on this evidence, and the corraborating x-ray structure of $UO_2Q_2.HQ$(66), it seems very likely that the HQ molecule in $UO_2T_2.HQ$ is coordinated to the central uranium atom through the phenolate oxygen only.

The experimental yield of the $UO_2T_2.HQ$ adduct (Table III) is quite high (ca. 90%), and shows the possibility of being quantitative

## TABLE III

## CALCULATED AND EXPERIMENTAL YIELDS OF ADDUCT CHELATES FORMED BY INTERACTION OF SELECTED LIGANDS WITH $UO_2T_2.H_2O$

| LIGAND | INITIAL WEIGHT OF $UO_2T_2.H_2O$ TAKEN (mg) | EXPECTED PRODUCT | YIELD (mg)* | |
|---|---|---|---|---|
| | | | Calculated | Found |
| TROPOLONE (HT) | 107.14 | $UO_2T_2.HT$ | 131.81 | 126.44<br>(78.2%) |
| 8-HYDROXYQUINOLINE (HQ) | 106.20 | $UO_2T_2.HQ$ | 135.27 | 132.15<br>(89.3%) |
| α-PICOLINIC ACID (HPic) | 106.75 | $UO_2T_2.HPic$ | 132.40 | 104.44<br>(-) |

* Weight loss due to solubility of $UO_2T_2.H_2O$ and the adduct chelate in the solvent medium, and weight gains due to the possibility of coprecipitated reagent, were not accounted for in the above calculations. The % yield was calculated as follows: $\frac{126.44-107.14}{131.81-107.14} \times 100\% = 78.2\%$.

under refined experimental conditions.

It appears that the HPic did not displace the water in $UO_2T_2.H_2O$ (Table III). In fact, the data clearly indicate weight loss of the starting bis chelate due to solubility in the aqueous medium. In the i.r. spectrum (not shown), no $\overset{+}{N}$-H---O bands were present to indicate complexation. Such bands have been found to occur in the spectrum of the $UO_2Pic_2$.HPic adduct*, and have definite diagnostic value for the extra HPic molecule.

## IV.B. Thorium (IV) Tropolonate Complexes

### IV.B.a. Composition of the tetrakis thorium (IV)-tropolone complex.

The reports of Muetterties⁽⁴⁶⁾ and Selbin and Ortego⁽⁴⁷⁾ have failed to mention the presence of coordinated solvents in $ThT_4$, even though nine-coordinate $ThT_4$.DMSO⁽⁴⁶⁾ and $ThT_4$.DMF⁽⁴⁹⁾ solid solvates have been reported (HISTORICAL INTRODUCTION, Section B). In this thesis the preparation of the tetrakis chelate from a 50% aqueous methanol medium (EXPERIMENTAL, Section E.1.c.), and from aqueous medium (EXPERIMENTAL, Section E.1.a.), resulted in the methanol and aquo solvates,respectively.

Muetterties did not report analytical data in his preparation of $ThT_4$ from aqueous methanol, but the data reported by Selbin and Ortego showed the %C and %H to be high for the assigned formula $ThT_4$, suggesting the presence of coordinated or lattice methanol. Metal-ion analyses were not reported. Drying conditions for $ThT_4$, as reported by Muetterties (80°C and atmospheric pressure for 4 hours) differed from those described in this thesis (50°C and 6-7 mm Hg for 14 hours), but otherwise the procedures were essentially identical. Analytical data

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* Unpublished work, this laboratory.

for the methanol and aquo solvates (Table IV) show that the best agreement is with the formulae $ThT_4.CH_3OH$ and $ThT_4.H_2O$.

I.r. spectra for $ThT_4.H_2O$ (Figure VIIa, APPENDIX) and $ThT_4.CH_3OH$ (Figure VIIIa, APPENDIX) show the presence of the solvent molecules. In the $ThT_4.H_2O$ spectrum, the O-H stretch band (broad, weak intensity) at about 3375 $cm^{-1}$ and the $H\overset{O}{\wedge}H$ bending mode (broad shoulder, very weak) at about 1600 $cm^{-1}$ are indicative of lattice or coordinated water$^{(56)}$. The spectrum of $ThT_4.D_2O$ (Figure VIIb, APPENDIX) shows a shift of the antisymmetric and symmetric stretch bands to 2400 $cm^{-1}$($^{\nu}H/\nu_D = 1.40$) and to 2300 $cm^{-1}$ ($^{\nu}H/\nu_D = 1.47$). Two peaks associated with the $D\overset{O}{\wedge}D$ bending mode are located at 1315 $cm^{-1}$ (sharp, weak intensity, $^{\nu}H/\nu_D = 1.26$) and at 1270 $cm^{-1}$ (sharp, medium intensity, $^{\nu}H/\nu_D = 1.31$). Of significance is the broad shoulder band at 753 $cm^{-1}$ in the $ThT_4.H_2O$ spectrum, which is absent in the spectra of $ThT_4.D_2O$ and $ThT_4.HT$ (Figure IX, APPENDIX). This band arises from wagging, twisting and rocking modes in the water molecule activated by coordination to the metal-ion$^{(58,59)}$, and is also found in the $UO_2T_2.H_2O$ spectrum (Figure IIa, APPENDIX).

In the spectrum of $ThT_4.CH_3OH$ (Figure VIIa, APPENDIX), methanol bands corresponding to $\nu_{O-H}$ (broad, moderate intensity) at 3100 $cm^{-1}$, $\nu_{C-H}$ (medium broad, weak intensity) at 2800 $cm^{-1}$, and $\nu_{C-O}$ (sharp, moderate intensity) at 1030 $cm^{-1}$ are evident. These bands are shifted to lower frequency than those in free methanol$^{(61,63)}$. The methanol in $ThT_4 . CH_3OH$ is thus likely a coordinated or lattice component. In the spectrum of $ThT_4 . CH_3OD$ (Figure VIIb, APPENDIX), the $\nu_{O-D}$ band (broad, weak intensity) at 2300 $cm^{-1}$ ($^{\nu}H/\nu_D = 1.35$) and the disappearance of the $\nu_{O-H}$ band at 3100 $cm^{-1}$ further verify the presence of methanol in the

## TABLE IV

## ANALYTICAL DATA FOR POSSIBLE SOLVATES OF TETRAKIS (TROPOLONATO) THORIUM (IV)

a. PRECIPITATION FROM AQUEOUS MEDIUM

| COMPOUND | C(%) | H(%) | Th(%) |
|---|---|---|---|
| $ThT_4$ | 46.94 | 2.81 | 32.39 |
| $ThT_4.H_2O$ | 45.79 | 3.02 | 31.59 |
| $ThT_4.2H_2O$ | 44.69 | 3.22 | 30.84 |
| FOUND | 45.84 | 2.99 | 31.96 |

b. PRECIPITATION FROM 50% AQUEOUS METHANOL MEDIUM

| COMPOUND | C(%) | H(%) | Th(%) |
|---|---|---|---|
| $ThT_4.CH_3OH$ | 46.41 | 3.22 | 30.92 |
| $ThT_4.2CH_3OH$ | 46.16 | 3.62 | 29.73 |
| FOUND | 45.90 | 3.23 | 31.20 |

bis chelate. The $\nu_{C-H}$ band appears at 2825 $cm^{-1}$ (very weak) in the $ThT_4.D_2O$ spectrum, a negligible shift from its position in the aquo solvate.

Although there is no i.r. evidence to distinguish between coordinated and lattice methanol in the $ThT_4.CH_3OH$ chelate, it is quite likely that the solvent molecule is coordinated since an x-ray crystal structure determination of $ThT_4$.DMF and $ThB_4.H_2O$ (B = γ-isopropyltropolone anion) have shown the DMF and $H_2O$ molecules to be coordinated to the central $Th^{4+}$ ion (although not as strongly as the tropolonate oxygen donor atoms)(49). In $ThT_4.CH_3OH$ and $ThT_4.H_2O$, the donor atoms are probably arranged in a monocapped square-antiprismatic coordination polyhedron, just as observed in the $ThT_4$.DMF and $ThB_4.H_2O$ molecules. This coordination polyhedron has also been shown by an x-ray study to apply to $ThQ_4$.2DMSO in which only one DMSO molecule is coordinated(73).

Thermogravimetric analysis of $ThT_4.H_2O$ and $ThT_4.CH_3OH$ (Figures IIA, IIB) shows initial loss of solvent at the same temperature (75°C). The weight loss is complete at 125°C for the $H_2O$ solvate and at 175°C for the $CH_3OH$ solvate, to give $ThT_4$. Decomposition to $ThO_2$ occurs at about 500°C. Thermogravimetric data for loss of solvent in both solvate chelates are shown in Table V.

### IV.B.b. Composition of the pentakis thorium (IV)-tropolone complex.

The bright yellow pentakis chelate $ThT_4$.HT, prepared from aqueous solution (EXPERIMENTAL, Section E.1.e.), is a further example of similarities in Th(IV) and U(VI) tropolonate chemistry. Analytical data presented for this chelate (EXPERIMENTAL, Section E.1.e.) are in excellent agreement with the composition $ThT_4$.HT, and are more satisfactory than for the $UO_2T_2$.HT complex (RESULTS AND DISCUSSION,Section A.b.). There

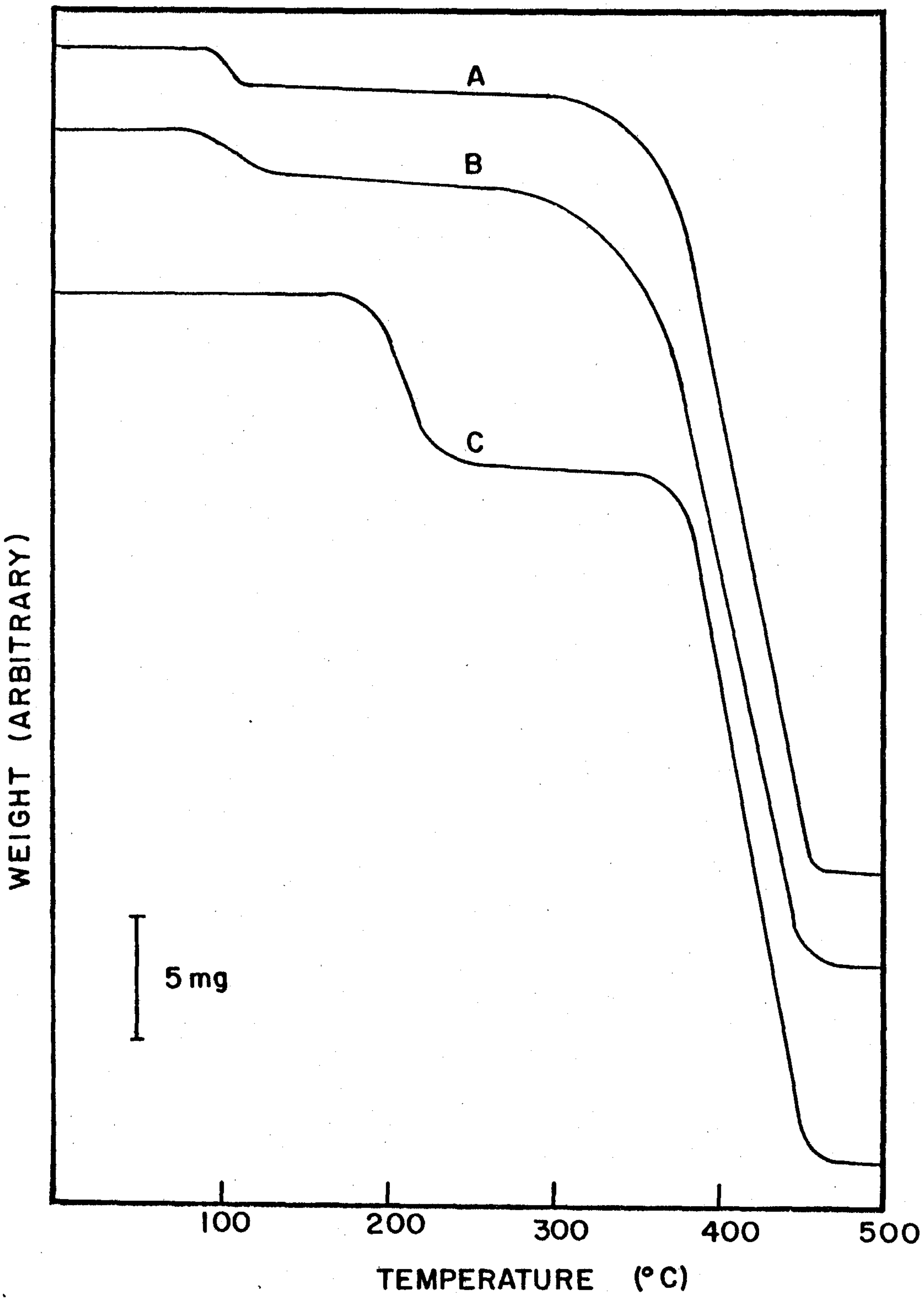

Figure II THERMOGRAMS OF Th(IV) COMPLEXES OF TROPOLONE

A. $ThT_4.H_2O$ (initial weight 52.0 mg)
B. $ThT_4.CH_3OH$ (initial weight 52.4 mg)
C. $ThT_4.HT$ (initial weight 52.0 mg)

## TABLE V

## THERMOGRAVIMETRIC DATA FOR THORIUM (IV) TROPOLONATE COMPLEXES

| COMPOUND | SAMPLE WEIGHT | WEIGHT LOSS REGIONS | | | |
|---|---|---|---|---|---|
| | (mg) | Temp. Range (°C) | Reaction | Weight Loss (mgs) | % Weight Loss |
| $ThT_4 \cdot H_2O$ | 52.0 | 75 - 125 | $ThT_4 \cdot H_2O \rightarrow ThT_4$ | Calc.: 1.3<br>Found: 1.5 | Calc.: 2.5<br>Found: 2.9 |
| | | 275 - 475 | $ThT_4 \rightarrow ThO_2$ | Calc.: 31.9<br>Found: 31.8 | Calc.: 63.2<br>Found: 63.0 |
| $ThT_4 \cdot CH_3OH$ | 52.4 | 75 - 175 | $ThT_4 \cdot CH_3OH \rightarrow ThT_4$ | Calc.: 2.2<br>Found: 2.3 | Calc.: 4.3<br>Found: 4.4 |
| | | 300 - 500 | $ThT_4 \rightarrow ThO_2$ | Calc.: 31.6<br>Found: 31.4 | Calc.: 63.2<br>Found: 62.7 |
| $ThT_4 \cdot HT$ | 52.0 | 150 - 250 | $ThT_4 \cdot HT \rightarrow ThT_4$ | Calc.: 7.6<br>Found: 6.9 | Calc.: 14.6<br>Found: 13.3 |
| | | 300 - 500 | $ThT_4 \rightarrow ThO_2$ | Calc.: 28.5<br>Found: 28.2 | Calc.: 63.2<br>Found: 62.5 |

is no indication that the chelate is deficient in adduct ligand, as has been found in the compound $ThQ_4.HQ$(74).

As in the i.r. spectrum of $UO_2T_2.HT$ (Figure IV, APPENDIX), the spectrum of $ThT_4.HT$ (Figure IX, APPENDIX) definitely shows the presence of the phenolic proton in the additional tropolone molecule. Bands at 1487 $cm^{-1}$ (sharp, shoulder, low intensity), and at 1275 $cm^{-1}$ (sharp, high intensity), have been found to originate in the C-O-H group(41,57). Although definite assignments of these bands are uncertain, the former band closely corresponds to the O-H deformation vibrations in enolized β-diketones(75). The broad band of medium intensity centered at 730 $cm^{-1}$ is a combination band assigned to C-C stretching, C-H out-of-plane deformation and O-H out-of-plane deformation modes(57). The broad band centered at about 3000 $cm^{-1}$, also found for $UO_2T_2.HT$ (RESULTS AND DISCUSSION, Section A.b.), corresponds to hydrogen-bonded $\nu_{O-H}$. This band overlaps with the very weak bands at 2950 $cm^{-1}$ and 2800 $cm^{-1}$ which correspond to tropolone C-H stretch(60).

Based on the x-ray structures for several other nona-coordinate thorium(IV) chelates(49,73), it would indeed be surprising if the adduct molecule in $ThT_4.HT$ were not coordinated.

The thermogravimetric curve for $ThT_4.HT$ (Figure IIC) shows the loss of the HT molecule over the range 150 - 250°C, as for the $UO_2T_2.HT$ chelate. By contrast, the analogous 8-hydroxyquinoline chelate, $UO_2Q_2.HQ$, was found to be more thermally stable than $ThQ_4.HQ$(76). Thermogravimetric data for loss of HT from $ThT_4.HT$ (Table V) indicates a deficiency of the adduct ligand, but this is unsupported, however, by the analytical data discussed earlier.

### IV.B.c. Thermal reactions.

Thermal conversion of the solvates $ThT_4.H_2O$ and $ThT_4.CH_3OH$ at temperatures ascertained from thermogravimetric data, showed trends similar to those for the corresponding U(VI) solvates. Although analytical data were not obtained for the residues from thermal conversion, the products were characterized by i.r. (not shown). Both spectra showed residual intensities of solvent (RESULTS AND DISCUSSION, Section B.a.), indicating incomplete conversion under the conditions studied. It should be possible to obtain pure $ThT_4$ under appropriate thermal conditions. The i.r. spectra (not shown) of the trapped solvents identified them as water and methanol.

Analytical data for the thermal conversion of the bright yellow $ThT_4.HT$ to the pale yellow $ThT_4$ (EXPERIMENTAL, Section E.2.b.) are satisfactory. The spectrum of the residue (Figure X, APPENDIX) shows the disappearance of the O-H and C-O-H bands ascribed earlier to the bound HT (RESULTS AND DISCUSSION, Section B.b.), but the presence of bands at 3350 $cm^{-1}$ (broad, low intensity) and at about 1660 $cm^{-1}$ (broad, shoulder, very low intensity) correspond to the O-H stretching and $H\overset{O}{\diagup\,\diagdown}H$ bending modes of coordinated or lattice water (RESULTS AND DISCUSSION, Section B.a.). The $ThT_4$ has apparently picked up water. The hygroscopic nature of $ThT_4$ is not unusual in view of the tendency of the Th(IV) in tetrakis chelates to attain nona-coordination.

### IV.B.d. Ligand addition reactions.

The ability of ligands to displace the water molecule in $ThT_4.H_2O$ has been confirmed in the present work only for the addition of HT to form $ThT_4.HT$ (EXPERIMENTAL, Section E.3.a.). The i.r. spectrum of the product (not shown) was identical to that for $ThT_4.HT$ (Figure IX, APPENDIX). Under the reported conditions, the foreign ligands HQ

(EXPERIMENTAL, Section E.3.b.) and HPic (EXPERIMENTAL, Section E.3.c.) did not undergo addition. In fact, the only report of addition to Th(bidentate)$_4$ chelates is that of HQ to ThQ$_4$, for which the mechanism of ligand addition was investigated by [$^{14}$C]-HQ tracer techniques(76).

## IV.C. Scandium (III) Tropolonate Complexes

### IV.C.a. Composition of the tris scandium (III)-tropolone complex.

Attempts by Muetterties and Wright(11) to prepare ScT$_3$ by the concentration of a hot chloroform-methanol solution of the tetrakis chelate ScT$_3$.HT yielded a product for which the analytical data (Table VI) were poor. The low %Sc and %C values, and high %H value suggest the formula ScT$_3$.X where X is an organic moiety with a C:H ratio less than that found in tropolone. In view of the solvent used, it is possible that X is methanol or chloroform, or perhaps both. A comparison of the analytical data obtained by Muetterties and Wright for ScT$_3$ with expected values for ScT$_3$ and ScT$_3$.xCH$_3$OH shows the data best fit the formula ScT$_3$.0.5CH$_3$OH (Table VI). It is possible that the composition was ScT$_3$.CH$_3$OH, but that the stringent drying conditions reported by these authors ("vacuum-dried at 80°C") resulted in partial loss of CH$_3$OH. The tris chelate prepared from aqueous medium as described in this thesis (EXPERIMENTAL, Section F.1.b.) yielded analytical data in satisfactory agreement with the formula ScT$_3$ (Table VI).

The procedure of Muetterties and Wright was repeated in this work (EXPERIMENTAL, Section F.1.a.). The i.r. spectrum of the compound (Figure XIa, APPENDIX) exhibited bands corresponding to methanol C-H stretch at 2700 cm$^{-1}$ (low intensity) and C-O stretch at 1020 cm$^{-1}$ (sharp, medium intensity), indicating the presence of coordinated or lattice methanol. These bands are slightly shifted to lower wavenumbers

# TABLE VI

## ANALYTICAL DATA FOR POSSIBLE SOLVATES OF TRIS (TROPOLONATO) SCANDIUM (III)

| COMPOUND | C(%) | H(%) | Sc(%) |
|---|---|---|---|
| $ScT_3$ | 61.78 | 3.70 | 11.01 |
| $ScT_3.0.5CH_3OH$ | 60.86 | 4.04 | 10.60 |
| $ScT_3.CH_3OH$ | 60.01 | 4.35 | 10.21 |
| FOUND | 60.6 * | 3.98 * | 10.5 * |
|  | 60.45** | 3.66** | 10.46** |

* By Muetterties and Wright

** This work

compared to corresponding bands in the spectrum of $UO_2T_2.CH_3OH$ (Figure IIIa, APPENDIX) and $ThT_4.CH_3OH$ (Figure VIIa, APPENDIX), implying perhaps that the $CH_3OH$ molecule is bound more strongly in the Sc(III) compound than in the U(VI) and Th(IV) compounds. Coordination of the $CH_3OH$ to Sc(III) implies hepta-coordination around the scandium. Hepta-coordination has been suggested previously(77) for the complexes $ScQ_3.HQ$ (HQ = 2-methyl and 4-methyl-8-hydroxyquinoline) but has not been demonstrated in any Sc(III) complex to date. (There are several examples of hexa and a few of octa-coordination(78).)

An interesting feature of the methanol solvate i.r. spectrum is the absence of the broad band at ca. 3100 $cm^{-1}$ corresponding to the methanol $\nu_{O-H}$. This observation suggests that the proton is involved in very strong hydrogen bonding, as in bis (dimethylglyoximato) nickel(II)(79).

Anderson et al. have reported the preparation of a mixture of the $HScT_4$ and $ScT_3$ solid chelates from primarily an aqueous medium, but no analytical data were given. In the present study, the tris chelate was prepared from 75% $H_2O$ - $CH_3OH$ medium (EXPERIMENTAL, Section F.1.b.), and shown to be unsolvated, as discussed above. The absence of methanol or water in the chelate is substantiated by i.r. evidence (Figure XIb, APPENDIX).

The thermogram for $ScT_3$ (Figure III) shows only one weight loss region (occurring in the 300-550°C range), corresponding to decomposition to the oxide. There is no evidence of ligand deficiency in $ScT_3$, at least as based on theoretical and experimental weight losses (Table VII). Thermal dehydration of $ScQ_3.H_2O$, by comparison, resulted in a slightly sub-stoichiometric $ScQ_3$ compound(77).

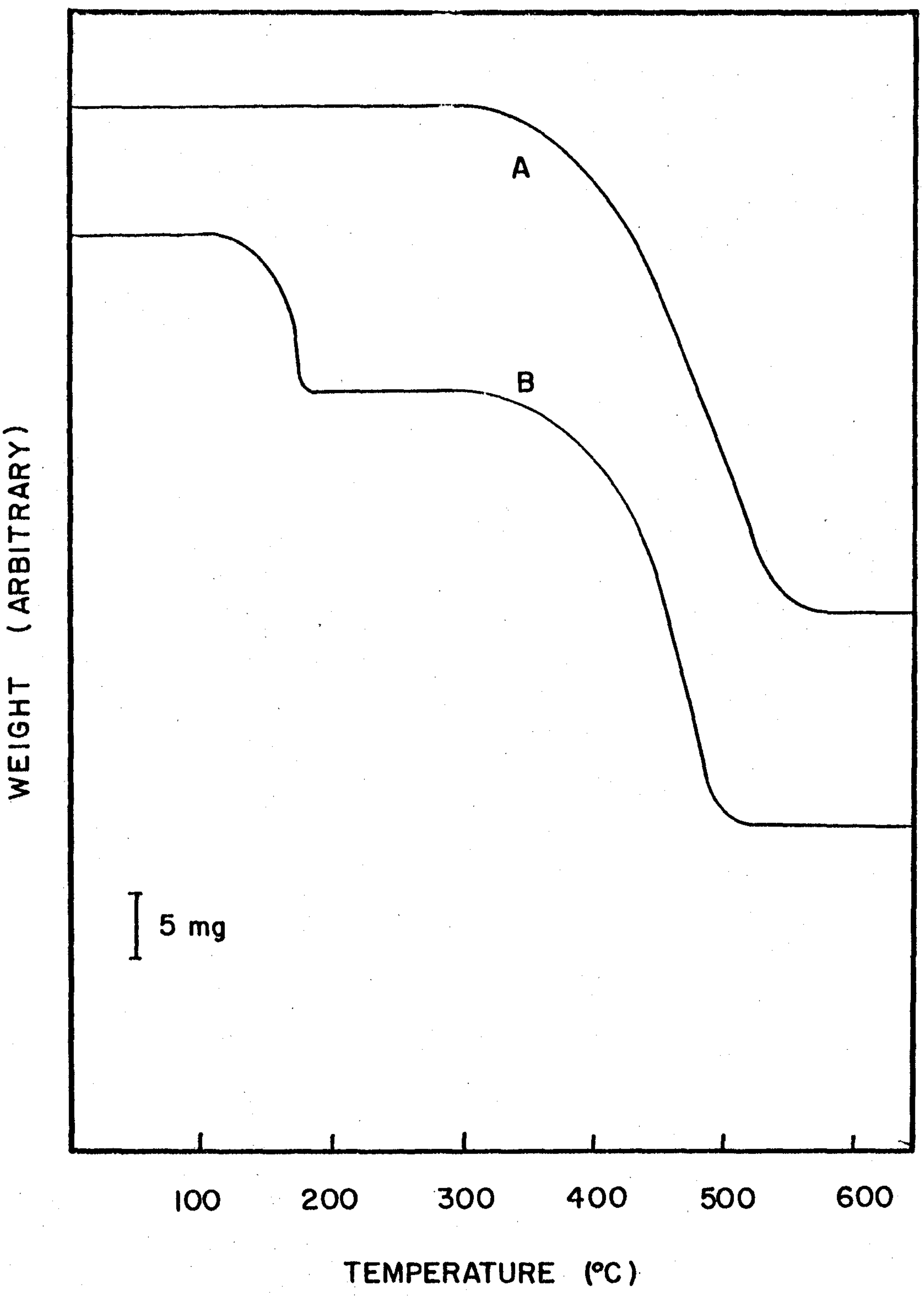

Figure III THERMOGRAMS OF Sc (III) COMPLEXES OF TROPOLONE

A. $ScT_3$ (initial weight 46.6 mg)

B. $ScT_3$.HT (initial weight 52.3 mg)

# TABLE VII

## THERMOGRAVIMETRIC DATA FOR SCANDIUM (III) TROPOLONATE COMPLEXES

| COMPOUND | SAMPLE WEIGHT (mg) | WEIGHT LOSS REGIONS | | | |
|---|---|---|---|---|---|
| | | Temp. Range (°C) | Reaction | Weight Loss (mgs) | % Weight Loss |
| $ScT_3$ | 46.6 | 300 - 550 | $ScT_3 \rightarrow Sc_2O_3$ | Calc.: 38.7<br>Found: 39.2 | Calc.: 83.1<br>Found: 84.1 |
| $ScT_3.HT$ | 52.3 | 125 - 175 | $ScT_3.HT \rightarrow ScT_3$ | Calc.: 12.0<br>Found: 11.8 | Calc.: 23.0<br>Found: 22.6 |
| | | 300 - 525 | $ScT_3 \rightarrow Sc_2O_3$ | Calc.: 33.7<br>Found: 33.7 | Calc.: 83.1<br>Found: 83.2 |

## IV.C.b. Composition of the tetrakis scandium (III)-tropolone chelate.

Muetterties and Wright(11) first synthesized $ScT_3.HT$, and because they were able to prepare the sodium salt, they formulated the compound as $H[ScT_4]$ and the salt as $NaScT_4$, implying the existence of the anion $ScT_4^-$ in which all tropolone ligands are bidentate. Their analytical data for $NaScT_4$ are in excellent agreement with the calculated, but no data was given for the compound $H[ScT_4]$. In the present work, the analytical data presented for the tetrakis chelate precipitated directly from aqueous methanol (EXPERIMENTAL, Section F.1.c.) are in excellent agreement with the formula $ScT_3.HT$.

The i.r. spectrum of $ScT_3.HT$ (Figure XII, APPENDIX) shows the absence of the C-O-H absorption bands characteristic of the additional HT molecule, and which are evident in the $UO_2T_2.HT$ and $ThT_4.HT$ spectra (RESULTS AND DISCUSSION, Sections A.b. and B.b.), suggesting that the proton is strongly hydrogen-bonded. I.r. stretching frequency dependence on intramolecular atomic distances have been reviewed(80), and for a tropolone O---O donor atom separation of 2.48 Å, an O-H stretching frequency of 1975 $cm^{-1}$ is predicted. A very small, broad band appears at this frequency in the $ScT_3.HT$ spectrum, and has been reported by others(81) as well.

Recent x-ray crystal structure determinations of $H[ScT_4]$(81,82) have shown the compound to exist as a hydrogen-bonded dimer with each scandium coordinated to the eight tropolone oxygen atoms arranged in a dodecahedron environment. The two dodecahedra are held together by almost linear O-H---O hydrogen bonds, in which the O-H and O---H bond distances are 1.03 and 1.43 Å, respectively. Hydrogen-bonding to this extent may account for the differences between the i.r. spectrum of

H[$ScT_4$] and the spectra of $UO_2T_2$.HT and $ThT_4$.HT (where the $\nu_{O-H}$ frequency occurred at ca. 3000 $cm^{-1}$). X-ray molecular structure determinations of the U(VI) and Th(IV) adducts would be expected to reveal a lesser degree of hydrogen-bonding than for H[$ScT_4$].

The thermogram for H[$ScT_4$] (Figure IIIb) shows loss of HT in the range 125-175°C, significantly lower than the 150-250°C range for $UO_2T_2$.HT and $ThT_4$.HT. Subsequent decomposition of $ScT_3$ to the oxide occurs in the range 300-525°C. Thermogravimetric data (Table VII) show excellent agreement with the calculated weight losses.

### IV.C.c. Thermal reactions.

On the basis of the i.r. spectrum of the residual product (Figure XIII, APPENDIX), it was found that $ScT_3$ is obtainable by thermal treatment of $ScT_3$.HT under conditions described earlier (EXPERIMENTAL, Section F.2.b.). The spectrum is identical with that of $ScT_3$ (Figure XIa, APPENDIX) and the very small, broad band at 1975 $cm^{-1}$ assigned to $\nu_{O-H}$ in the $ScT_3$.HT spectrum is absent.

### IV.C.d. Ligand addition reactions.

Of the bidentate ligands used for addition reactions to $ScT_3$ (EXPERIMENTAL, Section F.3.), only HT underwent addition. The i.r. spectrum of the product (not shown) was identical to that of $ScT_3$.HT (Figure XII, APPENDIX). No further characterization of the product was made.

## IV.D. Suggestions for Further Work

(i) The composition of reported U(VI), Th(IV) and Sc(III) complexes of tropolone derivatives should be re-examined for the presence of bound solvent. Also, the ability of these derivatives to form adducts should be studied to determine possible steric effects.

(ii) The structure of the various U(VI) and Th(IV) complexes reported in this work should be examined by three-dimensional x-ray analysis.

(iii) The addition of bidentate ligands to the thermal products $UO_2T_2$ and $ThT_4$ reported in this thesis would be of interest.

(iv) Attempts should be made to prepare other solvates by reacting the thermal conversion products $UO_2T_2$, $ThT_4$ and $ScT_3$ with solvents of varying polarity.

(v) The techniques described in this work should be extended to the tropolone adducts of other metal-ions (e.g., protactinium (V) and plutonium (VI)) reported in the literature.

(vi) The stability constants of the U(VI) and Sc(III) chelates reported in this thesis have yet to be determined.

# CHAPTER V

## SUMMARY

(i) The "solvate" chelates $UO_2T_2.CH_3OH$, $ThT_4.CH_3OH$ and $ScT_3.0.5CH_3OH$, and not $UO_2T_2$, $ThT_4$ and $ScT_3$, were obtained by previously-reported procedures. The compositions were determined by elemental, infrared and thermogravimetric analyses.

(ii) The aquo solvates of U(VI) and Th(IV) tropolonates have been prepared and shown to have the formulae $UO_2T_2.H_2O$ and $ThT_4.H_2O$, respectively.

(iii) The unsolvated $ScT_3$ chelate has been prepared and characterized.

(iv) The previously-reported adduct chelates $UO_2T_2.HT$ and $ScT_3.HT$ have been prepared by new procedures. In addition, the new adduct $ThT_4.HT$ has been reported in this thesis.

(v) Infrared evidence indicates that the acidic proton of the additional tropolone ligand in the above-mentioned adducts is hydrogen-bonded. The hydrogen-bonding appears to be stronger for the Sc(III) adduct than for the Th(IV) and U(VI) adducts.

(vi) Thermal conditions for obtaining the chelates $UO_2T_2$ and $ThT_4$ from either the solvate or adduct chelates of U(VI) and Th(IV) tropolonates have been reported. Similarly, the thermal conversion of $ScT_3.HT$ to $ScT_3$ has been described.

(vii) Attempts to displace the water molecule in the $UO_2T_2.H_2O$ and $ThT_4.H_2O$ solvates with selected bidentate ligands have been outlined. Also, attempts to add these ligands to $ScT_3$ have been described. All three metal tropolonates are readily converted to their corresponding tropolone adducts but the only case of addition of a foreign bidentate ligand is that of 8-hydroxyquinoline to the U(VI) tropolonate to yield $UO_2T_2.HQ$.

# VI. APPENDIX

## INFRARED SPECTRA OF URANIUM (VI), THORIUM (IV) AND SCANDIUM (III) COMPLEXES OF TROPOLONE

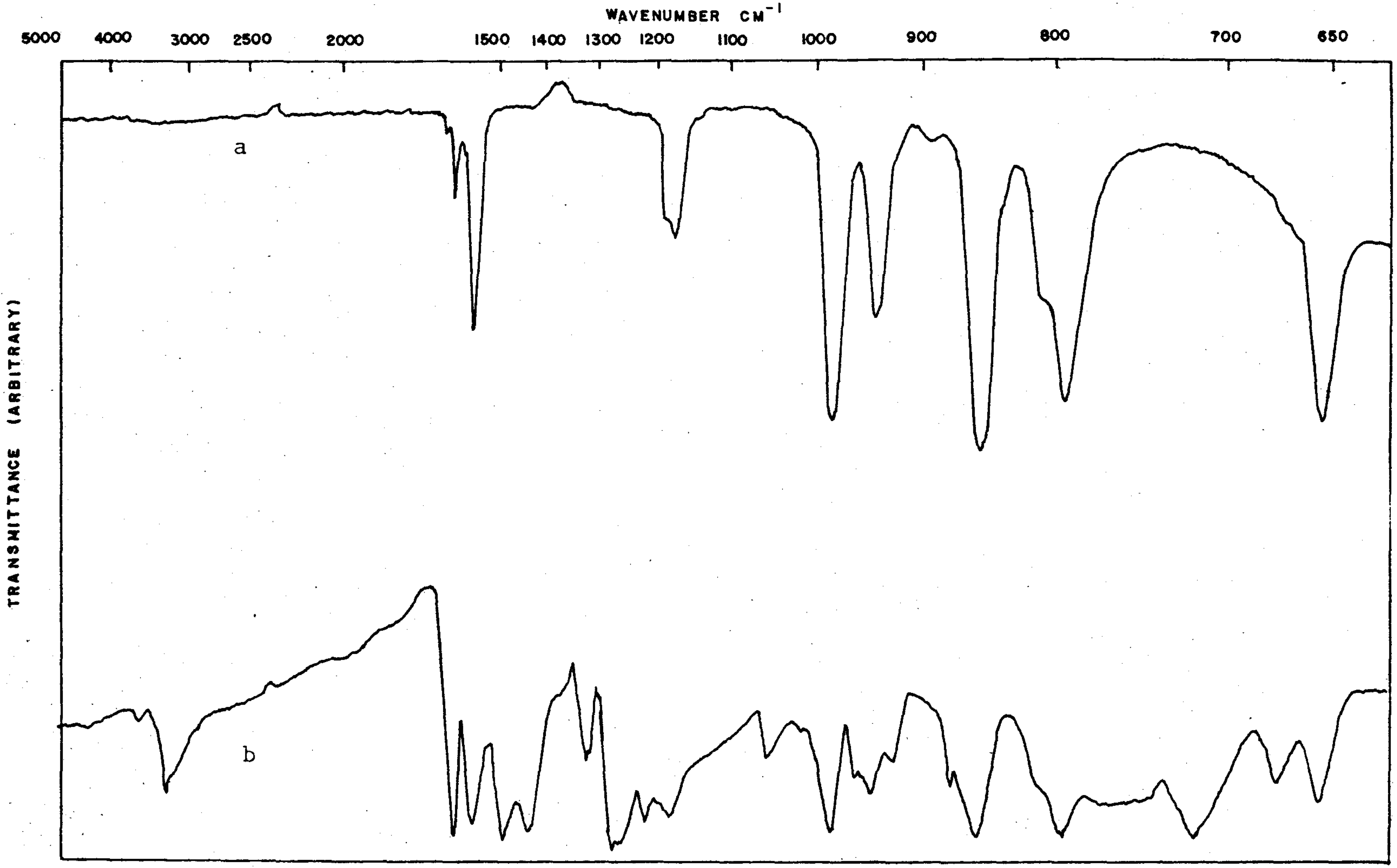

Figure I Infrared Spectra of Hexachloro-1,3-Butadiene and Tropolone

a. Hexachloro-1,3-Butadiene

b. Tropolone

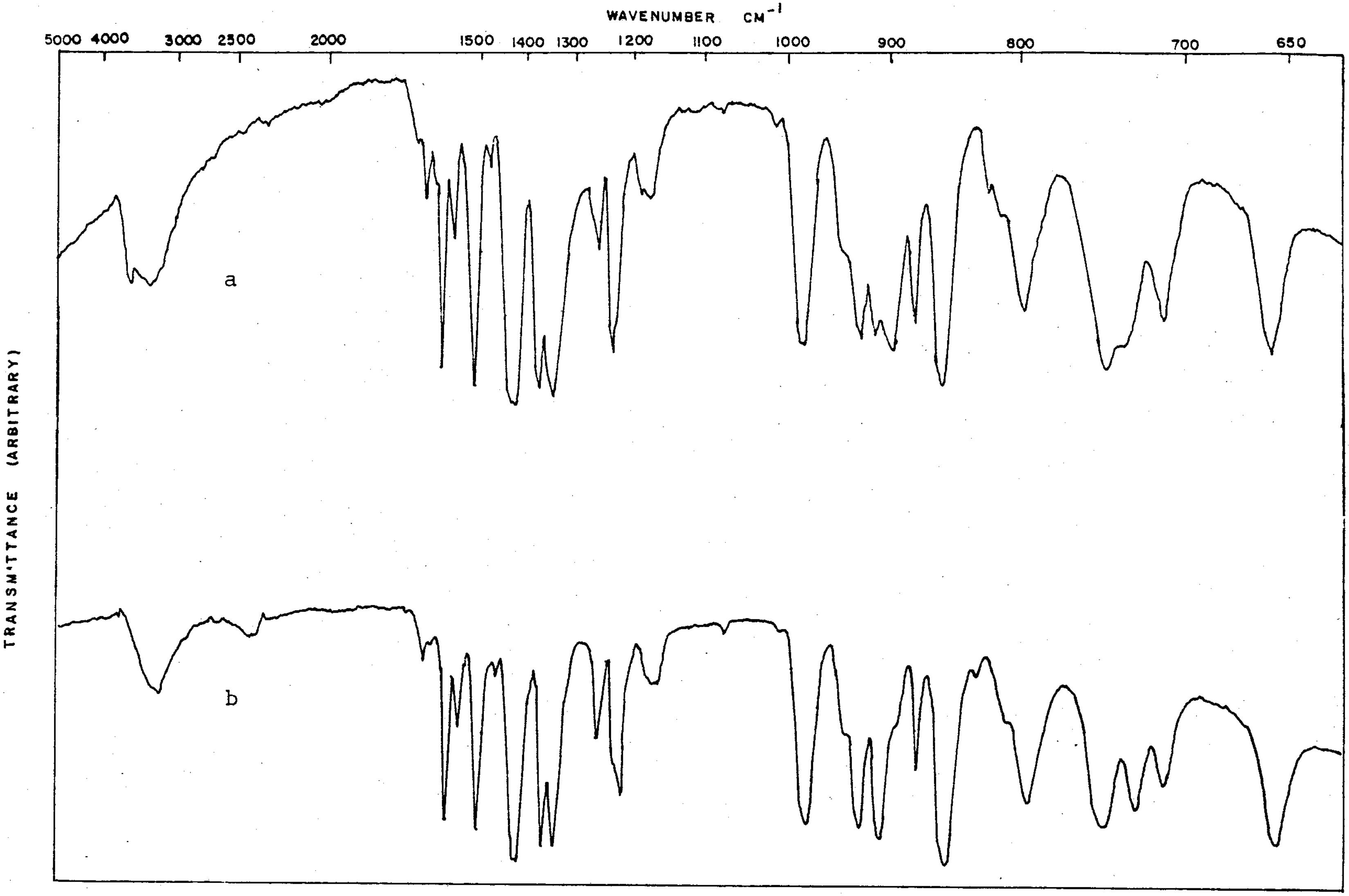

Figure II Infrared Spectra of Bis (Tropolonato) Dioxouranium (VI) Precipitated from Aqueous and $D_2O$ Media

a. $UO_2T_2.H_2O$

b. $UO_2T_2.D_2O$

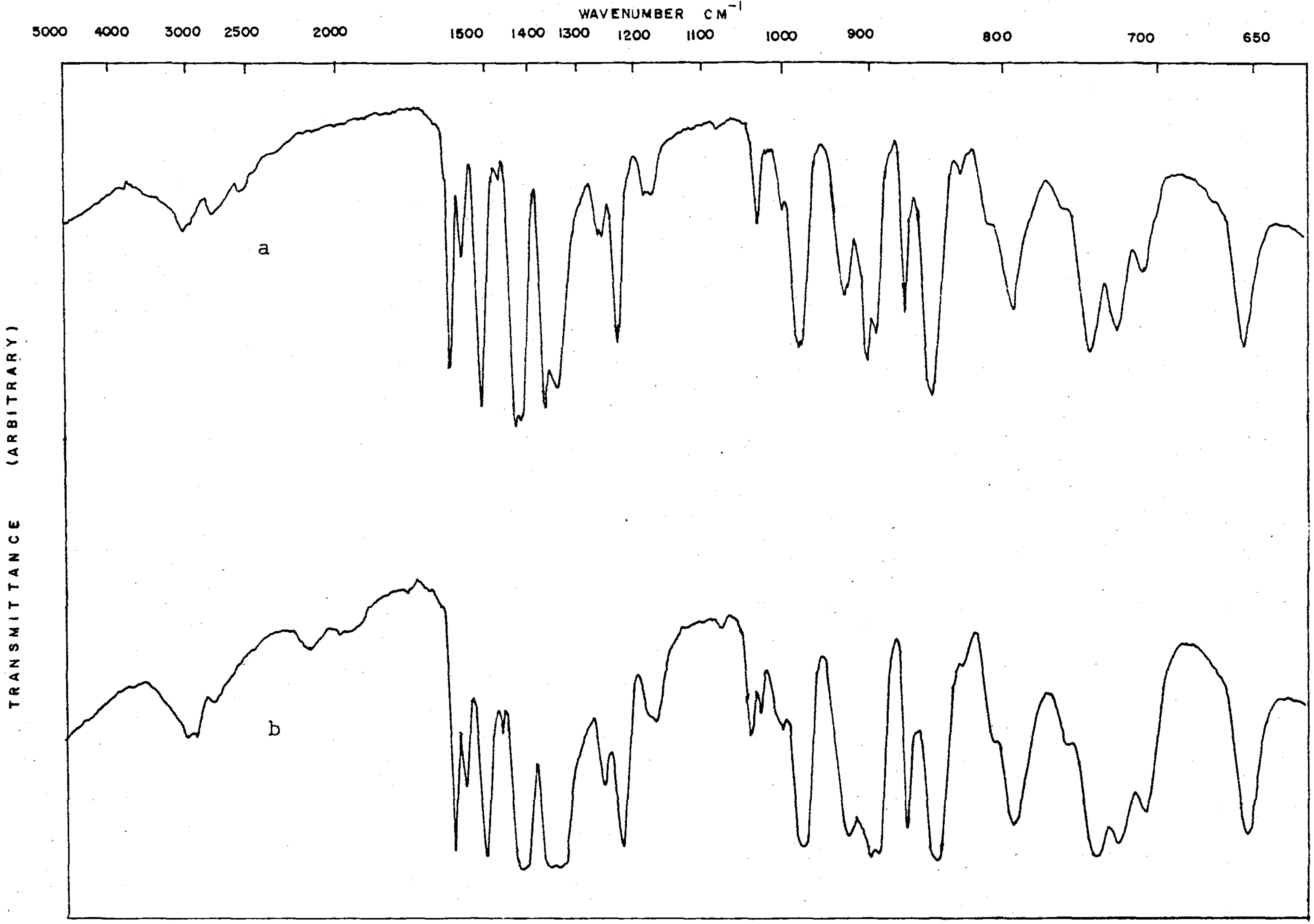

Figure III Infrared Spectra of Bis (Tropolonato) Dioxouranium (VI) Precipitated from Methanol and $CH_3OD$ Media

a. $UO_2T_2 \cdot CH_3OH$

b. $UO_2T_2 \cdot CH_3OD$

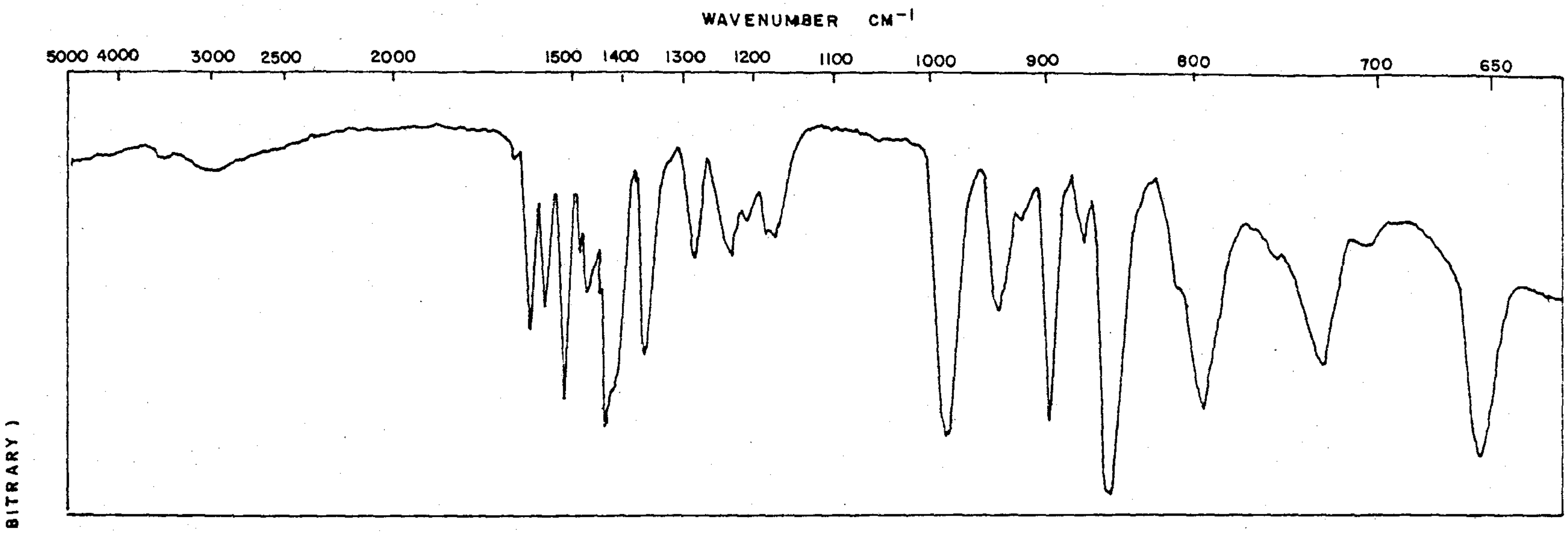

Figure IV Infrared Spectrum of Tris (Tropolonato) Dioxouranium (VI)

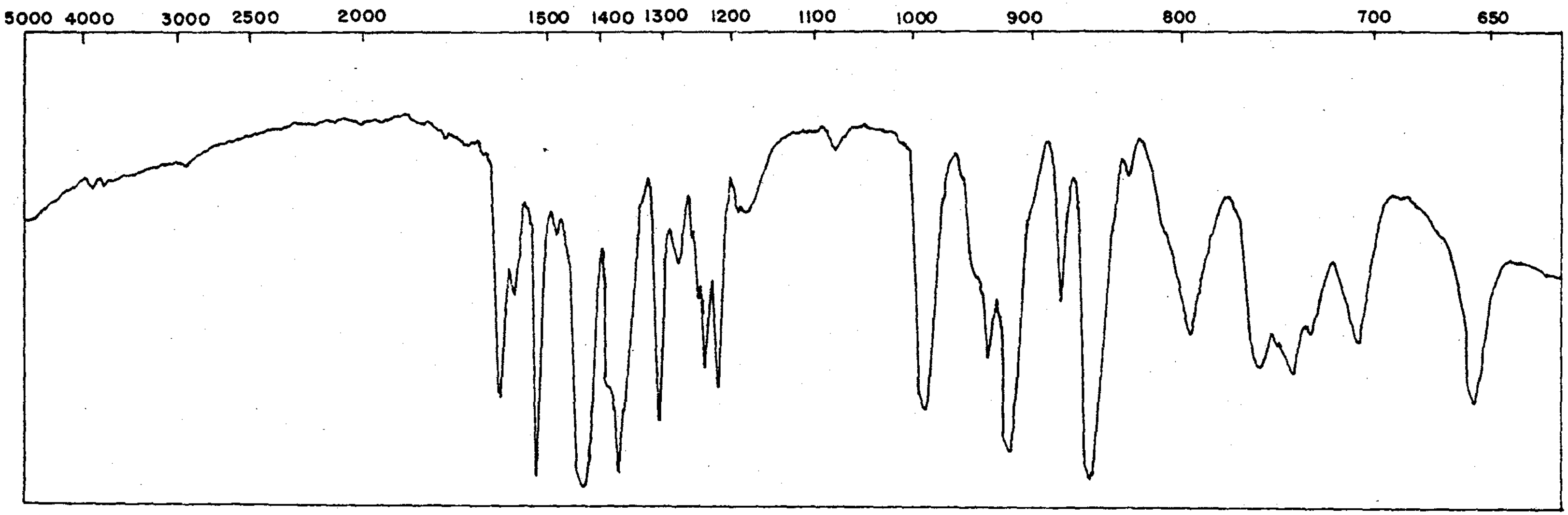

Figure V Infrared Spectrum of the Thermal Conversion Product Bis (Tropolonato) Dioxouranium (VI)

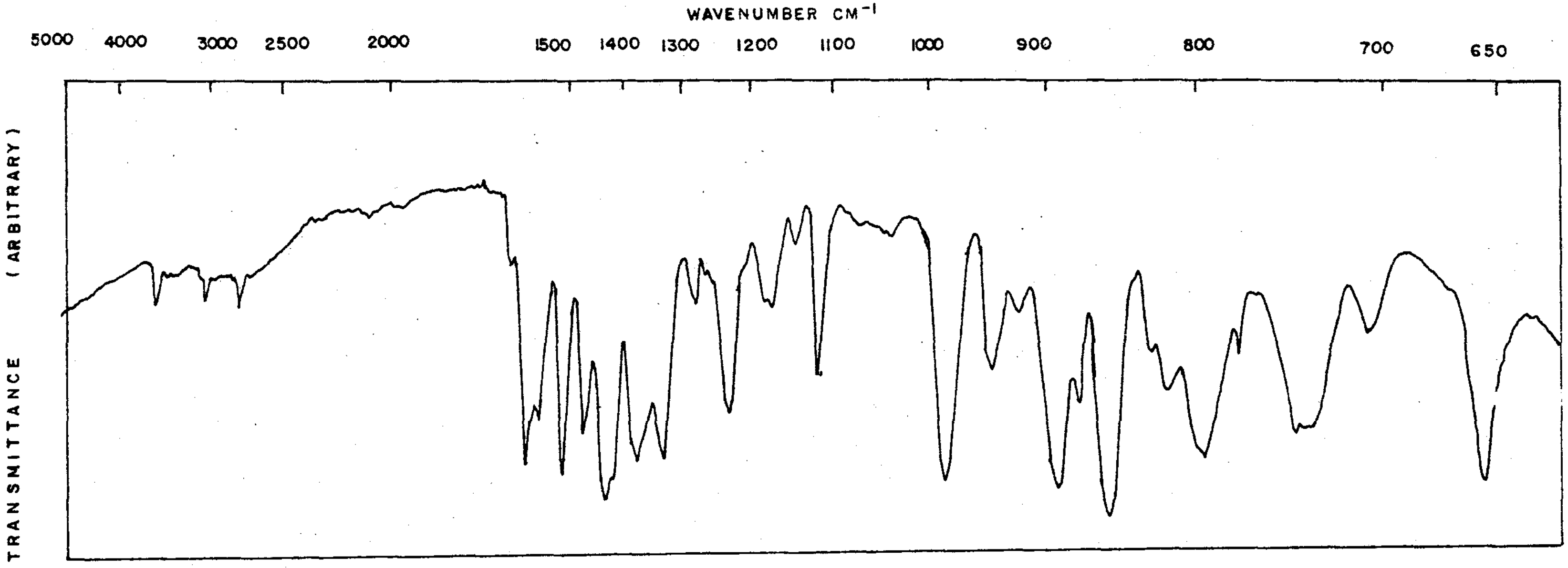

Figure VI Infrared Spectrum of Bis (Tropolonato) (8-Hydroxyquinoline) Dioxouranium (VI)

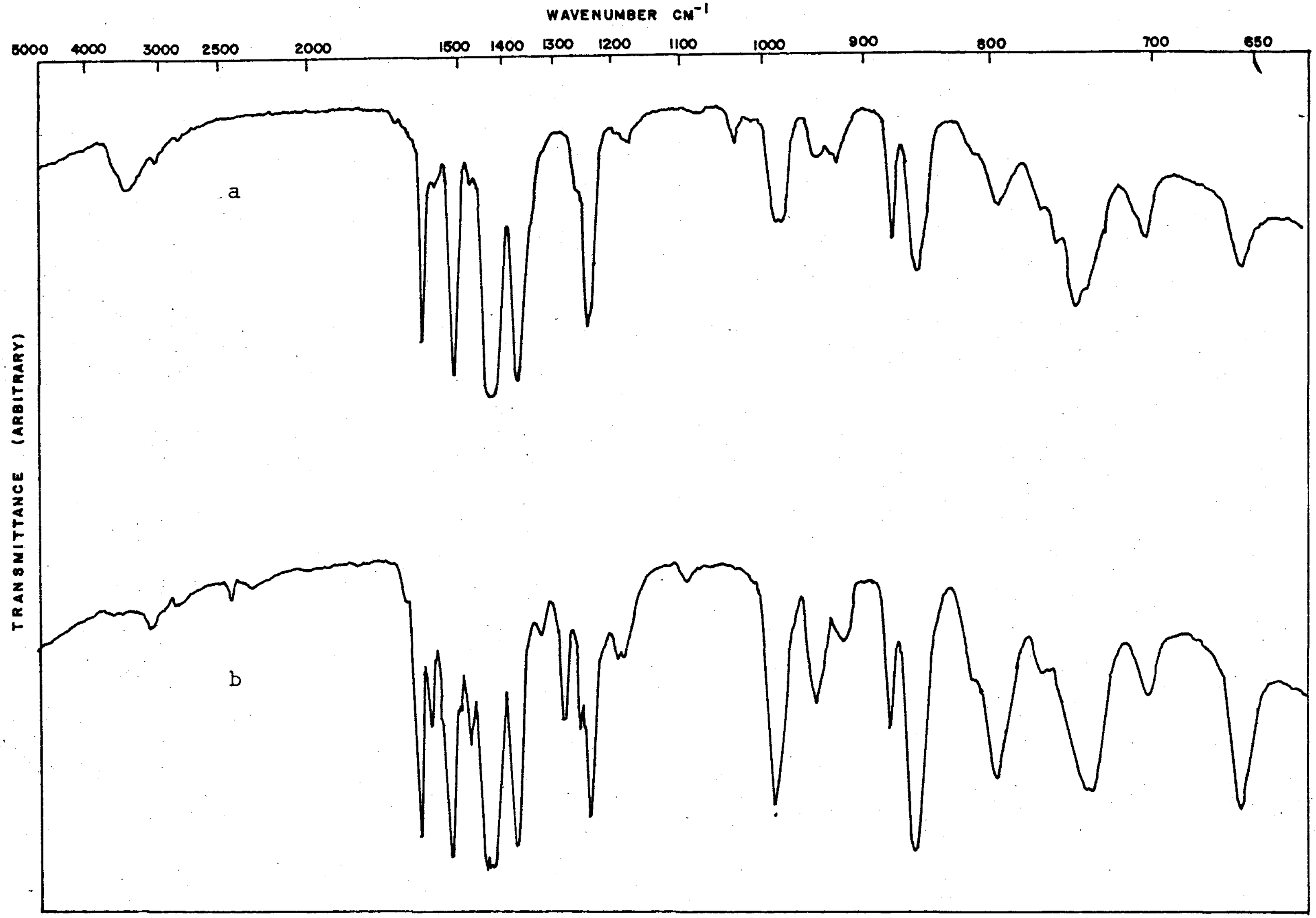

Figure VII Infrared Spectra of Tetrakis (Tropolonato) Thorium (IV) Precipitated from Aqueous and $D_2O$ Media

a. $ThT_4 \cdot H_2O$

b. $ThT_4 \cdot D_2O$

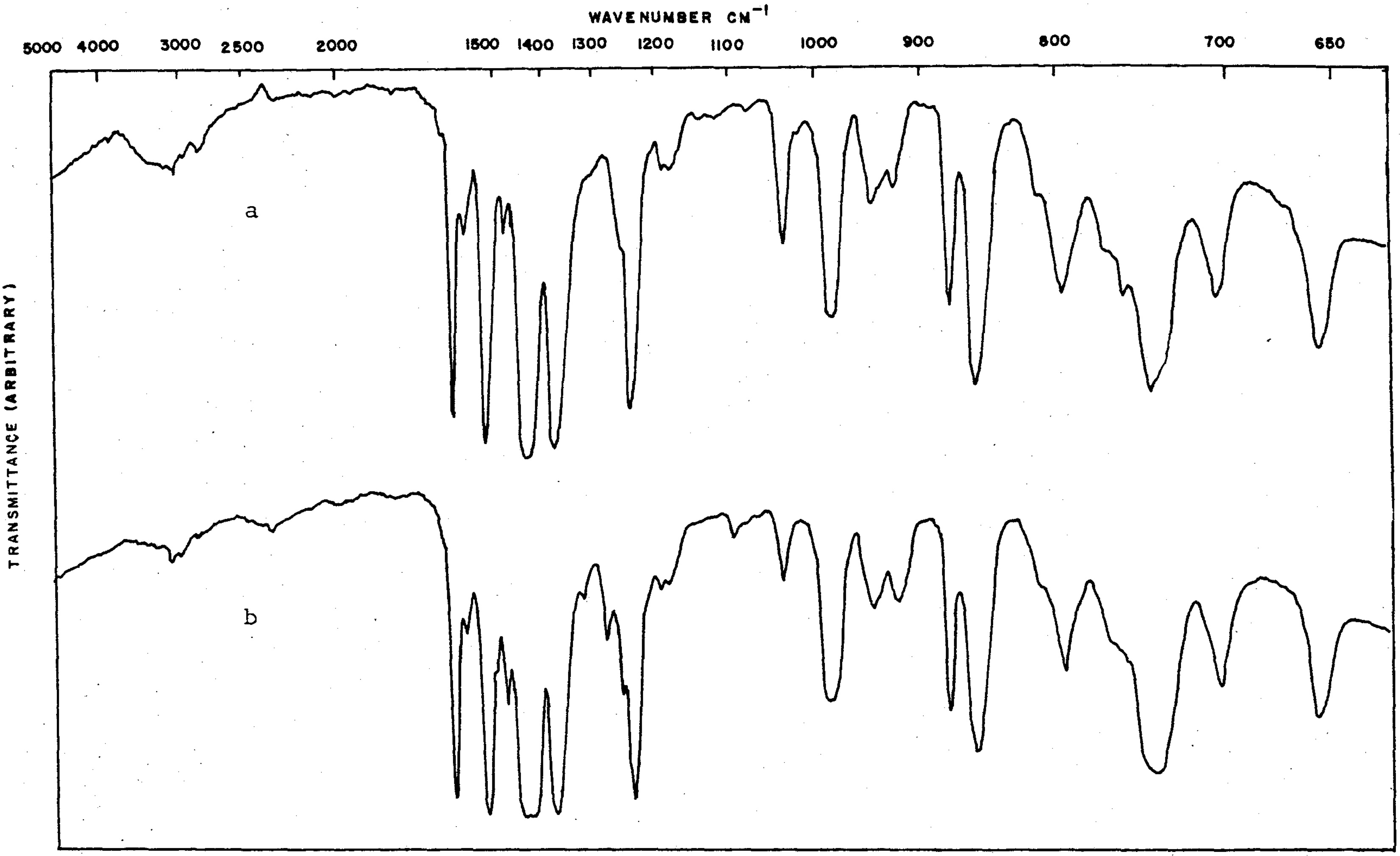

Figure VIII Infrared Spectra of Tetrakis (Tropolonato) Thorium (IV)

Precipitated from 50% Aqueous Methanol and from 50% $D_2O$-$CH_3OD$ Media

a. $ThT_4 \cdot CH_3OH$

b. $ThT_4 \cdot CH_3OD$

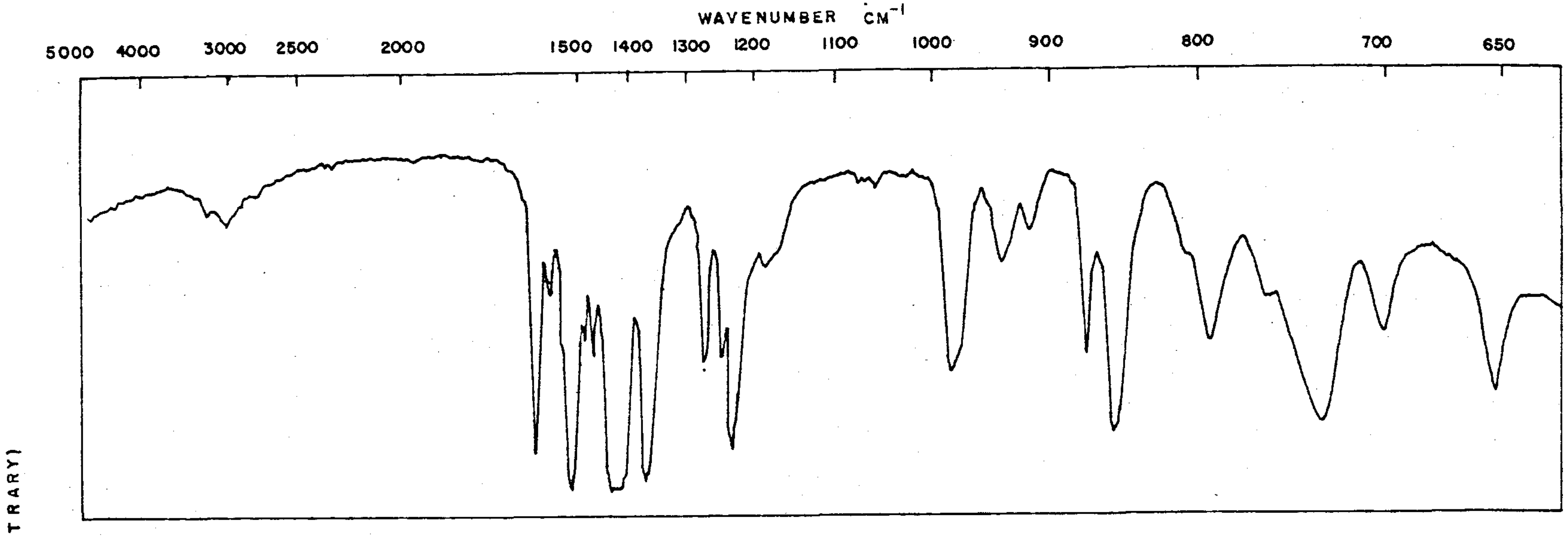

Figure IX Infrared Spectrum of Pentakis (Tropolonato) Thorium (IV)

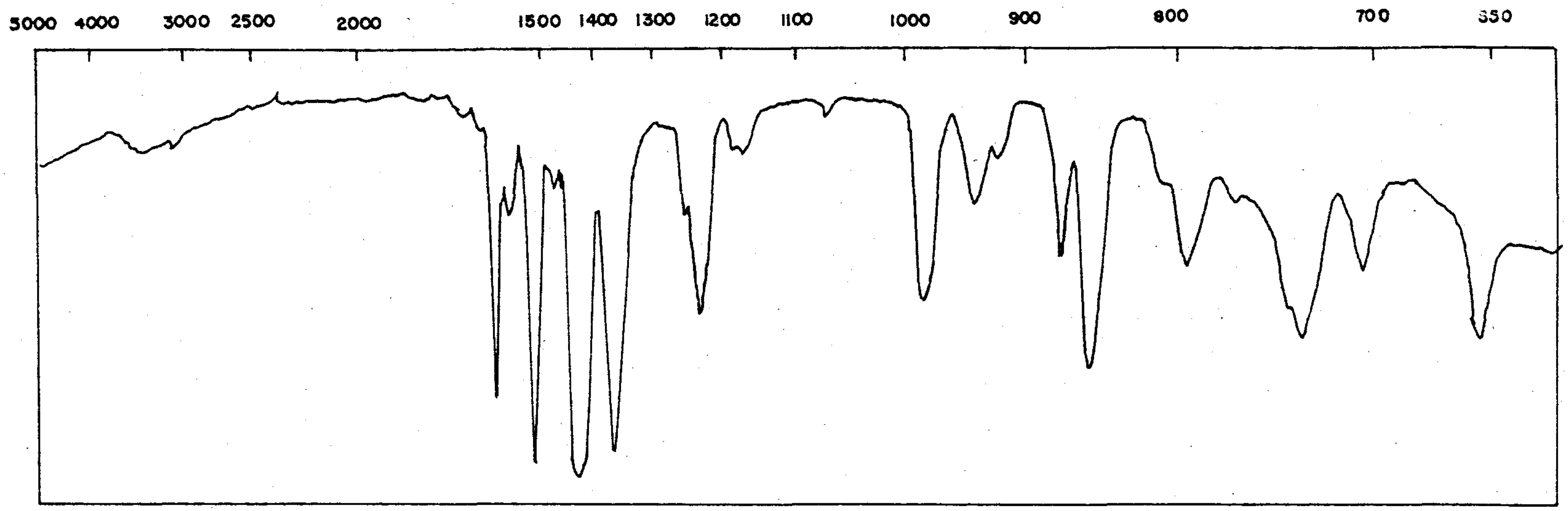

Figure X Infrared Spectrum of the Thermal Conversion Product Tetrakis (Tropolonato) Thorium (IV)

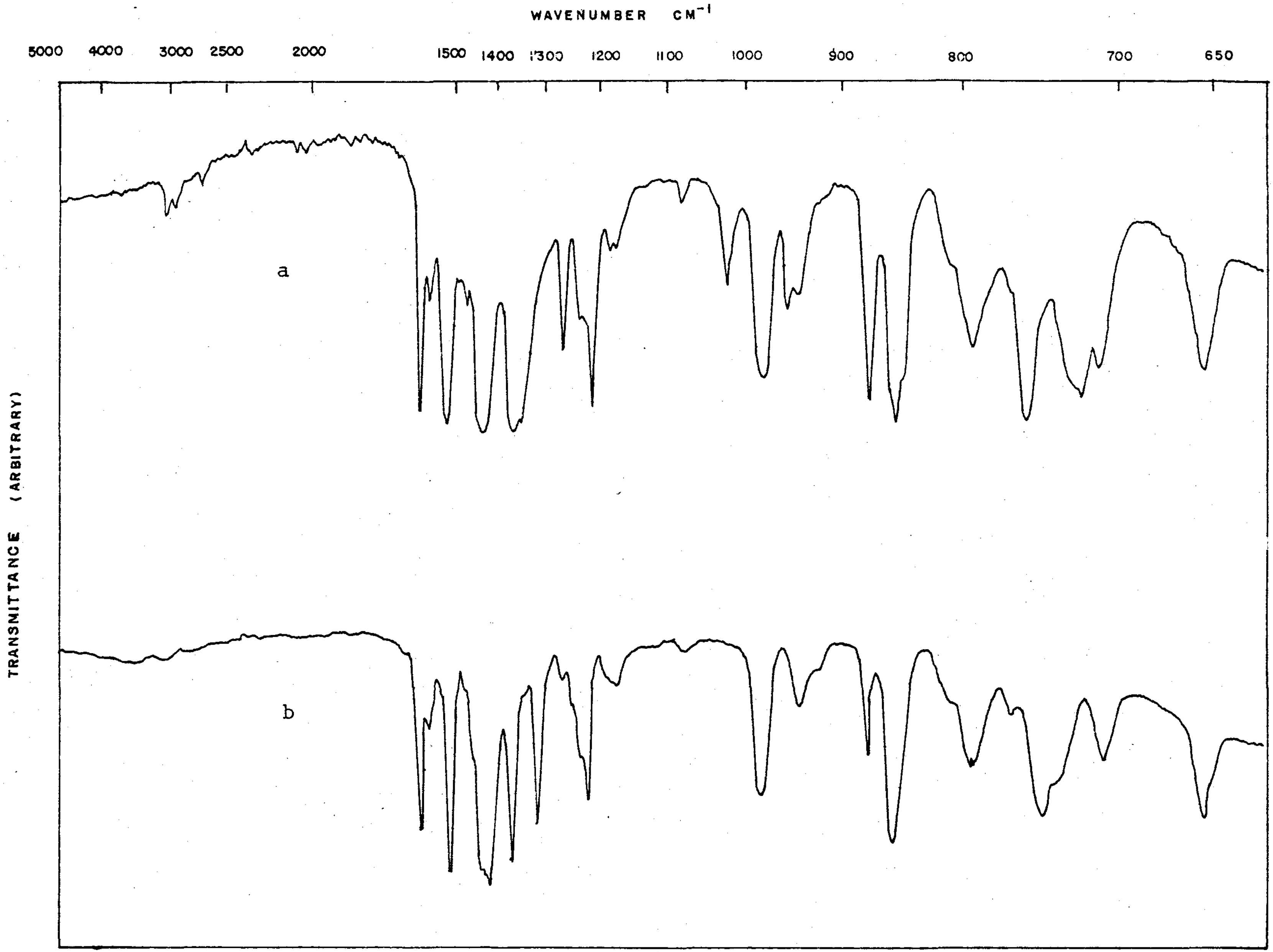

Figure XI Infrared Spectra of Tris (Tropolonato) Scandium (III)

a. $ScT_3 \cdot 0.5CH_3OH$, prepared by the method of Muetterties and Wright

b. $ScT_3$

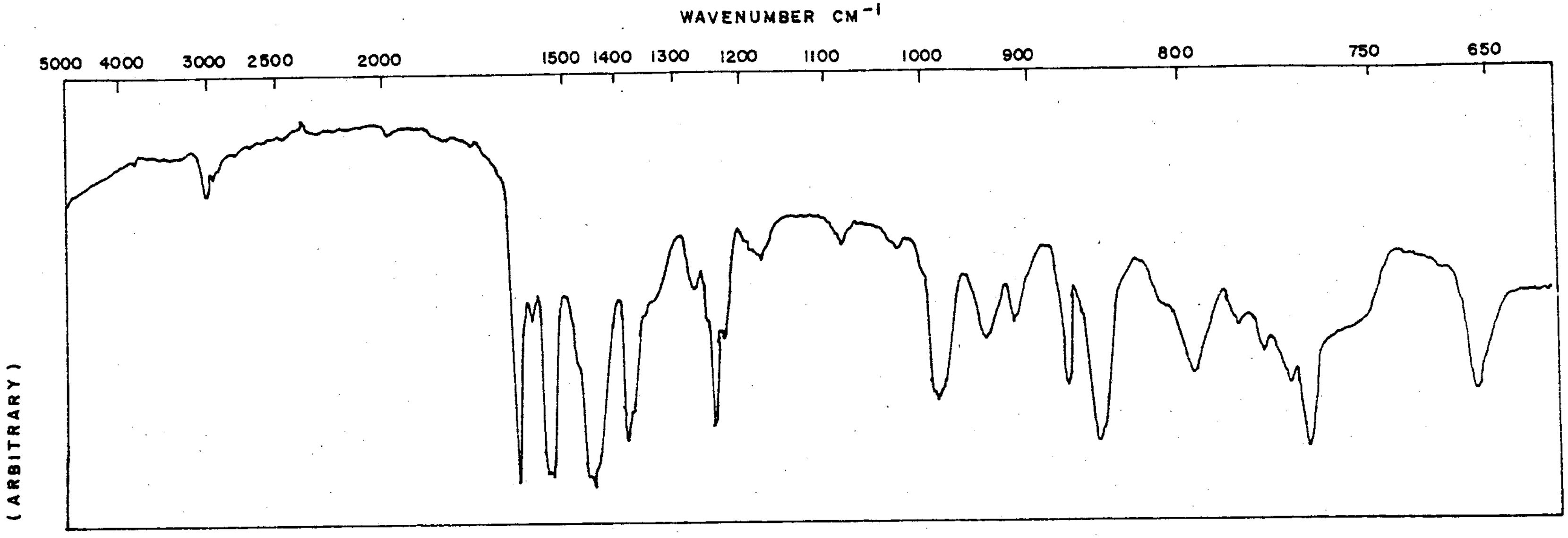

Figure XII Infrared Spectrum of Tetrakis (Tropolonato) Scandium (III)

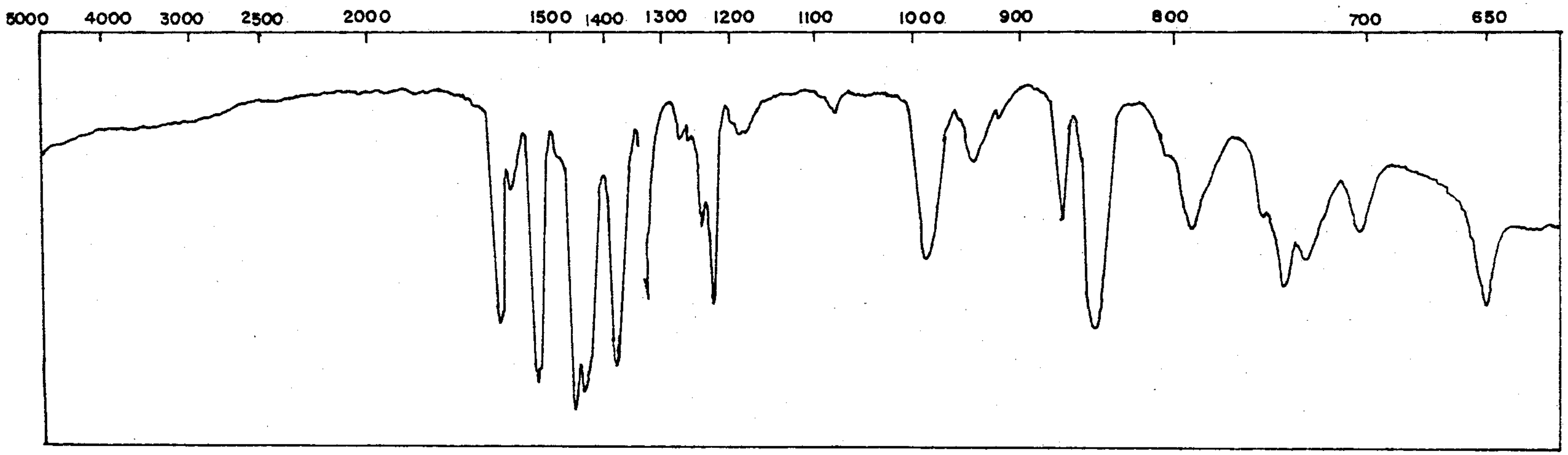

Figure XIII Infrared Spectrum of the Thermal Conversion Product Tris (Tropolonato) Scandium (III)

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