URANIUM(VI) AND SCANDIUM(III) COMPLEXES

OF

8-HYDROXYQUINOLINE AND DERIVATIVES

URANIUM(VI) AND SCANDIUM(III) COMPLEXES OF 8-HYDROXYQUINOLINE AND DERIVATIVES

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SCOPE AND CONTENTS:

New uranium(VI) complexes of 8-hydroxyquinoline ligands of formulae $UO_2(R\text{-}Q)_2 \cdot R\text{-}QH$ have been prepared. In these compounds, the additional ligand is likely bonded as a zwitterion. Appropriate substitution in the 2- and 7-positions lead to interesting steric effects. Some uranium(VI) complexes reported in the literature have been re-examined and found to be incorrectly formulated.

The scandium(III) complex of 8-hydroxyquinoline obtained from aqueous solution was found to be $Sc(C_9H_6NO)_3 \cdot H_2O$ and not $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ as previously reported. In the absence of water, $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ was obtained. New scandium(III) complexes of formulae $Sc(R\text{-}Q)_3 \cdot R\text{-}QH$ and $Sc(R\text{-}Q)_3 \cdot H_2O$ have been prepared.

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I. GENERAL INTRODUCTION

The usefulness of metal chelates in medicine and chemistry is now generally recognised.[1,2] In medicine, the treatment of lead poisoning by the calcium chelate of EDTA, and the applications of the chelating agent, 8-hydroxyquinoline, to therapeutic science are illustrations of the use of chelate compounds.

In chemistry, progress in the study of metal chelates has received an added impetus because of its many applications to biology and analytical chemistry. Interest in the structure and properties of chelates has led to a greater understanding of other metal complexes of biological importance, and of chemical problems such as exist in analytical chemistry.

In analytical chemistry, the wide attention given to chelates stems from the unusual versatility of these compounds. For example, chelating agents have been used extensively in qualitative,[3] gravimetric,[4] titrimetric[5,6] and spectrophotometric[7] analysis, and in ion-exchange[8] and solvent extraction[9,10] separations. Bidentate dimethylglyoxime and 8-hydroxyquinoline, and hexadentate EDTA are examples of important reagents* in analytical methods.

Normally, mono-protonated bidentate ligands, HChel, react with a metal-ion of charge z+ according to the reaction:

$$M^{z+} + zHChel = M(Chel)_z + zH^+$$

The number of reacting ligands and of released protons are equal to

*The terms "reagent", "ligand" and "8-hydroxyquinoline" (or derivative thereof) are used interchangeably throughout this thesis.

the metal-ion charge. With several metal-ions, however, certain ligands react as follows:

$$M^{z+} + (z + n)HChel = M(Chel)_z \cdot nHChel + zH^+$$

The number of reacting ligands is one or more (n) than the charge on the metal-ion, and the resulting complex has additional molecule(s) of reagent, which retain their proton(s) to preserve charge neutrality. For example, uranium(VI) yields adducts* with α-picolinic acid,[11] tropolone,[12] acetylacetone[13] and 8-hydroxyquinoline[14] that contain one extra molecule of reagent.

During the past thirty years, considerable attention has been directed toward the adduct complexes of 8-hydroxyquinoline. The solid uranium(VI), thorium(IV) and scandium(III) adducts have been used in chemical analysis for several years, although the recent advent of modern techniques has diminished their analytical importance. Studies of the complexes, however, continue to appear regularly in the literature. The X-ray single crystal studies of the uranium(VI)[15] and silver(I)[16] complexes, and several examinations of the composition of the uranium(VI)[17-21] and thorium(IV) complexes[20,22-25] are recent examples. Furthermore, several new adducts of hydroxyquinoline, such as the yttrium(III),[26] antimony(III)[27] and sodium(I)[28] complexes, have been reported.

Although a significant effort has been made to determine the composition and structure of various solid adducts, little research has been done on the factors that govern the formation of the adduct complexes. The purpose of this work is to investigate these factors by

*As stated in the SUMMARY, the term "adduct" is an inaccurate description of the complexes, but is used in this thesis for consistency with the literature.

a study of the reactions of uranium(VI) and scandium(III) with 8-hydroxyquinoline and its derivatives. In particular, study is given to: (i) a comparison of the products formed when the metal-ions are precipitated from solution by various substituted 8-hydroxyquinolines, and (ii) a careful re-examination of the composition of the 8-hydroxyquinoline complex of scandium(III).

8-Hydroxyquinoline is a compact ligand with a small preferred separation between its two donor atoms ("bite") and is, therefore, capable of generating high coordination-number complexes. The higher coordinate species are usually defined as polyhedra in which an atom is within bonding distance of seven or more other atoms. In view of the current research in the area of high coordination-number polyhedra,[29,30] information concerning the chemistry of adduct complexes is of particular interest.

II. HISTORICAL INTRODUCTION

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

Under appropriate conditions, reaction between uranium(VI) and 8-hydroxyquinoline in aqueous solution yields a brick-red adduct with the assigned formula, $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$. This compound has been used for the quantitative determination of uranium for many years.[31] The compound was first prepared by Hecht and Reich-Rohrwig,[14] and since this early work it has been reported extensively in the literature.[32] A recent X-ray single crystal study showed that the extra molecule is coordinated to the uranium atom but, unlike the two bidentate ligands, through the phenolate oxygen only.[15] Infrared studies located the acidic proton on the ring nitrogen atom of the monodentate ligand.[17] It is likely hygrogen-bonded to the phenolate oxygen of the neighbouring bidentate ligand.

Investigations pertaining to the uranium(VI) complexes of 8-hydroxyquinoline derivatives have not been as extensively reported as those of the parent ligand. Previous research has been concerned for the most part with the preparation and properties of compounds precipitated from solution. The compounds that have been reported are summarized in Table I and are discussed in more detail below.

Moeller and Ramaniah[39] reported the formation of complexes of 5,7-dichloro- and 5,7-dibromo-8-hydroxyquinoline. According to these workers, it is possible to precipitate both the tris and bis complexes if the initial ligand-to-metal ratio in solution is adjusted to the

TABLE I

SOLID COMPOUNDS OF URANIUM(VI) WITH 8-HYDROXYQUINOLINE DERIVATIVES

8-Hydroxyquinoline Derivative	Compound	Reference
2,3-dimethyl-	insoluble precipitate	33
2-methyl-	$UO_2(C_{10}H_8NO)_2 \cdot C_{10}H_9NO$	34-38
5,7-di-X- (X = Cl or Br)	$UO_2(C_9H_4NOX_2)_2 \cdot C_9H_5NOX_2$	37-40
	$UO_2(C_9H_4NOX_2)_2$	38,39
5,7-diiodo-	$UO_2(C_9H_4NOI_2)_2 \cdot C_9H_5NOI_2$	41
5-chloro-7-iodo	$UO_2(C_9H_4NOClI)_2$	39
5-iodo-	$UO_2(C_9H_5NOI)_2 \cdot C_9H_6NOI$	37
7-(α-anilobenzyl)-	$UO_2(C_{22}H_{17}N_2O)_2 \cdot C_{22}H_{18}N_2O$	42

appropriate stoichiometric value. These results are in conflict with the work of Bullwinkel and Noble[43] who found that it was not possible to prepare the normal bis complex of 8-hydroxyquinoline by precipitation from solution. Moeller and Ramaniah suggested, from absorption spectral studies, that the extra molecule in the tris complexes is held by lattice forces. Subsequently, Wendlandt et al.[37,38,40] studied the compounds by thermogravimetric, vapour pressure and X-ray powder diffraction methods. Under thermogravimetric conditions, it was not possible to remove the extra molecule of reagent from the tris complex according to the reaction:

$$UO_2(C_9H_4NOX_2)_2 \cdot C_9H_5NOX_2(solid) \overset{\Delta}{=} UO_2(C_9H_4NOX_2)_2(solid) + C_9H_5NOX_2(gas)$$

The heats of dissociation for the same reaction were determined for the tris 5,7-dichloro- and 5,7-dibromo-8-hydroxyquinoline complexes (ΔH = 25.0 and 27.6 kcal $mole^{-1}$, respectively) by vapour pressure methods. Although both these values are higher than that for the dissociation of 8-hydroxyquinoline from its adduct (ΔH = 21.8 kcal $mole^{-1}$), no conclusions regarding these results were drawn. It was also reported that the tris and bis complexes of each 5,7-dihalo-8-hydroxyquinoline are crystallographically different (monoclinic and triclinic, respectively). This result is different from that for the tris and bis complexes of the parent ligand, where the introduction of the extra molecule distorts the unit cell of the bis complex to one of lower symmetry.[44]

With 5,7-diiodo-8-hydroxyquinoline, a tris complex is formed.[41] Under thermogravimetric conditions, it was not possible to remove the extra molecule of reagent from the tris complex.

In the various studies of the 5,7-dihalo-8-hydroxyquinoline complexes, the basic formulae assigned by Moeller and Ramaniah were assumed to be correct. In the present study, it will be shown that these formulae are incorrect.

Phillips, Emery and Price[34] found that 2-methyl-8-hydroxyquinoline formed a tris complex. The composition of the compound was determined by gravimetry. Subsequently, Wendlandt et al.[35-38] studied the tris complex by thermogravimetric, infrared, differential thermal analysis, calorimetric, vapour pressure and X-ray powder diffraction methods. No conclusions regarding the bonded nature of the extra molecule were drawn. In the present work, the acidic proton of the tris complex is located by an infrared study.

Phillips et al.[42] also prepared the tris complex of 7-(α-anilobenzyl)-8-hydroxyquinoline; however, very little data was given to confirm the composition of the compound.

In a potentiometric titration study, Irving and Rossotti[45] determined the formation constants* for the reaction of uranium(VI) with several alkyl-substituted 8-hydroxyquinolines and found that the value of the first formation constant for the complex of 7-methyl-8-hydroxyquinoline is lower than that of the parent ligand. Therefore, according to these workers, the methyl group exhibits a steric effect. In the present work, titrations with 7-tert -butyl-8-hydroxyquinoline show that this suggestion is incorrect.

In this thesis, the following studies on the uranium(VI) complexes of 8-hydroxyquinoline derivatives have been made.

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*The equilibrium formation constants are defined by the concentrations of species.

(i) The new uranium(VI) complexes of 5-methyl-, 5-chloro-, 5-phenyl- and 7-phenyl-8-hydroxyquinoline have been prepared and characterized as adducts by elemental analysis and infrared spectroscopy.

(ii) The new uranium(VI) complexes of 7-methyl-, 2,7-dimethyl- and 7-tert-butyl-8-hydroxyquinoline have been prepared and shown by elemental and infrared analysis to have formulae of the type, $UO_2(R\text{-}Q)_2 \cdot Y$, where R-Q represents the anion of the 8-hydroxyquinoline derivative and Y is a small coordinating species (e.g., H_2O, NH_3) present in solution. The failure of the adduct complexes to form has been attributed to inter-ligand steric interactions.

(iii) The bis and tris 5,7-dihalo-8-hydroxyquinoline complexes proposed by Moeller and Ramaniah are shown by elemental, infrared and X-ray powder diffraction analysis to be incorrect. The compounds have formulae of the type $UO_2(C_9H_4NOX_2)_2 \cdot OC(CH_3)_2$.

(iv) The thermal products of the general reaction,

$$UO_2(R\text{-}Q)_2 \cdot Y(\text{solid}) \overset{\Delta}{=} UO_2(R\text{-}Q)_2(\text{solid}) + Y(\text{gas})$$

have been characterized by elemental and infrared analysis.

(v) The acidic proton of the uranium(VI) adduct of 2-methyl-8-hydroxyquinoline has been located by infrared spectroscopy. Attempts to prepare complexes with 2-n-butyl-, 2-phenyl- and 2-(2'-thienyl)-8-hydroxyquinoline were unsuccessful. The precipitates consisted largely of hydrolysed species of uranium and free reagent.

(vi) The formation of complexes with 2-substituted 8-hydroxyquinolines was studied at 25°C in 50% v/v aqueous dioxane of ionic strength 0.1 by the potentiometric titration method. Formation constants could be obtained only for the 2-methyl- and 2-n-butyl-8-hydroxyquinoline systems. The data are very suggestive of steric interactions between the 2-substituents and water in adjacent coordination sites of the metal-ion.

II.B. Scandium(III) Complexes of 8-Hydroxyquinoline and Derivatives

Previous research has been almost entirely concerned with the preparation and properties of compounds precipitated from solution. The compounds that have been reported are summarized in Table II and are discussed in more detail below.

In hot aqueous solution, scandium(III) and 8-hydroxyquinoline react under appropriate conditions of pH and concentration to give a lemon-yellow precipitate. Pokras and Bernays[46,47] were the first workers to prepare this compound to which they ascribed the formula, $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$, although the procedure prescribed for its synthesis is ambiguous. The composition of the adduct was largely assigned on the basis of gravimetry of precipitates, dried at 100-110°C, and elemental analysis. Precipitates were heated within this temperature range to remove "free" 8-hydroxyquinoline. The tetrakis adduct was also suggested by Moeller and Ramaniah,[50] again on the basis of elemental analysis.

Subsequently, Pokras and Bernays[47] recommended the compound as a separation and weighing form for the gravimetric determination of

TABLE II

SOLID COMPOUNDS OF SCANDIUM(III) WITH 8-HYDROXYQUINOLINE AND DERIVATIVES

8-Hydroxyquinoline Derivative	Compound	Reference
8-hydroxyquinoline	$Sc(C_9H_6NO)_3 \cdot C_9H_7NO$	37,38,40,44,46-51
	$[Sc(C_9H_6NO)_3]_2 \cdot C_9H_7NO$	49
	$[Sc(C_9H_6NO)_3]_2 \cdot 3C_9H_7NO$	49
	$Sc(C_9H_6NO)_3$	52
2-methyl-	$Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$	34-38
5,7-di-X- (X = Cl or Br)	$Sc(C_9H_4NOX_2)_3 \cdot C_9H_5NOX_2$	40,50
	$Sc(C_9H_4NOX_2)_3$	50
5,7-diiodo-	$Sc(C_9H_4NOI_2)_3$	41
5-chloro-7-iodo-	$Sc(C_9H_4NOClI)_3 \cdot C_9H_5NOClI$	50
	$Sc(C_9H_4NOClI)_3$	50
7-(α-anilobenzyl)-	$Sc(C_{22}H_{17}N_2O)_3$	42

scandium, because of the favourable (7.24% Sc) gravimetric factor. By cryoscopic methods, the same workers found that a solution of the compound in benzene is completely dissociated into the normal tris complex, $Sc(C_9H_6NO)_3$, and 8-hydroxyquinoline.[48] From the results of these studies, it was suggested that the extra molecule is bound by weak lattices forces in the molecular crystal. It is interesting to note that similar suggestions, concerning the binding of the extra molecule, were made during the earlier work on the uranium(VI) and thorium(IV) adducts.[39,53,54]

Van Tassel, Wendlandt and Sturm[44] determined the crystal unit cell dimensions of the tetrakis compound by X-ray powder crystallography, and attempted a non-aqueous titration of an acetonitrile solution of the compound. These workers found that the titration curve is very broad, with no discernible buffer region that could be ascribed to the proton in the complex. It was suggested that formation of a complex-anion in basic solution "would require the unlikely cation coordination-number of eight for scandium". The authors apparently favour the view that the additional molecule is a lattice component. Although octacoordination for scandium has not been rigorously established, it is reasonably certain that coordination-number eight exists in the tropolonate anion, $Sc(C_7H_5O_2)_4^-$, prepared as the sodium salt by Muetterties and Wright.[55]

Numerous attempts have been made to convert the tetrakis compound to the normal tris complex by a thermal reaction as follows:[37,40,46,47,51]

$$Sc(C_9H_6NO)_3 \cdot C_9H_7NO(solid) \overset{\Delta}{=} Sc(C_9H_6NO)_3(solid) + C_9H_7NO(gas)$$

Such reactions are established for the adducts of uranium(VI) and thorium(IV).[56] In no case was the normal tris complex obtained. (These results could be criticized in that the experiments that were performed were generally based upon gravimetric methods, rather than by analysis of the thermal products.) Also, differential thermal analysis has not revealed the removal of the extra molecule on the heating of the tetrakis compound.[38] Despite the result that the stoichiometry of the thermal reaction has not been observed, Wendlandt et al.[37] determined the heat of dissociation (ΔH = 17.0 kcal mole^{-1}) of the reaction by vapour pressure methods. No conclusions concerning the binding of the additional molecule were drawn.

Cardwell and Magee[49] studied the precipitation of scandium(III) with 8-hydroxyquinoline in homogeneous solution. The reagent was generated by the hydrolysis of 8-acetoxyquinoline. Two compounds were prepared, $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ and $[Sc(C_9H_6NO)_3]_2 \cdot C_9H_7NO$, precipitated at pH values of 6.5 and 8.8, respectively. A third scandium 8-hydroxyquinolate, $[Sc(C_9H_6NO)_3]_2 \cdot 3C_9H_7NO$, was prepared by a "solid-phase" reaction at 110°C between the tetrakis compound obtained at pH 6.5 and 8-hydroxyquinoline. As 8-hydroxyquinoline melts at 73°C, it is doubtful that the reaction occurred in the solid-phase. More likely, it occurred in molten 8-hydroxyquinoline. The compositions of the compounds were assigned on the basis of gravimetry of precipitates, and elemental analysis. As with the studies of previous workers, thermogravimetry of the two compounds precipitated from solution did not result in constant-weight levels corresponding to the normal tris

complex. The thermogram of the compound prepared by a "solid-phase" reaction did, however, exhibit a constant-weight level at 205°C corresponding to the tetrakis compound $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$. The infrared spectra of the three compounds, pressed in potassium bromide, were recorded in the range, 4000-400 cm^{-1}. Minor differences between the three spectra were discussed, but no clear conclusions regarding the binding of the additional 8-hydroxyquinoline in the compounds were drawn.

Petronio and Ohnesorge[52] prepared the scandium(III) complex of 8-hydroxyquinoline according to the procedure of Pokras and Bernays, and reported that the compound is not an adduct, but simply the normal tris complex. The authors pointed out that the differences in carbon, hydrogen and nitrogen contents of the adduct and normal compounds are small and that, therefore, the elemental analyses of previous workers are not definitive evidence for the adduct compound. Elemental analysis of several samples of the compound showed three significant features. Firstly, the results for carbon were considerably lower and those for hydrogen slightly higher than the theoretical values calculated for the normal chelate and for the adduct compositions. Secondly, the scandium analyses were much closer to the value calculated for the normal complex. Thirdly, the precision of the results was poor. The cause of the poor reproducibility was attributed to the hygroscopic nature of the compound. A molecular weight determination by vapour-phase osmometry compared favourably with the molecular weight of the normal complex. Results from a mole-ratio study, by ultraviolet absorption and fluorescent spectral methods, were consistent with the formation of a tris complex.

By similar techniques, the authors found that the compound dissociated in absolute ethanol solution to give a bis-chelate species and 8-hydroxyquinoline. Evidence was given to support the following dissociation reaction:

$$Sc(C_9H_6NO)_3 + 2C_2H_6O = Sc(C_9H_6NO)_2 \cdot OC_2H_5 \cdot OC_2H_6 + C_9H_7NO$$

The equilibrium constant of the reaction was 10^{-4}. From these studies, the approximate value of 10^9 was calculated for the third step-wise formation constant of the tris complex.

It is noticeable in the literature that all previous workers (except Cardwell and Magee who used a PFHS method) have quoted the procedure of Pokras and Bernays for the preparation of the scandium(III) complex of 8-hydroxyquinoline. In view of the ambiguous nature of the procedure, and the controversy that now exists, the composition of the complex was re-examined in the present work.

Phillips, Emery and Price[34] found that 2-methyl-8-hydroxyquinoline formed the tetrakis complex. The compound was precipitated from aqueous solution by the procedure used by Pokras and Bernays for the complex of the parent ligand. Subsequently, Wendlandt et al.[35-38] studied the compound by vacuum sublimation, infrared, thermogravimetric, differential thermal analysis and vapour pressure methods. Initially, it was reported that, unlike the adduct complex of the parent ligand, the tetrakis complex can be converted to the normal tris complex by heating at 80°C <u>in vacuo</u>. Later, however, the authors reported that a thermogram of the compound showed a first weight loss at 70°C, a break in the thermogram curve at 120-160°C, and then a constant-weight level corresponding to the normal

tris complex at 225°C. In differential thermal analysis studies, endothermic peaks were observed at 100°C, 150°C and 350°C. The peaks at 100°C and 150°C were attributed to the removal of the additional molecule from the tetrakis complex. These results appear to be somewhat inconsistent, even allowing for the different conditions of the experiments. In the studies by Wendlandt et al., no conclusions regarding the binding of the additional molecule were drawn. The complex was further examined in this thesis.

Moeller and Ramaniah[50] reported that both the tetrakis and tris complexes can be precipitated from aqueous acetone solution by 5,7-dichloro-, 5,7-dibromo- and 5-chloro-7-iodo-8-hydroxyquinoline. The tetrakis complexes cannot be converted to the normal tris complexes under thermogravimetric conditions.[40]

5,7-Diiodo-[41] and 7-(α-anilobenzyl)-8-hydroxyquinoline[42] apparently precipitate only the tris complexes.

In solution, there have been no determinations of the chelate formation constants of scandium(III) with 8-hydroxyquinoline, or its derivatives.

In this thesis, the following studies on the scandium(III) complexes of 8-hydroxyquinoline and derivatives have been made.

(i) The composition of the 8-hydroxyquinoline complex precipitated from aqueous solution has been re-examined and shown by analysis, infrared spectroscopy X-ray powder crystallography and thermogravimetric analysis to have the formula $Sc(C_9H_6NO)_3 \cdot H_2O$. The erroneous formulae proposed by other workers are explained.

(ii) The new scandium(III) complexes of 2-chloro-, 4-chloro- and

5-methyl-8-hydroxyquinoline have been prepared and shown by analysis and infrared spectroscopy to have formulae of the type $Sc(R\text{-}Q)_3 \cdot H_2O$.

(iii) The composition of the 2-methyl-8-hydroxyquinoline complex has been re-examined and shown by analysis, infrared spectroscopy, X-ray powder crystallography and thermogravimetric analysis to have the formula $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$.

(iv) The new scandium(III) complex of 4-methyl-8-hydroxyquinoline and the 8-hydroxyquinoline complex prepared from the reagent melt have been characterized as adducts by analysis, infrared spectroscopy and thermogravimetric analysis.

(v) The formation of adduct or tris complexes (with respect to the chelating ligand) of scandium(III) from aqueous solution has been correlated with the $\log {}^{C}K_{NH}$ values of the ligands.

(vi) The thermal products of several scandium(III) complexes have been characterized by analysis and infrared spectroscopy.

(vii) The 4-methyl-8-hydroxyquinoline adduct has been obtained by an addition reaction of the type,

$$Sc(C_{10}H_8NO)_3(\text{solid}) + C_{10}H_9NO(\text{solution}) = Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO(\text{solid})$$

in 1,2-dichloroethane as solvent.

(viii) Formation constants have been obtained for the complexation of 8-hydroxyquinoline and its 2- and 4-methyl-substituted derivatives by the potentiometric titration method (25°C, 50% v/v aqueous dioxane and ionic strength 0.1).

III. EXPERIMENTAL AND RESULTS

III.A. Apparatus

Certified volumetric ware was used when appropriate.

Weighings were made on a conventional analytical balance (Type B-6, E. Mettler, Zürich).

General laboratory measurements of pH were made with a Coleman Model Metrion IV pH meter (Coleman Instruments Corporation, Maywood, Illinois) fitted with suitable electrodes.

Infrared spectra were recorded with a Beckman IR-5 infrared spectrophotometer (Beckman Instruments Inc., Fullerton, California). Proton magnetic resonance spectra were recorded with one of Varian A-60, T-60, or HA-100 nuclear magnetic resonance spectrometers (Varian Associates, Palo Alto, California). Mass spectra were recorded on a Hitachi Perkin-Elmer RMU-6A mass spectrometer (Perkin-Elmer Corporation, Norwalk, Connecticut). Samples were introduced through an all-glass inlet system maintained at 200°C.

Thermograms were recorded on a Stanton HT-D automatic thermo-recording balance (Stanton Instruments Limited, London, England).

X-ray diffraction powder photographs were obtained by exposing samples in a 114.6 mm-diameter camera to Cu Kα radiation emitted by a Philips PW 1011 X-ray generator (Philips Scientific Equipment, Holland).

The potentiometric titration apparatus for the determination of protonation constants and chelate formation constants consisted of a titration cell, a pH meter, two ten-millilitre microburets and a

constant-temperature water bath. The pH meter was a Radiometer Model PHM4 (Radiometer, Copenhagen, Denmark) equipped with a Beckman E-3 (low sodium-ion error) glass electrode and saturated calomel electrode supplied by the Fisher Scientific Company.

When appropriate, a heated vacuum desiccator (P5, Precision Scientific Company, Chicago, Illinois) was used 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 an evacuating oil 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 modified Kjeldahl apparatus used for the determination of ammonia in the uranium(VI) complex of 7-methyl-8-hydroxyquinoline consisted of a 3-necked 100-ml flask fitted with an air inlet, condenser, and thistle funnel. The condenser was connected by tygon tubing to a small glass pipette.

III.B. Reagents

All common laboratory chemicals were either reagent-grade or sufficiently pure for the purpose intended.

Uranyl nitrate hexahydrate (Fisher Scientific Company, Fair Lawn, New Jersey) and scandium chloride hexahydrate (Alfa Inorganics, Beverley, Massachusetts) were used without further purification. Stock solutions of scandium chloride containing 1.57 mg Sc/ml (0.035

millimoles/ml) were prepared from the hexahydrate salt and standardized with EDTA[57] before use.

1,2-Dichloroethane (Fisher Scientific Company) was dried before use by distillation over phosphorus pentoxide and then stored over type 4 A molecular sieves (British Drug Houses Ltd., Poole, England). Hexachloro-1,3-butadiene (Eastern Chemical Corporation, Newark, New Jersey), used to prepare mulls for infrared studies, was vacuum-distilled over barium oxide and then stored over molecular sieves. Spectrally-pure benzene (J. T. Baker Chemical Company, Phillipsburg, New Jersey) was used in vapour-phase osmometry without further purification. The deuterium oxide (Columbia Organic Chemicals Company, Columbia, South Carolina) used in infrared studies was 99.7% pure. Dimethylsulfoxide-d_6, acetic-acid-d_4 and acetone-d_6 (Stohler Isotope Chemicals, Montreal) were used as supplied.

The chemicals used in potentiometric titration studies were as given below.

Reagent-grade 1,4-dioxane (Fisher Scientific Company) 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.

Carbonate-free sodium hydroxide was prepared as given by Kolthoff and Sandell.[58] The sodium hydroxide solution (∿0.1 M) was standardized by titration against 25-ml portions of a standard potassium hydrogen phthalate solution using phenolphthalein indicator.

A solution of perchloric acid (∿0.01 M) containing sodium perchlorate

(0.21 M) was used in the potentiometric titrations. The hydrogen-ion concentration of this solution was determined by potentiometric titration with standard sodium hydroxide solution (0.1 M).

A standard uranium nitrate solution (0.01 M) was prepared by dissolving the required weight of the dried salt in deionized water.

A scandium chloride solution (~0.01 M) was prepared and standardized with EDTA.

The organic ligands used in this work were either purchased, available in the laboratory, or synthesized, as indicated below.

8-Hydroxyquinoline (oxine, 8-quinolinol). 8-Hydroxyquinoline (Fisher Scientific Company) was steam-distilled and recrystallized from aqueous ethanol solution to give white needles, mp, 72-73°C.

2-n-Butyl-8-hydroxyquinoline hydrochloride. 2-n-Butyl-8-hydroxyquinoline was synthesized by the procedure of Kaneko and Ueno.[59] The oily product was dissolved in dry ether and hydrogen chloride gas was passed through the solution to give a pale-yellow precipitate. The solid was filtered, washed with dry ether, and repeatedly recrystallized from absolute ethanol to give pale-yellow crystals, mp, 176-179°C.

Calculated for $C_{13}H_{16}NOC\ell$: 65.68% C, 6.78% H, 5.89% N, 14.91% Cℓ.

Found*: 65.48% C, 6.78% H, 5.80% N, 14.93% Cℓ.

2-Phenyl-8-hydroxyquinoline. 2-Phenyl-8-hydroxyquinoline was synthesized by the method of Irving, Butler and Ring.[60] The product

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*All microanalyses (C, H, N, Cℓ and Br) reported in this thesis were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engleskirchen, West Germany.

was recrystallized from 95% v/v ethanol to give flesh-coloured flakes, mp, 58°C.

5,7-Dichloro-8-hydroxyquinoline. 5,7-Dichloro-8-hydroxyquinoline (Eastman Organic Chemicals, Rochester, New York) was twice recrystallized from acetone to give cream-coloured crystals, mp, 174-175°C.

5,7-Dibromo-8-hydroxyquinoline. 5,7-Dibromo-8-hydroxyquinoline (Matheson, Coleman and Bell, Norwood, Ohio) was twice recrystallized from acetone to give white needles, mp, 196-197°C.

4-Chloro-8-hydroxyquinoline. 4-Chloro-8-hydroxyquinoline was synthesized by the procedure of Pinnington.[61] The product was steam-distilled and recrystallized from aqueous ethanol to give white needles, mp, 142-143°C.

7-Phenyl-8-hydroxyquinoline. 7-Phenyl-8-hydroxyquinoline was synthesized by the general method of Vorozhtsov and Troshchenko.[62] The intermediate product, 2-nitro-6-phenyl phenol, was reduced to 2-amino-6-phenyl phenol with sodium hydrosulphite. Amounts of the final product were steam-distilled, when required, to give white needles, mp, 144-145°C.

7-tert-Butyl-8-hydroxyquinoline. The starting compound for the synthesis of 7-tert-butyl-8-hydroxyquinoline, 2-tert-butyl-phenol (Aldrich Chemical Company, Ltd., Milwaukee, Wisconsin), was converted to 2-nitro-6-tert-butyl phenol by the method of Dearden and Forbes.[63]

Thirty grams of 2-nitro-6-tert-butyl phenol were dissolved in 200 ml of 2 M sodium hydroxide and the deep red solution warmed to 70-80°C. Solid sodium hydrosulfite was added in 0.5 g quantities, with continuous

stirring, until the colour of the solution became yellow. A white solid, 2-amino-6-tert-butyl phenol, was obtained when the solution was neutralized with 50% v/v acetic acid solution. The amine was filtered, washed with cold water, and then dried quickly over phosphorus pentoxide in a vacuum desiccator. No attempt was made to characterize the amine as it is very readily oxidised on exposure to air. The product was immediately used to prepare 7-tert-butyl-8-hydroxyquinoline by the Skraup reaction.

Twenty-one grams of 2-amino-6-tert-butyl phenol, 15 g of 2-nitro-6-tert-butyl phenol and 72 g of glycerol were thoroughly mixed in a 3-necked 250-ml flask equipped with thermometer, condenser and mechanical stirrer. Twenty-two millilitres of concentrated sulfuric acid were added to the mixture in the flask over a period of 20 minutes. The contents of the flask were heated gently to 130-140°C, and kept at this temperature for 4 hours. The viscous black product was cooled to 70-80°C and then transferred to a 1-litre 3-necked flask. Water was added to the flask and the mixture steam-distilled to remove unchanged 2-nitro-6-tert-butyl phenol. The residue was then neutralized with sodium hydroxide solution and further steam-distilled to give white 7-tert-butyl-8-hydroxyquinoline. The product was again steam-distilled, and then recrystallized from aqueous ethanol to give white needles, mp, 92-93°C. Yield, 6.5 g (25%).

Calculated for $C_{13}H_{15}NO$: 77.58% C, 7.51% H, 6.96% N.

Found: 77.48% C, 7.51% H, 6.98% N.

III.C. Characterization of 8-Hydroxyquinoline Derivatives

The purity of 2-n-butyl-8-hydroxyquinoline was confirmed by

elemental analysis (above). The new reagent, 7-tert-butyl-8-hydroxyquinoline, was characterized by elemental analysis (above), and infrared, mass and proton magnetic resonance spectrometry. The infrared spectrum showed absorption bands characteristic of the functional groups (OH, $C(CH_3)_3$). The mass spectrum showed that the m:e ratio of the parent-ion agreed with the calculated molecular weight. The PMR spectrum is summarized in Table III.

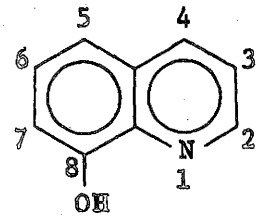
In addition to the spectrum of 7-tert-butyl-8-hydroxyquinoline, the spectra of all the 8-hydroxyquinoline derivatives used in this work were recorded. The results of these spectra served to confirm the structure of the compounds, particularly those synthesized by previous colleagues in this laboratory. The spectra were recorded at either 60 or 100 Mc, with carbon tetrachloride as solvent, and tetramethylsilane as internal reference. The spectra are summarized in Table III, and selected spectra are reproduced in Appendix A.

III.D. Bromination of 8-Hydroxyquinoline Derivatives

The direct determination of 7-methyl-, 5-methyl-, 4-chloro- and 2-chloro-8-hydroxyquinoline, present in a number of metal complexes described in this work, was required. Since 8-hydroxyquinoline and some derivatives were shown to be readily determined bromometrically by Corsini and Graham,[64] their procedure was used with some modification for the above compounds. In the present studies, the time between the addition of the standard bromate solution and of the iodide was varied. The liberated iodine was titrated with standard thiosulphate solution. White crystalline precipitates were observed

TABLE III

PROTON MAGNETIC RESONANCE SPECTRA OF 8-HYDROXYQUINOLINE DERIVATIVES



Coupling Constants for Appropriate Protons

(c/s)

$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{5,6}$	$J_{5,7}$	$J_{6,7}$
4.0	1.5	8.5	8.5	2.0	8.0

Substituent(s) R	Chemical shifts* (ppm)						
	H_2	H_3	H_4	H_5	H_6	H_7	H_R
H	8.76		8.04				
2-chloro-	-		7.94				
2-methyl-	-		7.79				2.59 (CH_3)
2-n-butyl-	-		7.95				2.95 (α-CH_2) 0.98 (CH_3)
2-phenyl-							
4-chloro-	8.58		-			7.15	
4-methyl-	8.53		-				2.66 (CH_3)
5-chloro-	8.77	7.51	8.48	-	7.47	7.03	
5-methyl-	8.68	7.34	8.17	-	7.16	6.93	2.55 (CH_3)
5-phenyl-	8.78		8.25	-		7.18	
7-methyl-	8.64		7.92	7.05	7.21	-	2.43 (CH_3)
7-phenyl-	8.75		8.10			-	

TABLE III (Cont'd.)

Substituent(s) R	Chemical Shifts*(ppm)						
	H_2	H_3	H_4	H_5	H_6	H_7	H_R
7-t-butyl-	8.64	7.23	7.97	7.11	7.45	-	1.53[$C(CH_3)_3$]
2,7-dimethyl-	-		7.74			-	2.53(2-CH_3) 2.40(7-CH_3)
5,7-dichloro-	8.82	7.52	8.48	-	7.58	-	

*Dashes represent chemical shifts not assigned due to substitution of position. Blanks represent chemical shifts not assigned because of the complexity of the spectrum.

during the titrations of 2-chloro-8-hydroxyquinoline. The crystals were identified as 2-chloro-5,7-dibromo-8-hydroxyquinoline. The results of the bromometric titrations are given in Table IV. Further comment on the applicability of the bromometric titration of the above compounds to the analysis of metal complexes is given in the DISCUSSION.

III.E. Potentiometric Determination of Protonation Constants

Potentiometric titrations were performed in a 250-ml jacketted titration cell; water at 25.0±0.1°C was circulated through the outer jacket. The cell was fitted with a lucite cover with holes for the glass and calomel electrodes, a nitrogen inlet tube, a thermometer and two 10-ml burets.

The general procedure was as follows: purified-grade nitrogen gas was bubbled through the solution which was to be titrated. The contents of the cell were stirred magnetically. The tip of the sodium hydroxide buret was placed below the surface of the solution during a titration. The buret was gravity filled from a 4-litre polyethylene bottle. The contents of both the buret and the bottle were protected from atmospheric carbon dioxide by absorption tubes filled with ascarite.

The pH meter was standardized immediately before use with Beckman standard buffer solutions of pH 4.01 and 7.00.

The titration procedure was as follows: a weighed amount of the 8-hydroxyquinoline derivative was placed in the titration cell and dissolved in 5.0 ml of 1,4-dioxane. Next, 5.0 ml of water and 50.0 ml of 0.01 M perchloric acid solution (0.21 M in sodium perchlorate) were

TABLE IV

BROMOMETRIC TITRATION OF 8-HYDROXYQUINOLINE DERIVATIVES

Derivative	Time (mins)				
	1	3	5	8	11
7-methyl-monobromination (%)	98.8	100.2	100.9	101.6	
5-methyl-monobromination (%)	95.4	98.8	101.0	102.5	104.0
4-chloro-dibromination (%)	98.7	99.8	100.2	100.0	
2-chloro-dibromination (%)*		97.2	97.7		97.5

*Precipitated 2-chloro-5,7-dibromo-8-hydroxyquinoline observed during the titration.

pipetted into the cell, followed by 50.0 ml of 1,4-dioxane. The electrodes were inserted into the solution, and nitrogen gas was bubbled through until the contents of the cell reached 25.0°C. The titration was then performed by the addition of small increments of sodium hydroxide. With each addition of base, an equal volume of 1,4-dioxane was added, and the P value (pH meter reading) of the solution was recorded. Attainment of equilibrium was rapid in every titration.

The Van Uitert and Haas correction factor,[65] $\log U_{H^+}$, is given by

$$\log U_{H^+} = p_cH - P \qquad (1)$$

where $p_cH = -\log [H^+]$. The value of p_cK_w is given by

$$p_cK_w = p_cH + p_cOH \qquad (2)$$

where $p_cK_w = -\log K_w$, and $p_cOH = -\log [OH^-]$. The values of p_cK_w (15.37) and $\log U_{H^+}$ (-0.08±0.01) for 50% v/v aqueous 1,4-dioxane were determined as described elsewhere.[66]

The protonation constants, $\log {}^cK_{OH}{}^*$ and $\log {}^cK_{NH}{}^*$, are defined by

$${}^cK_{NH} = \frac{[H_2L^+]}{[HL][H^+]} \qquad (3)$$

$${}^cK_{OH} = \frac{[HL]}{[L^-][H^+]} \qquad (4)$$

---

*All constants determined in this work are equilibrium concentration constants.

where L^- represents the 8-hydroxyquinoline (or derivative thereof) -anion. The constants were calculated from the intercept and slope of a linear least-squares fit to the general equation,[66]

$$\frac{\bar{p}}{(\bar{p}-1)[H^+]} = {}^{c}K_{OH}\,{}^{c}K_{NH}\frac{(2-\bar{p})[H^+]}{(\bar{p}-1)} - {}^{c}K_{OH} \qquad (5)$$

where $\bar{p}$ represents the average number of protons bound to each ligand molecule. Values of $\bar{p}$ in the ranges 0.2 - 0.8 and 1.2 - 1.8 were used in the calculations, which were performed with the aid of an IBM 7040 or CDC 6400 computer. The FORTRAM IV program employed for the calculations is listed in Appendix B. Representative titration data for each 8-hydroxyquinoline derivative are presented in Appendix C.

The protonation constants are given in Table V. The precision of the data points <u>within</u> any given titration is expressed as the parameter, σ, where

$$\sigma = \sqrt{\frac{\Sigma(\bar{p}_{exp} - \bar{p}_{calc})^2}{(N-1)}} \qquad (6)$$

and $\bar{p}_{exp}$ represents the experimental $\bar{p}$ values; $\bar{p}_{calc}$ represents the $\bar{p}$ values calculated from the determined protonation constants, and N is the number of data points.

The protonation constants of 2-n-butyl-8-hydroxyquinoline were obtained from the hydrochloride salt. The $\overset{+}{N}H$ groups of 2-(2'-thienyl)- and 2-chloro-8-hydroxyquinoline are too acid for potentiometric determination of $\log {}^{c}K_{NH}$. The value of $\log {}^{c}K_{OH}$ for 7-tert-butyl-8-hydroxyquinoline was estimated from data in the high ($\sim$13) pH region.

TABLE V

PROTONATION CONSTANTS OF 8-HYDROXYQUINOLINE DERIVATIVES

(Temp. 25.0°C, ionic strength 0.1, 50% v/v dioxane)

Derivative	$\text{Log}^{c}K_{NH}$	$\text{Log}^{c}K_{OH}$	σ
8-hydroxyquinoline	4.12	11.12	0.01
2-methyl-	4.75	11.60	0.01
4-methyl-	4.85	11.23	0.01
5-methyl-	4.27	11.44	0.01
7-methyl-	3.94	11.68	0.02
2-chloro-		10.65	
4-chloro-	2.83	10.38	0.01
2-n-butyl-	4.58	11.93	0.02
2-(2'-thienyl)-	(1.48)*	11.64	
2-phenyl-	2.36	11.77	0.01
7-tert-butyl-	2.50	13.4†	

*Value from reference (66).

†Estimated value.

III.F. Potentiometric Determination of Uranium(VI) and Scandium(III) Chelate Formation Constants

The chelate formation constants of uranium(VI) with 8-hydroxyquinoline, its 7-tert-butyl- derivative and several 2-substituted 8-hydroxyquinolines were determined potentiometrically. Similarly, formation constants for the scandium(III) complexes of 8-hydroxyquinoline and its 2- and 4-methyl- substituted derivatives were measured.

The titration procedure was the same as that used in the potentiometric determination of protonation constants except that 5.00 ml of a 0.01 M solution of uranium(VI) or scandium(III)-ion were added in place of 5.00 ml of water. The titrations were performed at molar ratios of ligand-to-metal in the range 5-7:1 for uranium(VI), and approximately 10:1 for scandium(III).

Typical chelate formation curves are shown in Figures 1, 2 and 3. Figure 2 shows that hydrolysed species of uranium precipitated in the titrations with the 2-substituted 8-hydroxyquinolines.

The general equations of Hearon and Gilbert[67] were employed for the calculation of the parameters $\bar{n}$ and [L], where $\bar{n}$ represents the average number of ligands bound to a metal-ion and [L] the molar concentration of ligand not bound to the metal-ion. The appropriate equations are as follows,

$$\bar{n} = \frac{C_L - [L](1 + {}^{c}K_{OH}[H^+] + {}^{c}K_{OH}\,{}^{c}K_{NH}[H^+]^2)}{C_M} \qquad (7)$$

$$[L] = \frac{C_L - [H^+] - [Na^+] + [Cl{O_4}^-] + [OH^-]}{{}^{c}K_{OH}[H^+] + 2\,{}^{c}K_{ON}\,{}^{c}K_{NH}[H^+]^2} \qquad (8)$$

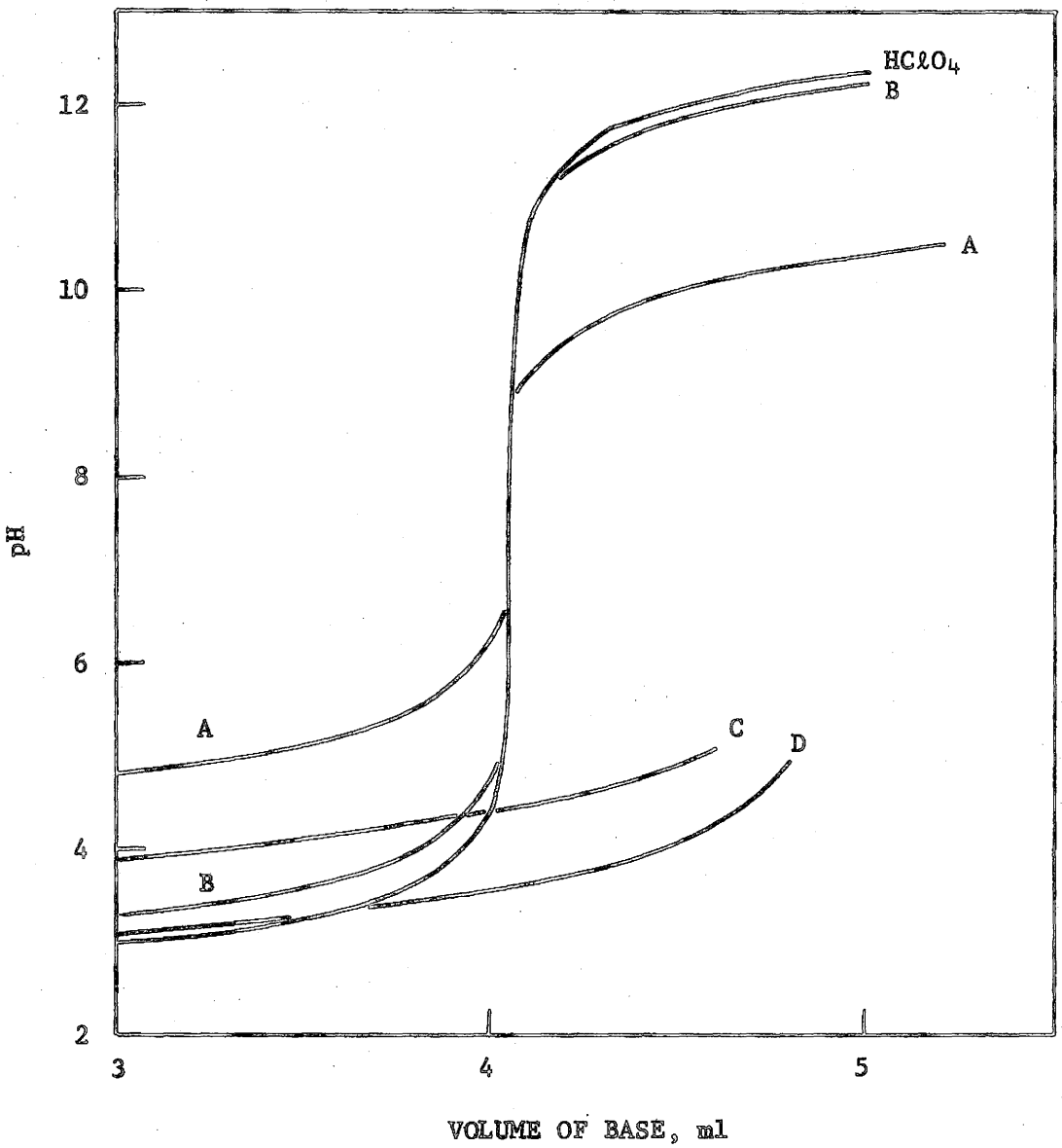


Figure 1. Titration curves of U(VI) chelates of 8-hydroxyquinoline and 7-tert -butyl-8-hydroxyquinoline in 50% v/v dioxane, 25°C, I = 0.1.

A. 8-Hydroxyquinoline ligand; B. 7-tert -Butyl-8-hydroxyquinoline ligand; C. U(VI) + 8-Hydroxyquinoline; D. U(VI) + 7-tert -Butyl-8-hydroxyquinoline.

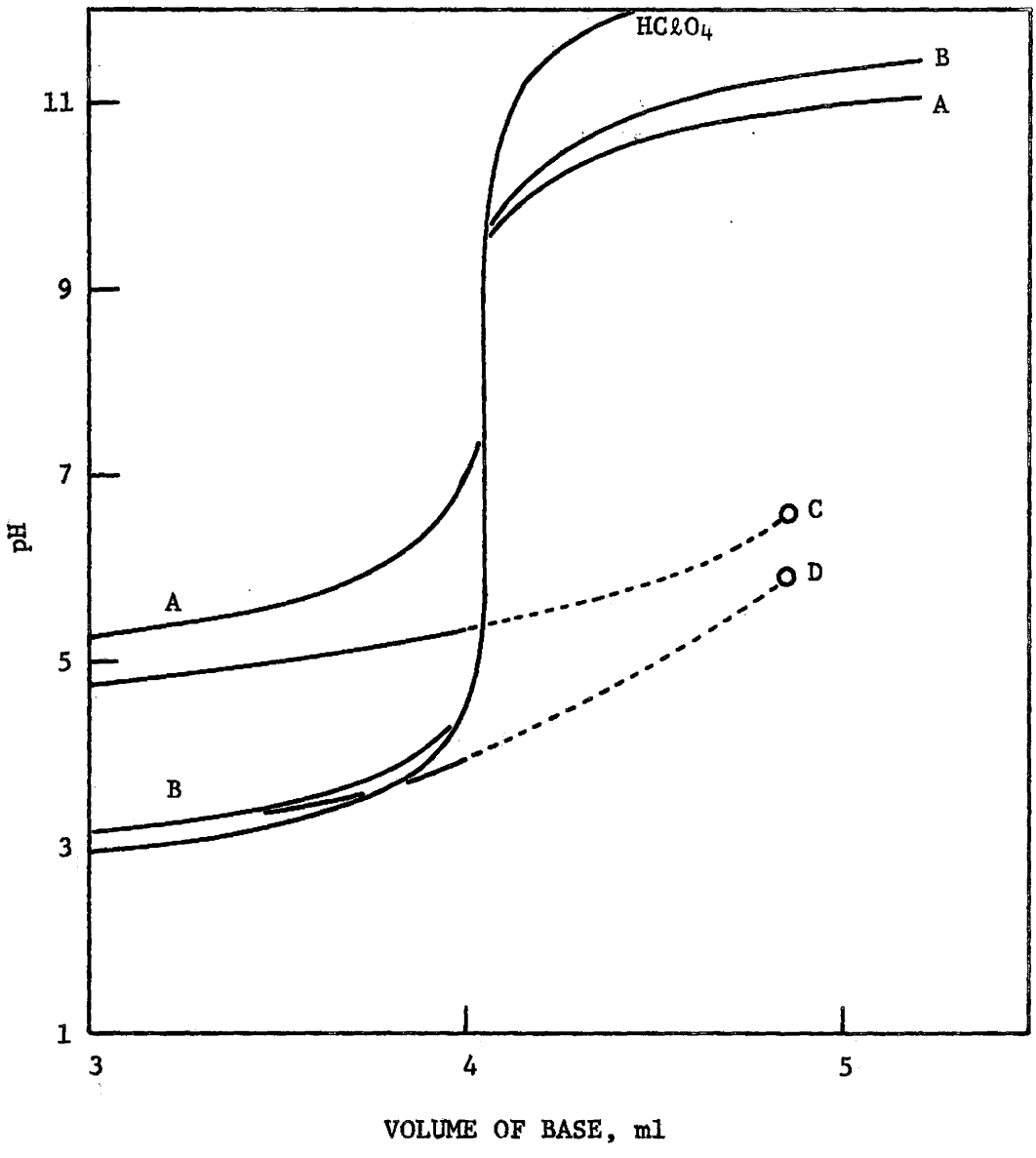


Figure 2. Titration curves of U(VI) chelates of 2-methyl- and 2-phenyl-8-hydroxyquinoline in 50% v/v dioxane, 25°C, I = 0.1. Dotted lines represent hydrolysis of U(VI); circles represent precipitation of hydrolysed uranium.

A. 2-Methyl-8-hydroxyquinoline ligand; B. 2-Phenyl-8-hydroxyquinoline ligand; C. U(VI) + 2-Methyl-8-hydroxyquinoline; D. U(VI) + 2-Phenyl-8-hydroxyquinoline.

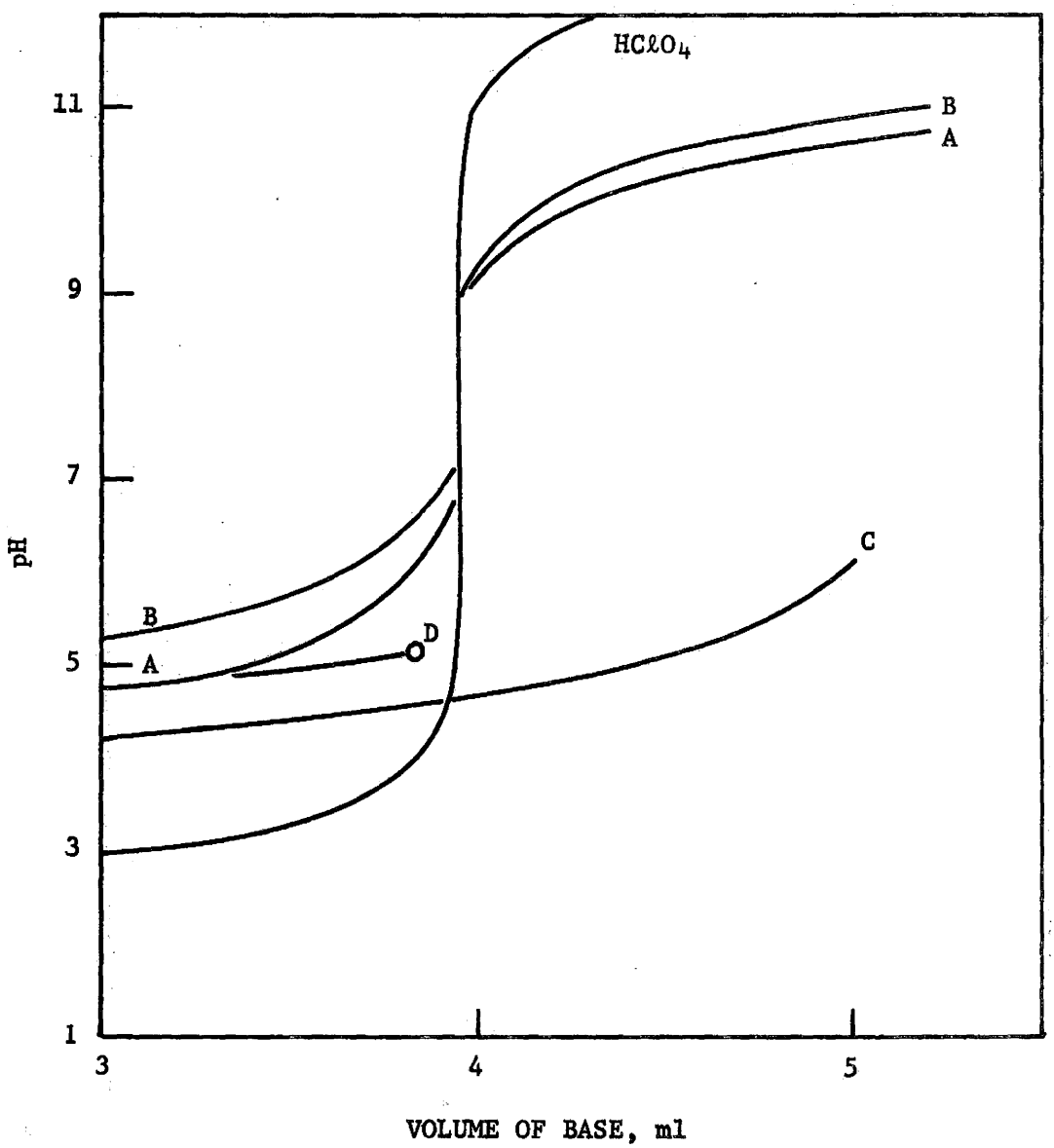


Figure 3. Titration curves of Sc(III) chelates of 8-hydroxyquinoline and 4-methyl-8-hydroxyquinoline in 50% v/v dioxane, 25°C, I = 0.1. Full circle represents precipitation of metal chelate.

A. 8-Hydroxyquinoline ligand; B. 4-Methyl-8-hydroxyquinoline Ligand; C. Sc(III) + 8-Hydroxyquinoline; D. Sc(III) + 4-Methyl-8-hydroxyquinoline.

where C_M and C_L are the analytical concentrations of the metal-ion and ligand, respectively, in moles per litre. The $\bar{n}$ and [L] parameters were calculated with the aid of an IBM CDC 6400 computer. The FORTRAN IV program for this purpose is listed in Appendix D.

The overall metal-chelate formation constants, ${}^{c}\beta_n$, are defined by

$$ {}^{c}\beta_n = \frac{[ML_n^{(z-n)+}]}{[M^{z+}][L^-]^n} \qquad n = 1,2,.....,N \qquad (9) $$

where M represents a metal-ion of charge z and coordination number N, and $[L^-]$ represents the ligand-anion. The overall constants were computed from titration data, corresponding to particular $\bar{n}$ and [L] values, by the FORTRAN IV computer program SCOGS.[68,69] The choice of data appropriate to particular $\bar{n}$ and [L] values was made by personal judgement; for example, data corresponding to the appearance of a precipitate during a titration was not included in the calculation of formation constants.

The overall formation constants and standard deviations estimated by SCOGS are given in Tables VI and VII. Also shown are the stepwise formation constants defined by

$$ {}^{c}K_n = \frac{[ML_n^{(z-n)+}]}{[ML_{n-1}^{(z-n+1)+}][L^-]} \qquad n = 1,2,.....,N \qquad (10) $$

and

$$ {}^{c}\beta_n = {}^{n}\Pi {}^{c}K_n \qquad (11) $$

These constants were calculated from the overall formation constants.

Uranium(VI) hydrolysis during the titrations with the 2-alkyl

TABLE VI

CHELATE FORMATION CONSTANTS FOR URANIUM(VI) COMPLEXES OF 8-HYDROXYQUINOLINE AND DERIVATIVES

(Temp. 25.0°C, ionic strength 0.1, 50% v/v dioxane)

Derivative	$\bar{n}$ Range	$\text{Log}^{c}\beta_1$*	σ	$\text{Log}^{c}\beta_2$	σ	$\text{Log}^{c}K_2$
8-hydroxyquinoline	0.37-1.51	11.42	0.01	21.09	0.01	9.67
2-methyl-	0.31-0.71	10.28	0.07	-	-	-
2-n-butyl-	0.25-0.57	10.39	0.09	-	-	-
7-tert-butyl-	0.41-1.45	13.39	0.01	24.97	0.04	11.58

*$\text{Log}^{c}\beta_1 = \text{Log}^{c}K_1$.

TABLE VII

CHELATE FORMATION CONSTANTS FOR SCANDIUM(III) COMPLEXES OF 8-HYDROXYQUINOLINE AND DERIVATIVES

(Temp. 25.0°C, ionic strength 0.1, 50% v/v dioxane)

Derivative	$\bar{n}$ Range	$Log^{c}\beta_1$ *	σ	$Log^{c}\beta_2$	σ	$Log^{c}\beta_3$	σ	$Log^{c}K_2$	$Log^{c}K_3$
8-hydroxyquinoline	0.54-2.58	11.26	0.01	20.87	0.01	28.92	0.02	9.61	8.05
2-methyl-	0.33-1.85	11.18	0.05	19.8	0.1	28.3	0.1	8.6	8.5
4-methyl-	0.53-2.34	11.78	0.02	22.06	0.02	20.88	0.03	10.28	8.82

*$Log^{c}\beta_1 = Log^{c}K_1$

substituted 8-hydroxyquinolines necessitated consideration of limited ranges of $\bar{n}$ values, as shown in Table VI. Therefore, $\log {}^{c}K_2$ values could not be obtained in these instances. In the titrations with the 2-phenyl- and 2-(2'-thienyl)- substituted derivatives, hydrolysis was even more extensive and neither $\log {}^{c}K_1$ nor $\log {}^{c}K_2$ values could be obtained.

Representative chelate formation data are given in Appendix E.

III.G. Uranium(VI) Complexes of 8-Hydroxyquinoline Derivatives

III.G.1. Syntheses

III.G.1.a. Precipitation of the 7-methyl-, 5-methyl-, 7-phenyl- and 5-phenyl-8-hydroxyquinoline complexes by urea hydrolysis.

One hundred milligrams of uranyl nitrate hexahydrate (0.20 millimoles) were dissolved in 50 ml of water containing 2 drops of concentrated nitric acid, and the solution warmed to 70-80°C. A solution of the appropriate 8-hydroxyquinoline derivative (0.72 millimoles), dissolved in 1-2 ml of glacial acetic acid, was added dropwise with stirring. Next, 5.5 g of urea were added, the solution heated to boiling and then transferred to a steam-bath for 4-6 hours. The pH of the solution at this point was in the range 5.8-6.0. The suspension was filtered hot through a sintered glass crucible (porosity M), washed once with 90% v/v ethanol and several times with water at 70-80°C. The precipitate was dried in a stream of air for 1 hour and for 2 hours at 100°C.

The analytical data (Table VIII) are explained in the DISCUSSION.

TABLE VIII

ANALYSES OF URANIUM(VI) COMPLEXES PRECIPITATED BY UREA HYDROLYSIS

			Calculated (%)					Found (%)				
Derivative	Colour	Formula	C	H	N	U	Reag.	C	H	N	U*	Reag.†
7-methyl-	black	$UO_2(C_{10}H_8NO)_2 \cdot NH_3$ **	39.81	3.17	6.96	39.45	52.42	39.62	3.03	6.42	39.35	51.3
5-methyl-	brick-red	$UO_2(C_{10}H_8NO)_2 \cdot C_{10}H_9NO$	48.33	3.38	5.64	31.93	63.65	48.41	3.87	5.52	32.04	63.3
5-phenyl-	brick-red	$UO_2(C_{15}H_{10}NO)_2 \cdot C_{15}H_{11}NO$	58.01	3.35	4.51	25.55		57.87	3.39	4.42	25.12	
7-phenyl-	orange-brown	$UO_2(C_{15}H_{10}NO)_2 \cdot C_{15}H_{11}NO$	58.01	3.35	4.51	25.55		58.26	3.25	4.60	25.09	

*All uranium analyses were performed by ignition to U_3O_8.[70]

†All reagent-anions were analyzed bromometrically.[64]

**A modified Kjeldahl method[71] using the apparatus described in Section III.A. gave 2.4% NH_3 (calculated, 2.83%).

III.G.1.b. Precipitation of the 7-methyl-, 2,7-dimethyl- and 7-tert-butyl-8-hydroxyquinoline complexes by dilute base solution.

The procedure was similar to that in the previous Section III.G.1.a. except that the pH was raised by dropwise addition of either 0.2 M sodium hydroxide or 4 M ammonia solution until pH 7-8 was reached. The steam heating in this case served to remove contaminating reagent by distillation.

The analytical data (Table IX) are explained in the DISCUSSION.

III.G.1.c. Precipitation of the 7-tert-butyl- and 5-chloro-8-hydroxyquinoline complexes from aqueous acetone solution.

One hundred milligrams of uranyl nitrate hexahydrate were dissolved in 60 ml of water containing 2 drops of nitric acid. The solution was warmed to 50°C. Next, a solution of the appropriate 8-hydroxyquinoline derivative (0.72 millimole), dissolved in 40 ml of acetone, was added. A 4 M ammonia solution was added dropwise until the pH was 7, and the precipitate was filtered hot through a sintered glass crucible (porosity M). After washing once with ethanol (90% v/v) and several times with hot water, the precipitate was dried for 2 hours at 95°C.

The analytical data (Table X) are explained in the DISCUSSION.

III.G.1.d. Precipitation of the 2-substituted 8-hydroxyquinoline complexes.

The tris complex of 2-methyl-8-hydroxyquinoline was prepared as described previously.[34] The infrared spectrum of the compound was recorded.

All attempts to prepare the 2-n-butyl-, 2-phenyl- and 2-(2'-thienyl)-8-hydroxyquinoline complexes, using the procedure of Section

TABLE IX

ANALYSES OF URANIUM(VI) COMPLEXES PRECIPITATED BY DILUTE BASE SOLUTION

Derivative	Colour	Formula	Calculated (%) C	H	N	U	Found (%) C	H	N	U
7-methyl-	dark-brown	$UO_2(C_{10}H_8NO)_2 \cdot H_2O$	39.74	3.00	4.64	39.38	39.30	3.20	4.55	39.58*
7-methyl-	dark-brown	$UO_2(C_{10}H_8NO)_2 \cdot H_2O$	39.74	3.00	4.64	39.38	39.79	3.33	4.79	38.82†
2,7-dimethyl-	brick-red	$UO_2(C_{11}H_{10}NO)_2 \cdot H_2O$	41.78	3.51	4.43	37.63	43.19	3.71	4.17	35.00*
2,7-dimethyl-	brick-red	$UO_2(C_{11}H_{10}NO)_2 \cdot H_2O$	41.78	3.51	4.43	37.63	42.53	3.65	4.33	36.12†
7-t-butyl-	red-brown	$UO_2(C_{13}H_{14}NO)_2 \cdot C_{13}H_{15}NO$	53.73	4.97	4.82	27.30	53.69	5.13	5.09	27.92†
		$UO_2(C_{13}H_{14}NO)_2 \cdot H_2O$	45.35	4.39	4.07	34.57				

*Precipitated by dilute sodium hydroxide.

†Precipitated by aqueous ammonia.

TABLE X

ANALYSES OF URANIUM(VI) COMPLEXES PRECIPITATED FROM AQUEOUS ACETONE SOLUTION

Derivative	Colour	Formula	Calculated (%)					Found (%)				
			C	H	N	Cℓ	U	C	H	N	Cℓ	U
7-t-butyl-		$UO_2(C_{13}H_{14}NO)_2 \cdot H_2O$	45.35	4.39	4.07		35.47					
7-t-butyl-	red-brown	$UO_2(C_{13}H_{14}NO)_2 \cdot OC(CH_3)_2$	47.81	4.70	3.84		32.67	49.66	4.81	4.34		32.41
7-t-butyl-		$UO_2(C_{13}H_{14}NO)_2 \cdot C_{13}H_{15}NO$	53.73	4.97	4.82		27.30					
5-chloro-	orange-brown	$UO_2(C_9H_5NOCℓ)_2 \cdot C_9H_6NOCℓ$	40.19	2.00	5.21	13.18	29.50	40.17	1.86	5.16	13.05	29.42

III.G.1.c. resulted in pale yellow precipitates of uranium hydroxide contaminated with uncomplexed reagent.

III.G.2. Composition of the 5,7-Dihalo-8-hydroxyquinoline Complexes Precipitated from Aqueous Acetone Solution

The bis and tris 5,7-dichloro- and 5,7-dibromo-8-hydroxyquinoline complexes of uranium(VI) were prepared according to the procedures of Moeller and Ramaniah,[39] in which the stoichiometric amounts of each reagent required to yield the appropriate compounds were used. Crystallization of an appreciable amount of reagent was observed when the filtrate from the tris 5,7-dichloro-8-hydroxyquinoline precipitation was cooled to 15°C. No reagent was observed in the filtrate of the corresponding 5,7-dibromo-8-hydroxyquinoline precipitation.

The colours of the four compounds were red-brown. The analytical data are presented in Table XI.

Although the compounds are of poor crystallinity, the X-ray powder diffraction photographs of the four compounds were taken. The calculable d-spacings are listed in Table XII.

The "tris" 5,7-dichloro-8-hydroxyquinoline complex was also prepared by (i) a modified procedure and (ii) from deuterated solvents.

(i) One millilitre of a solution of uranyl nitrate hexahydrate in water (30.66 mgU/ml, 0.13 millimoles U) was diluted to 50 ml with water containing 3 drops of concentrated nitric acid. The solution was warmed to 50°C and 33 ml of a solution of 0.3% w/v 5,7-dichloro-8-hydroxyquinoline (0.47 millimoles) in acetone was added slowly with stirring. The temperature was raised to approximately 60°C, and 2 M

TABLE XI

ANALYSES OF URANIUM(VI) COMPLEXES OF 5,7-DIHALO-8-HYDROXYQUINOLINES PREPARED BY LITERATURE METHOD

		Calculated (%)					C:X	Found (%)					C:X
Derivative	Proposed Formula	C	H	N	X	U	Ratio	C	H	N	X	U	Ratio
5,7-dichloro-	$UO_2(C_9H_4NOCl_2)_2$	31.06	1.16	4.02	20.37	34.19	1.52:1	32.27	2.12	3.58	19.17	29.27	1.69:1
5,7-dichloro-	$UO_2(C_9H_4NOCl_2)_2 \cdot C_9H_5NOCl_2$	35.63	1.44	4.62	23.37	26.15	1.52:1	35.42	2.90	3.91	20.19	22.43	1.75:1
5,7-dibromo-	$UO_2(C_9H_4NOBr_2)_2$	24.74	0.92	3.21	36.57	27.24	0.68:1	26.91	1.67	2.79	34.42	24.48	0.78:1
5,7-dibromo-	$UO_2(C_9H_4NOBr_2)_2 \cdot C_9H_5NOBr_2$	27.55	1.11	3.57	40.74	20.23	0.68:1	28.44	1.14	2.89	39.68	21.49	0.72:1

TABLE XII

d-SPACINGS (Å) OF URANIUM(VI) COMPLEXES OF 5,7-DIHALO-8-HYDROXYQUINOLINES PREPARED BY LITERATURE METHOD

5,7-Dichloro- Complexes		5,7-Dibromo- Complexes	
"bis"	"tris"	"bis"	"tris"
9.95(s)*	9.96(s)	9.54(w)	10.40(m)
8.62(s)	8.61(s)	8.83(w)	8.85(s)
7.49(s)	7.48(s)	8.25(w)	7.90(m)
5.43(w)	6.45(w)	6.55(m)	6.86(s)
4.96(w)	5.43(w)	5.50(s)	3.30(s)
4.76(w)	4.98(w)	5.02(m)	5.19(w)
4.40(s)	4.42(s)	4.82(s)	4.92(s)
3.90(m)	3.85(m)	4.35(w)	4.53(w)
3.65(m)	3.73(m)	3.98(m)	4.38(w)
3.41(m)	3.64(m)	3.83(m)	4.18(s)
	3.39(s)	3.61(w)	3.99(m)
		3.49(s)	3.78(m)
			3.60(m)
			3.42(s)

*Diffraction line-intensity ratings are given by (s) - strong, (m) - medium, (w) - weak and (vw) - very weak.

ammonia added dropwise with stirring until the pH was 7. The red-brown precipitate was digested for a few minutes, filtered hot through a sintered glass crucible (porosity M), washed with warm 40% v/v aqueous acetone followed by several times with hot water, and then dried for 2 hours at 95°C.

Calculated for $UO_2(C_9H_4NOC\ell_2)_2 \cdot H_2O$: 30.27% C, 1.41% H, 3.92% N, 19.86% Cℓ, %C:%Cℓ ratio 1.52:1.

Calculated for $UO_2(C_9H_4NOC\ell_2)_2 \cdot OC(CH_3)_2$: 33.44% C, 1.87% H, 3.71% N, 18.80% Cℓ, %C:%Cℓ ratio 1.78:1.

Found: 33.28% C, 1.84% H, 3.87% N, 18.99% Cℓ, 30.65% U, %C:%Cℓ ratio 1.75:1.

(ii) Twenty-one milligrams of uranyl nitrate hexahydrate (0.04 millimoles) were dissolved in 30 ml of a 40% v/v solution of acetone in deuterium oxide containing 1 drop of concentrated nitric acid. The solution was warmed to 50°C and 30 mg of 5,7-dichloro-8-hydroxyquinoline (0.14 millimoles) were added with stirring. A saturated solution of ammonia-d_3 in deuterium oxide was added dropwise until the "pH" was approximately 7. The red-brown precipitate was filtered hot through a sintered glass crucible (porosity M), washed with 3 2-ml portions of deuterium oxide, and then dried for 5 hours at 95°C.

The complex was also prepared by substituting 30 ml of 40% v/v acetone-d_6 solution in deuterium oxide for the acetone solution. This compound was dried for 1 hour at 90°C.

Further comment concerning the 5,7-dihalo-8-hydroxyquinoline complexes is given in the DISCUSSION.

III.G.3. Thermal Reactions

Selected complexes prepared in Sections III.G.1. and III.G.2. were heated in the thermal reaction apparatus described earlier (Section III.A.). The residues were examined by elemental and infrared analysis. The compounds that were heated and the analyses of the residues are given below.

The dark-brown uranium(VI) complex of 7-methyl-8-hydroxyquinoline (Section III.G.1.b.), $UO_2(C_{10}H_8NO)_2 \cdot H_2O$, was heated for 3 hours at 200-210°C to yield a green-black compound.

Calculated for $UO_2(C_{10}H_8NO)_2$: 40.96% C, 2.75% H, 4.78% N, 40.59% U.

Found: 40.61% C, 2.96% H, 5.11% N, 41.62% U.

The red-brown complex of 7-tert-butyl-8-hydroxyquinoline prepared from aqueous solution (Section III.G.1.b.) was heated for 3 hours at 225°C. The product was black.

Calculated for $UO_2(C_{13}H_{14}NO)_2$: 46.57% C, 4.21% H, 4.18% N, 35.50% U.

Found: 45.83% C, 3.98% H, 4.52% N, 35.67% U.

The complex of 7-tert-butyl-8-hydroxyquinoline prepared from aqueous acetone solution (Section III.G.1.c.) was heated for 3 hours at 225°C. An infrared spectrum of the black residue was obtained.

The red-brown complex of 5,7-dichloro-8-hydroxyquinoline prepared by the modified procedure (Section III.G.2.) was heated for 3 hours at 200°C to yield a green-black product.

Calculated for $UO_2(C_9H_4NOCl_2)_2$: 31.06% C, 1.16% H, 4.02% N, 20.37% Cl, 34.19% U, %C:%Cl ratio 1.52:1.

Found: 30.81% C, 1.41% H, 3.83% N, 20.52% Cl, 33.50% U, %C:%Cl ratio 1.50:1.

The red-brown complex of 5,7-dibromo-8-hydroxyquinoline thought by Moeller and Ramaniah to be the tris complex (Section III.G.2.) was heated for 3 hours at 225°C.

Calculated for $UO_2(C_9H_4NOBr_2)_2$: 24.74% C, 0.92% H, 3.21% N, 36.57% Br, 27.24% U, %C:%Br ratio 0.68:1.

Found (green-black): 24.81% C, 1.09% H, 3.16% N, 36.74% Br, 26.25% U, %C:%Br ratio 0.68:1.

When the green-black residues of the 5,7-dihalo-8-hydroxyquinoline complexes were treated with a few drops of acetone, the original red-brown colours of the compounds were immediately restored. The infrared spectra of these red-brown compounds were identical to those of the original complexes before the thermal reactions. Furthermore, on standing in air for an extended period of time (∿1 year), the green-black residues reverted to their former red-brown colours.

III.G.4. Infrared Spectra

Samples of the compounds for infrared study were prepared as mulls in anhydrous hexachloro-1,3-butadiene. Where it was appropriate, the mulls were prepared under dry-box conditions. All spectra were recorded from 5000-630 cm^{-1} using sodium chloride windows (6 mm). The spectra were calibrated against a polystyrene film.

The spectra of the complexes prepared in Section III.G.1. are given in Figures 1 and 2, Appendix F.* For purposes of comparison, the spectrum of the 8-hydroxyquinoline adduct is included in Figure 2. The spectra of the 5,7-dihalo-8-hydroxyquinoline complexes that were prepared according

*All infrared spectra are reproduced in Appendix F.

to the literature method are presented in Figure 3. The spectra of the 5,7-dichloro-8-hydroxyquinoline complexes that were prepared by the modified procedure and from deuterated solvents are given in Figure 4. The spectra of the thermal products (Section III.G.3) are reproduced in Figure 5.

III.F. Scandium(III) Complexes of 8-Hydroxyquinoline and Derivatives

III.F.1. Syntheses

III.F.1.a. Precipitation of the 2-chloro-8-hydroxyquinoline complex.

Ten millilitres of stock scandium chloride solution (0.35 millimoles Sc) were pipetted into a 400-ml beaker. Next, 500 mg of 2-chloro-8-hydroxyquinoline (2.79 millimoles) dissolved in 18 ml of acetone, 80 ml of water and 10 ml of 2 M acetic acid were added to the scandium solution. The solution was warmed to 60-70°C, and 50 ml of a buffer solution containing 30 ml of 2 M ammonium acetate solution and 20 ml of 2 M ammonia solution were added dropwise with stirring. The suspension was stirred for a further ten minutes. The pale-yellow precipitate was filtered hot through a sintered glass crucible (porosity M), washed copiously with cold water, and then dried for 4 hours at 90°C in vacuo. The pH of the filtrate was 8.5.

Calculated for $Sc(C_9H_5NOC\ell)_3 \cdot C_9H_6NOC\ell$: 5.91% Sc, 93.95% $C_9H_5NOC\ell$.

Calculated for $Sc(C_9H_5NOC\ell)_3 \cdot H_2O$: 7.51% Sc, 89.48% $C_9H_5NOC\ell^-$.

Found: 7.11% Sc,* 89.9% $C_9H_5NOC\ell^-$, $C_9H_5NOC\ell^-$:Sc ratio 3.2:1.†

*All scandium determinations were performed as follows. The solid to be analysed (∿0.1 g) was wet-oxidised with concentrated nitric acid (20 ml), and subsequently with fuming perchloric acid (4 ml). The colourless residue was diluted with water and the pH of an aliquot adjusted to ∿2.5. The aliquot was then titrated with standard EDTA solution, using xylenol orange as an indicator.(57)

†All ligand:Sc ratios are molar ratios.

III.F.1.b. Precipitation of the 4-chloro-8-hydroxyquinoline complex.

The procedure was similar to that in Section III.F.1.a., except that the acetone contained 628 mg of 4-chloro-8-hydroxyquinoline (3.50 millimoles), and the yellow precipitate was dried for 4 hours at 100°C in vacuo. The pH of the filtrate was 8.5.

Calculated for $Sc(C_9H_5NOC\ell)_3 \cdot H_2O$: 7.51% Sc, 89.48% $C_9H_5NOC\ell^-$.

Found: 7.43% Sc, 88.0% $C_9H_5NOC\ell^-$, $C_9H_5NOC\ell^-$:Sc ratio 3.0:1.

III.F.1.c. Precipitation of the 5-methyl-8-hydroxyquinoline complex.

The procedure was similar to that in Section III.F.1.a., except that the acetone contained 557 mg of 5-methyl-8-hydroxyquinoline (3.50 millimoles), and the yellow precipitate was dried overnight at 95°C in vacuo. The pH of the filtrate was 8.5.

Calculated for $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$: 6.62% Sc, 93.23% $C_{10}H_8NO^-$.

Calculated for $Sc(C_{10}H_8NO)_3 \cdot H_2O$: 8.36% Sc, 88.28% $C_{10}H_8NO^-$.

Found: 8.07% Sc, 89.5% $C_{10}H_8NO^-$, $C_{10}H_8NO^-$:Sc ratio 3.2:1.

III.F.1.d. Precipitation of the 4-methyl-8-hydroxyquinoline complex.

Ten millilitres of stock scandium chloride solution (0.35 millimoles Sc) were pipetted into a beaker containing 90 ml of water. The solution was warmed to 70-80°C, and 0.33 g of 4-methyl-8-hydroxyquinoline (2.07 millimoles) in 10 ml of 2 M acetic acid was added. The reagent was dissolved by stirring in the bulk solution for 15 minutes. Fifty ml of a buffer solution containing 30 ml of 2 M ammonium acetate solution and 20 ml of 2 M ammonia solution were added dropwise with stirring. The resulting suspension was stirred for 1 hour. The yellow precipitate was then filtered hot through a sintered glass crucible (porosity M), washed with 200 ml of water at

70-80°C, and dried overnight at 95°C *in vacuo*. The pH of the filtrate was 8.5.

Calculated for $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$: 6.62% Sc, 93.23% $C_{10}H_8NO^-$.

Found: 6.57% Sc, 92.5% $C_{10}H_8NO^-$, $C_{10}H_8NO^-$:Sc ratio 4.00:1.

III.F.1.e. Precipitation of the 8-deuteroxyquinoline complex.

Twenty milligrams of scandium chloride hexahydrate (0.08 millimoles) were dissolved in 20 ml of deuterium oxide. Fifty milligrams of 8-deuteroxyquinoline (0.34 millimoles) were dissolved in a minimum amount of acetic acid-d_4 and the resulting yellow solution added, with deuterium oxide washings, to the scandium solution. The solution was warmed to 70-80°C, and with stirring, a saturated solution of ammonia-d_3 in deuterium oxide was added dropwise until the "pH" was approximately 8.5. The yellow precipitate was stirred for a few minutes, filtered hot through a sintered glass crucible (porosity M), washed with 3 2-ml portions of deuterium oxide at 70-80°C, and then dried overnight at 40°C *in vacuo*.

III.F.1.f. Preparation of the 8-hydroxyquinoline complex from molten reagent.

One hundred milligrams of $Sc(C_9H_6NO)_3 \cdot H_2O$ (0.20 millimoles), prepared from aqueous solution as described below (Section III.F.2.), were thoroughly mixed with 145 mg of 8-hydroxyquinoline (1.00 millimoles). The mixture was ground to a fine powder and placed in an air oven at 90°C. As the yellow powder reached the temperature of the melting point of the reagent (∿73°C) its colour became orange. Above 80°C, a homogeneous melt was obtained, which was heated for a further 30 minutes at 90°C. On cooling, an orange glass was obtained. This material was ground to

a fine powder and placed in a vacuum desiccator at 100°C. Excess reagent was then removed by heating *in vacuo* overnight at this temperature. The solid was reground and the heating process repeated to yield a bright-orange powder.

Calculated for $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$: 7.22% Sc, 92.62% $C_9H_6NO^-$.

Found: 7.05% Sc, 92.3% $C_9H_6NO^-$, $C_9H_6NO^-$:Sc ratio 4.08:1.

III.G.1.g. Preparation of the 8-deuteroxyquinoline complex from molten reagent.

8-Deuteroxyquinoline was prepared by melting 8-hydroxyquinoline in an atmosphere of deuterium oxide.

Twenty milligrams of $Sc(C_9H_6NO)_3 \cdot D_2O$ (0.04 millimoles), prepared as described in Section III.F.1.e., were ground with 58 mg of 8-deuteroxyquinoline (0.40 millimoles). The powder was placed in a 10-ml beaker, which was in turn placed in a 50-ml ground glass-stoppered bottle containing 5 ml of deuterium oxide. The bottle was stoppered and heated for 5 mins. at 80°C. The ground product was heated *in vacuo* overnight at 60°C to remove most of the excess 8-deuteroxyquinoline. The remaining excess reagent was removed in a similar manner to that described in Section III.F.1.f. The final product was an orange powder.

III.F.2. Composition of the 8-Hydroxyquinoline Complex

Four different procedures were used to prepare the scandium(III) complex.

(i) In the first procedure, varying amounts of 8-hydroxyquinoline were added to a given amount of the metal-ion. The procedure was as follows.

Ten millilitres of stock scandium chloride solution (0.35 millimoles

Sc) were pipetted into a 400-ml beaker containing 100 ml of water. The solution was warmed to 70-80°C, and 10 ml of a 5.0, 3.5, 3.0, 2.5 or 2.0% w/v solution of 8-hydroxyquinoline in 2 M acetic acid was added (3.45, 2.41, 2.07, 1.72 and 1.38 millimoles of reagent, respectively). Forty-five ml of a buffer solution (30 ml of 2 M ammonium acetate solution and 15 ml of 2 M ammonia solution) were added dropwise with stirring, and the resulting suspension stirred for 1 hour. The lemon-yellow precipitate was filtered hot, washed with 100 ml of water at room temperature, and dried overnight at 40°C in vacuo. The pH of the filtrate was in the range 7.8-8.0.

Each precipitation was done in duplicate. The dried precipitates were analysed for 8-hydroxyquinoline and scandium; the results are given in Table XIII. The calculated analyses for several possible compositions are given in Table XIV.

The procedure using 3.45 millimoles of 8-hydroxyquinoline (i.e., a ligand-to-metal ratio of 9.9:1) closely approximated that used by Pokras and Bernays.[47] The resulting complex is hereafter referred to as Pokras and Bernays' compound. These workers suggested that the compound could be freed of water and contaminating reagent by heating for 2-5 hours at 100-110°C in an air-oven (i.e., to constant weight). The data of Table XV show, however, that this compound slowly loses weight continuously.

(ii) In the second procedure, the compound was precipitated from mixed aqueous organic solvents. In one experiment, 100 ml of 16% v/v aqueous ethanol was substituted for 100 ml of water, and in another, 100 ml of 16% v/v aqueous acetone was used. In both experiments, 3.45

TABLE XIII

EFFECT OF REAGENT CONCENTRATION AND SOLVENT ON THE COMPOSITION OF THE SCANDIUM(III) COMPLEX OF 8-HYDROXYQUINOLINE

(Dried at 40°C in vacuo; Sc taken, 0.35 millimoles)

Solvent	Reagent Conc. in 2 M HOAc (% w/v)	C_9H_7NO:Sc Ratio Used	$C_9H_6NO^-$ Found (%)*	Sc Found (%)*	Sum (%)	$C_9H_6NO^-$:Sc Ratio Found
aqueous	5.0	9.9:1	90.1	6.97	97.1	4.03:1
			90.0	6.87	96.8	4.08:1†
aqueous	3.5	6.9:1	89.5	7.22	96.7	3.86:1
			89.9	7.06	97.0	3.96:1
aqueous	3.0	5.9:1	89.0	7.27	96.3	3.82:1
			89.4	7.22	96.6	3.86:1
aqueous	2.5	4.9:1	87.0	8.92	95.9	3.04:1
			87.4	8.66	96.1	3.14:1
aqueous	2.0	4.0:1	87.2	8.98	96.2	3.03:1
			87.5	8.99	96.5	3.04:1
10% v/v aqueous ethanol	5.0	9.9:1	89.5	7.04	96.5	3.97:1
			89.3	7.13	96.4	3.91:1
10% v/v aqueous acetone	5.0	9.9:1	87.9	8.19	96.1	3.25:1
			87.6	7.72	95.3	3.54:1

*For the $C_9H_6NO^-$ and Sc determinations, the precision was ±0.1 and ±0.02%, respectively. The errors are discussed in Section IV.G.

†This compound was prepared by the procedure of Pokras and Bernays; found: 67.00% C, 4.09% H, 8.65% N.

TABLE XIV

CALCULATED ANALYSES OF POSSIBLE SCANDIUM(III) COMPLEXES OF 8-HYDROXYQUINOLINE

Compound	C (%)	H (%)	N (%)	Sc (%)	$C_9H_6NO^-$ (%)
$Sc(C_9H_6NO)_3$	67.93	3.80	8.80	9.42	90.58
$Sc(C_9H_6NO)_3 \cdot H_2O$	65.46	4.07	8.48	9.07	87.29
$Sc(C_9H_6NO)_3 \cdot NH_3$	65.59	4.27	11.33	9.09	87.46
$Sc(C_9H_6NO)_3 \cdot C_9H_7NO$	69.45	4.05	9.00	7.22	92.62

TABLE XV

HEATING OF POKRAS AND BERNAYS' COMPOUND AT 105°C

(Initially dried at 40°C *in vacuo*.)

Total Time (hrs)	Wt. of Compound (mg)	Wt. Difference from Original (mg)
0	84.5	-
1.0	83.9	0.6
5.5	82.9	1.6
19.5	81.9	2.6
43.0	80.8	3.7
67.5	79.5	5.0
91.5	78.5	6.0
114.5	77.7	6.8
159.5	76.6	7.9
207.5	75.0	9.5
255.0	74.0	10.5
688.0	68.8	14.3

millimoles of 8-hydroxyquinoline was used and the final pH values were 7.9. The analyses of the compounds are included in Table XIII.

(iii) In the third procedure, the compound was prepared by procedure (i), except that 7.35 ml of scandium chloride solution (0.26 millimoles Sc) was substituted for the 10-ml aliquot, the reagent was added as 10 ml of a 2.26% w/v solution in 2 M acetic acid (1.56 millimoles reagent; reagent:scandium molar ratio 6:1) and the precipitate was washed with 100 ml of water at 70-80°C. The final pH was 7.9. The compound was prepared twice.

Samples of the compound were dried overnight at 40°C, for 3 hours at 100°C, and for 14 hours at 100°C in vacuo. The analyses are given in Table XVI.

Compound C (dried 100°C/14 hrs) of Table XVI was heated in an air-oven for a total of 161 hours at 105°C with periodic cooling and weighing. The results (Table XVII) served as a comparison with the air-heating of Pokras and Bernays' compound (Table XV).

(iv) In the fourth procedure, the final pH of precipitation was varied but kept below a value of 7.0. The procedure was as follows.

Ten millilitres of the stock scandium chloride solution (0.35 millimoles Sc) were pipetted into a 400-ml beaker containing 100 ml of water. The solution was warmed to 70-75°C and 10 ml of a 2.26% v/v solution of 8-hydroxyquinoline in 2 M acetic acid added (1.56 millimoles; reagent:scandium molar ratio 4.5:1).A buffer solution (1.33 M in ammonium acetate and 0.67 M in ammonia) was added dropwise until the required pH was obtained (pH paper). The suspension was stirred for 15 minutes at 70-75°C. The yellow precipitate was filtered hot, washed with three

TABLE XVI

EFFECT OF DRYING CONDITIONS ON THE COMPOSITION OF THE COMPLEX PREPARED BY PROCEDURE (iii)

(Sc taken, 0.26 millimoles; C_9H_7NO:Sc molar ratio used, 6:1)

Drying Condition (in vacuo)	$C_9H_6NO^-$ Found (%)	Sc Found (%)	Sum (%)	$C_9H_6NO^-$:Sc Ratio Found
*A. 40°C/4 hrs	86.6	9.01	95.6	3.00:1
	86.7	9.01	95.7	3.00:1
B. 100°C/3 hrs	87.1	9.05	96.2	3.00:1
*C. 100°C/14 hrs	87.4	9.06	96.5	3.00:1

*Elemental analyses: A. 65.84% C, 4.00% H, 8.75% N.

C. 65.24% C, 4.17% H, 8.59% N.

TABLE XVII

HEATING OF COMPLEX PREPARED BY PROCEDURE (iii) AT 105°C

(Initially dried at 40°C *in vacuo*)

Total Time (hrs)	Wt. of Compound (mg)	Wt. Difference from Original (mg)
0	107.8	-
1	107.7	0.1
20	107.5	0.3
67	107.3	0.5
112	106.9	0.9
161	106.7	1.1

portions of water at room temperature, and then dried in vacuo overnight at 100°C. The pH of the filtrate was accurately determined at room temperature with a pH meter.

The analyses of the compounds are given in Table XVIII.

The 100 Mc proton magnetic resonance spectra of the compound prepared at pH 6.2 (ligand-to-metal ratio 2.70:1), and of the compound prepared according to procedure (iii) (dried at 100°C/14 hours) are shown in Figure 4.

The compound prepared at pH 6.2 was sufficiently soluble in organic solvents for molecular-weight determination by vapour-phase osmometry. Initially, the osmometer was calibrated with solutions of benzil in benzene of known concentrations. The molecular weight found was 760±50 (average of seven determinations).

Further studies of the scandium(III) complexes are presented later in the EXPERIMENTAL AND RESULTS. The compounds prepared by procedure (iii) (dried 100°C/14 hours) and precipitated at pH 6.2 are shown in the DISCUSSION to have the formulae $Sc(C_9H_6NO)_3 \cdot H_2O$ and $Sc(C_9H_6NO)_{2.7}(OAc)_{0.3}$, respectively.

III.F.3. Composition of the 2-Methyl-8-hydroxyquinoline Complex

The details given by Phillips et al.[34] for the preparation of the complex are incomplete. In this work, the compound was prepared by the following three procedures.

(i) Varying amounts of 2-methyl-8-hydroxyquinoline were added for a given amount of the metal-ion. The procedure was as follows. Ten millilitres of stock scandium chloride solution (0.35 millimoles Sc) were pipetted into a 400-ml beaker containing 100 ml of water.

TABLE XVIII

EFFECT OF pH ON THE COMPOSITION OF THE SCANDIUM(III) COMPLEX OF 8-HYDROXYQUINOLINE

(Dried at 100°C *in vacuo*; Sc taken, 0.35 millimoles; C_9H_7NO:Sc molar ratio used, 4.5:1)

pH	$C_9H_6NO^-$ Found (%)	Sc Found (%)	Sum (%)	$C_9H_6NO^-$:Sc Ratio Found
5.0	83.4	10.08	93.5	2.58:1
	83.5	10.03	93.5	2.60:1
5.4	84.6	9.91	94.5	2.66:1
5.8	84.6	9.84	94.4	2.68:1
	84.2	9.89	94.1	2.66:1
6.2	85.2	9.86	94.9	2.70:1
6.6	86.1	9.72	95.8	2.76:1
	86.1	9.74	95.8	2.76:1
6.8	86.2	9.67	95.9	2.78:1
7.0	87.0	9.04	96.0	3.00:1

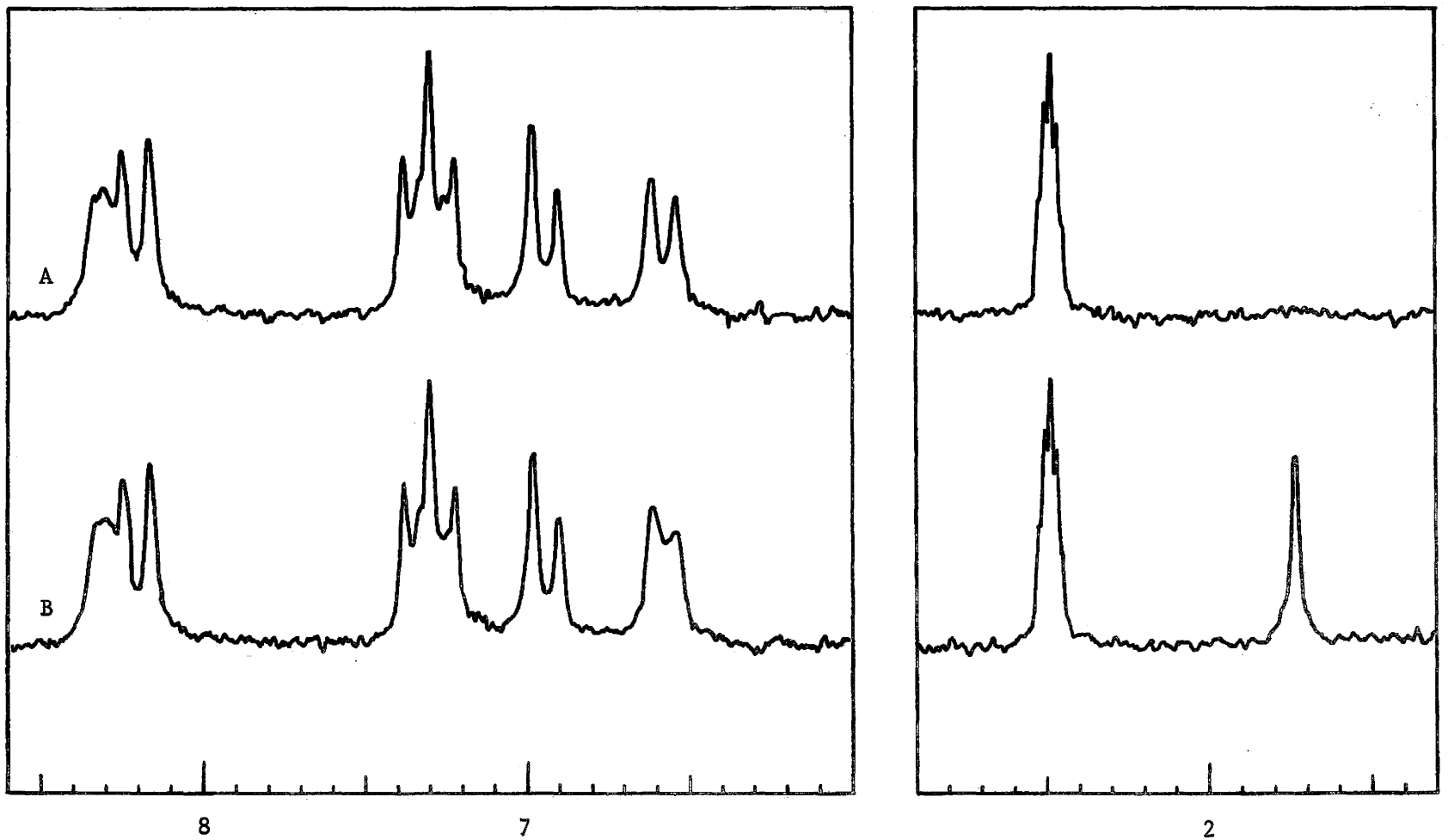


Figure 4. Proton magnetic resonance spectra of Sc(III) complexes of 8-hydroxyquinoline in dimethysulfoxide-d_6. Dimethylsulfoxide absorption at 2.48 ppm in both spectra. A. $Sc(Q)_3 \cdot H_2O$; B. $Sc(Q)_{2.7}(OAc)_{0.3}$.

The solution was warmed to 70-80°C and 10 ml of a 5.6, 3.3 or 2.3% w/v solution of 2-methyl-8-hydroxyquinoline in 2 M acetic acid was added (3.51, 2.07 and 1.44 millimoles of reagent, respectively). Fifty ml of buffer solution (30 ml of 2 M ammonium acetate solution and 20 ml of 2 M ammonia solution) were added dropwise with stirring, and the resulting suspension was stirred for 30 minutes. The bright yellow precipitate was filtered hot, washed with 100 ml of water at room temperature, and dried overnight at 40°C in vacuo. The pH values of the filtrates were in the range 8.3-8.5.

The analyses of the compounds are given in Table XIX. The calculated analyses of several possible scandium complexes of 2-methyl-8-hydroxyquinoline are given in Table XX.

(ii) Procedure (i) was repeated substituting 100 ml of 18% v/v aqueous acetone solution for 100 ml of water, and using 3.51 millimoles of reagent. The final pH value was 8.5. The analyses of two compounds prepared in this manner are included in Table XIX.

(iii) In this procedure, the final pH of precipitation was varied but kept below a value of 7.0. The procedure for each preparation was similar to that in (i) except that 2.07 millimoles of reagent were used and the buffer solution was added dropwise until the required pH was reached. The pH values of the filtrate were determined accurately with a pH meter. The analyses of the compounds are given in Table XXI.

None of the compounds prepared by the three procedures above could be washed with water at 70-80°C. The scandium(III) complex of 2-methyl-8-hydroxyquinoline is hydrolysed by water at this temperature. For example, a compound with the initial ligand-to-metal ratio of 4.00:1

TABLE XIX

EFFECT OF REAGENT CONCENTRATION AND SOLVENT ON THE COMPOSITION OF THE SCANDIUM(III) COMPLEX OF 2-METHYL-8-HYDROXYQUINOLINE

(Dried at 40°C *in vacuo*; Sc taken, 0.35 millimoles)

Solvent	Reagent Conc. in 2 M HOAc (% w/v)	$C_{10}H_9NO$:Sc Ratio Used	$C_{10}H_8NO^-$* Found (%)	Sc Found (%)	Sum (%)	$C_{10}H_8NO^-$:Sc Ratio Found
aqueous	5.6	10:1	90.0	6.09	96.1	4.20:1
			89.4	6.12	95.5	4.15:1
aqueous	3.3	5.9:1	88.4	6.26	94.7	4.01:1
aqueous	2.3	4.1:1	88.3	7.16	95.5	3.50:1
10% v/v aqueous acetone	5.6	10:1	88.3	6.28	94.6	3.99:1
			88.5	6.29	94.8	4.00:1

*For the $C_{10}H_8NO^-$ determinations, the precision was ±0.1%. The error is discussed in Section IV.G.

TABLE XX

CALCULATED ANALYSES OF POSSIBLE SCANDIUM(III) COMPLEXES OF 2-METHYL-8-HYDROXYQUINOLINE

Compound	Sc (%)	$C_{10}H_8NO^-$ (%)
$Sc(C_{10}H_8NO)_3$	8.65	91.35
$Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$	6.62	93.23
$Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$	6.29	88.53

TABLE XXI

EFFECT OF pH ON THE COMPOSITION OF THE SCANDIUM(III) COMPLEX OF 2-METHYL-8-HYDROXYQUINOLINE

(Dried at 40°C <u>in vacuo</u>; Sc taken, 0.35 millimoles; $C_{10}H_9NO$:Sc molar ratio used, 5.9:1)

pH	$C_{10}H_8NO^-$ Found (%)	Sc Found (%)	Sum (%)	$C_{10}H_8NO^-$:Sc Ratio Found
5.5	88.3	6.27	94.6	4.00:1
6.5	88.5	6.29	94.8	4.00:1
7.0	88.5	6.28	94.8	4.00:1

was washed with 1 litre of water at 70-80°C in 25-ml portions. The ligand-to-metal ratio of the dried residue was 1.6:1.

Further studies of the 2-methyl-8-hydroxyquinoline complex, shown in the DISCUSSION to have the formula $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$, are presented later in the EXPERIMENTAL AND RESULTS.

III.F.4. Thermal Studies

III.F.4.a. Thermogravimetry.

The main purpose of the thermogravimetric studies was to obtain information concerning the thermal stability and composition of selected scandium(III) complexes that were prepared in Sections III.F.1., III.F.2., and III.F.3.

Samples of the compounds were placed in a small silica crucible and heated in the thermobalance at an initial heating rate of 1°C per minute (average) to approximately 160°C, and thereafter, at 6°C per minute. The compounds were heated in air at atmospheric pressure to the constant-weight level associated with scandium oxide (~550-600°C). All thermograms were corrected for the buoyancy of the crucible.

The thermograms of the various 8-hydroxyquinoline complexes are given in Figure 5. The three curves represent the $Sc(C_9H_6NO)_3 \cdot H_2O$ compound (Section III.F.2., procedure (iii)), Pokras and Bernays' compound (Section III.F.2., procedure (i)), and the melt product, $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ (Section III.F.1.f.).

The thermograms of the 2-methyl-8-hydroxyquinoline complex, $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$ (Section III.F.3.) and the 4-methyl-8-hydroxyquinoline complex, $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$ (Section III.F.1.d.) are given in Figure 6.

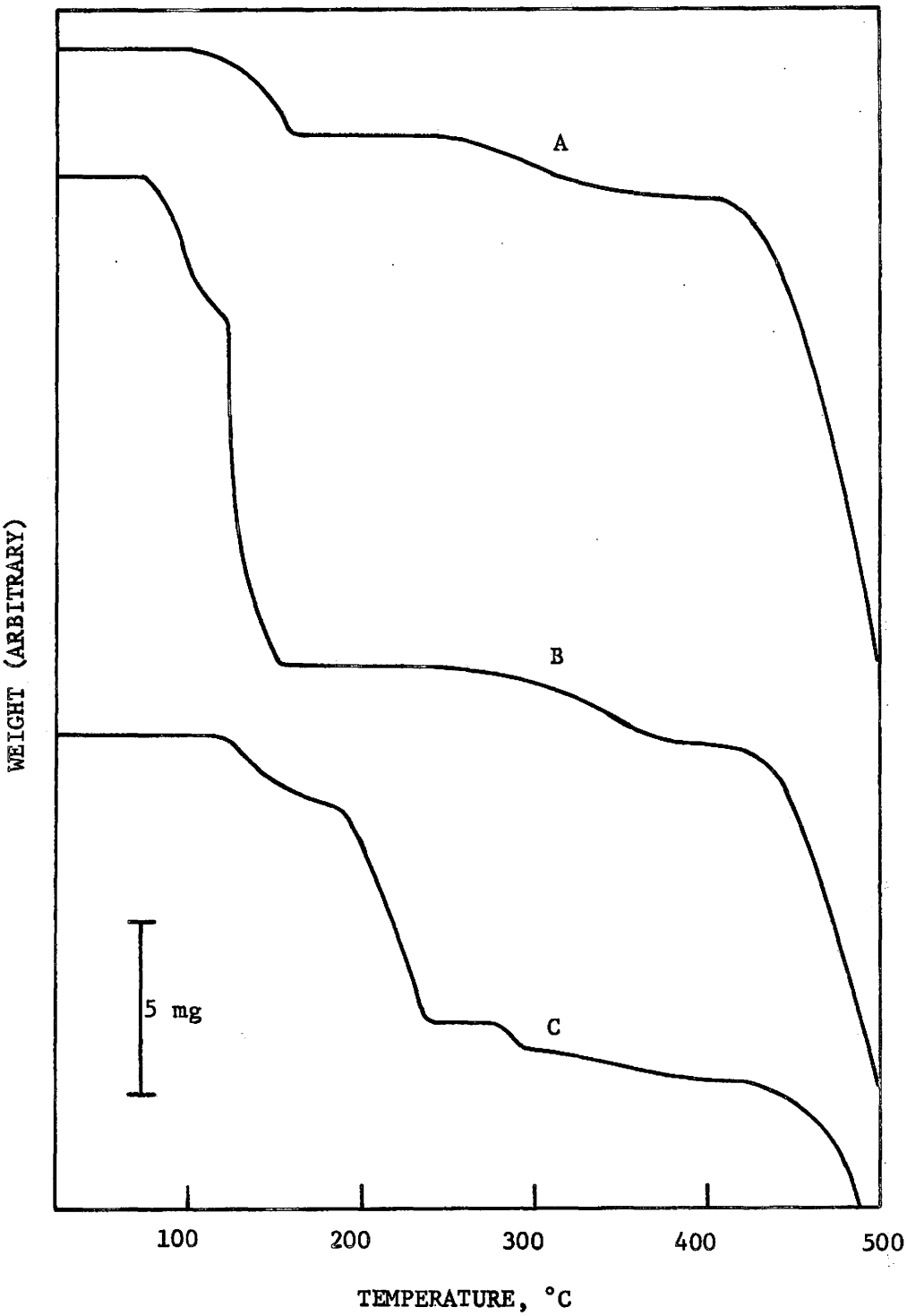


Figure 5. Thermograms of Sc(III) complexes of hydroxyquinoline. A. $Sc(Q)_3 \cdot H_2O$ (initial weight 58.9 mg); B. Pokras and Bernays' compound (58.6 mg); C. Melt product, $Sc(Q)_3 \cdot QH$ (32.9 mg).

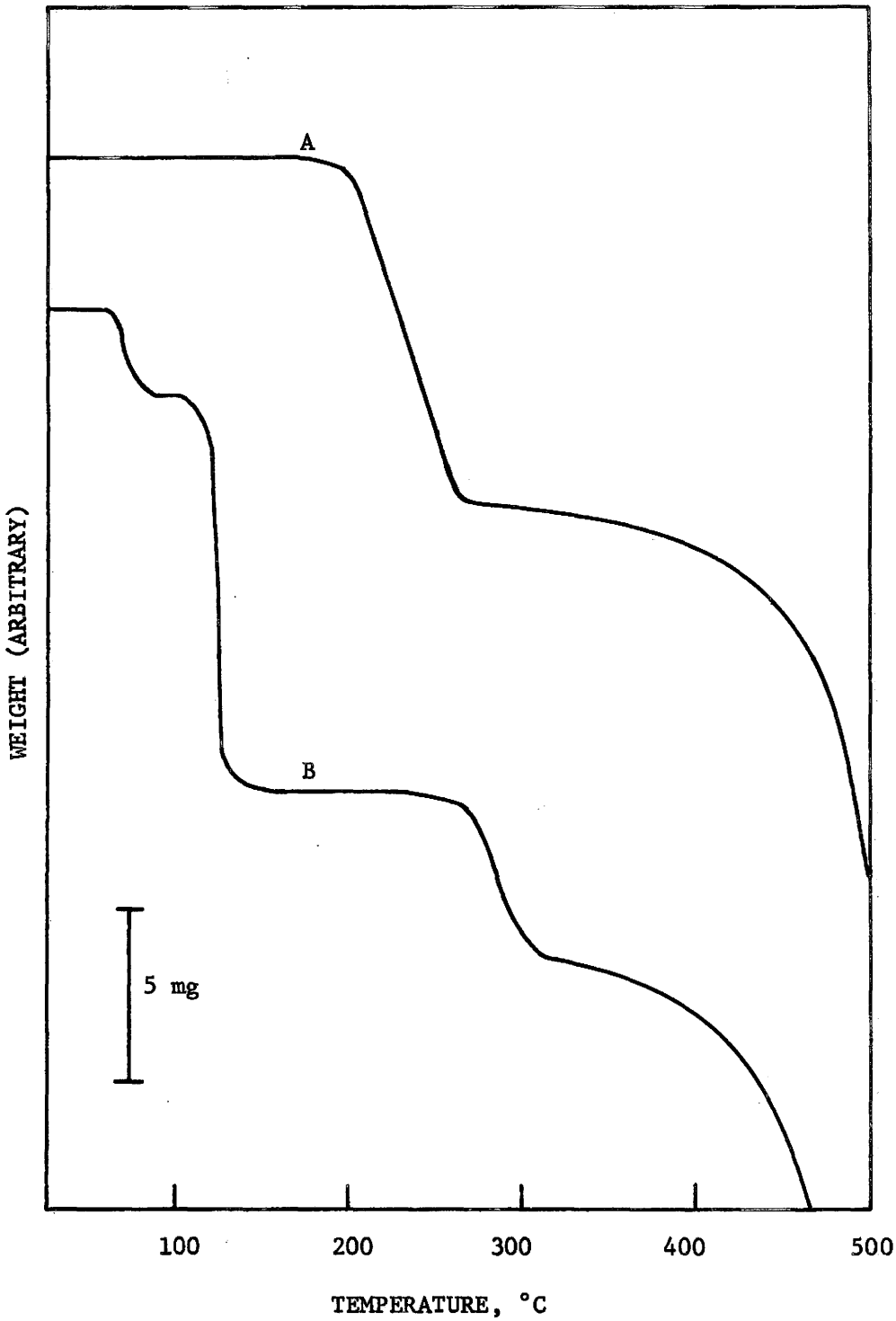


Figure 6. Thermograms of Sc(III) complexes of 2-methyl- and 4-methyl-8-hydroxyquinoline. A. $Sc(4\text{-Me-Q})_3 \cdot 4\text{-Me-QH}$ (45.6 mg); B. $Sc(2\text{-Me-Q})_3 \cdot 2\text{-Me-QH} \cdot 2H_2O$ (55.1 mg).

For convenience, the constant-weight levels of scandium oxide are omitted from Figures 5 and 6.

III.F.4.b. Thermal reactions.

Selected scandium(III) complexes were heated in the thermal reaction apparatus described earlier (Section III.A.) in order to obtain thermal products for further study. The thermograms (Section III.F.4.a., above) served as a guide for the selection of conditions.

The lemon-yellow 8-hydroxyquinoline complex, $Sc(C_9H_6NO)_3 \cdot H_2O$, was heated for varying times and temperatures (Table XXII). The sublimed 8-hydroxyquinoline collected in the U-tube was determined bromometrically. The analyses of the yellow residues and of the sublimed reagent are given in Table XXII.

The melt product, $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$, was heated slowly to 200°C. At ∿190°C, the compound appeared to bubble and melt. The dark-green fused residue became lime-green on crushing.

Calculated for $Sc(C_9H_6NO)_3$: 9.42% Sc, 90.58% $C_9H_6NO^-$.

Found: 8.83% Sc, 91.0% $C_9H_6NO^-$, $C_9H_6NO^-$:Sc ratio 3.21:1.

The 2-methyl-8-hydroxyquinoline complex $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$, was heated under conditions similar to those described for the 8-hydroxyquinoline complex. The analytical data are given in Table XXIII. The compounds heated below 90°C retained the bright-orange colour of the original compound. The residues at 135-140 and 165-170°C were each lime-green.

The yellow 4-methyl-8-hydroxyquinoline complex, $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$, was heated slowly to 230°C. At approximately 205°C the compound melted. The dark-green fused residue became lime-green on crushing.

TABLE XXII

THERMAL REACTIONS OF THE SCANDIUM(III) COMPLEX OF 8-HYDROXYQUINOLINE

(Calculated for $Sc(C_9H_6NO)_3$: 9.42% Sc, 90.58% $C_9H_6NO^-$)

Temp. (°C)	Wt. of Sample (mg)	Time of Heating (hrs)	Sublimed C_9H_7NO (mg)	$C_9H_6NO^-$ Found (%)	Sc Found (%)	Sum (%)	$C_9H_6NO^-$:Sc Ratio Found
*100	101.0	24	>0.1	87.4	9.06	96.5	3.00:1
160-165	101.4	15	3.3	88.8	9.60	98.4	2.88:1
165-170	94.2	23	3.5	89.1	9.71	98.8	2.86:1
165-170	100.8	24	3.4	89.2	9.70	98.9	2.87:1
180-185	97.4	10	1.5	89.5	9.54	99.0	2.92:1
180-185	99.6	27	1.4	89.6	9.57	99.2	2.92:1
200-210	101.7	6	1.5	89.3	9.59	98.9	2.90:1
200-210	104.1	18	1.4	89.4	9.53	98.9	2.91:1

*Control experiment for sublimed C_9H_7NO.

TABLE XXIII

THERMAL REACTIONS OF THE SCANDIUM(III) COMPLEX OF 2-METHYL-8-HYDROXYQUINOLINE

(Calculated for $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$: 6.62%, 93.23% $C_{10}H_8NO^-$;

Calculated for $Sc(C_{10}H_8NO)_3$: 8.65% Sc, 91.35% $C_{10}H_8NO^-$)

Temp. (°C)	Wt. of Sample (mg)	Time of Heating (hrs)	Sublimed $C_{10}H_9NO$ (mg)	Calc. Subl.* C_9H_7NO (mg)	$C_{10}H_8NO^-$ Found (%)	Sc Found (%)	Sum (%)	$C_{10}H_8NO^-$:Sc Ratio Found
75	98.4	2	1.0	-	91.9	6.66	98.6	3.93:1
90	108.1	1	0.9	-	92.0	6.66	98.7	3.93:1
135-140	214.5	2	44.2	47.8	90.6	8.49	99.1	3.05:1
165-170	206.0	5	43.6	45.9	91.1	8.58	99.7	3.02:1

*The calculated amount of reagent obtained from the reaction:

$$Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O \xrightarrow{\Delta} Sc(C_{10}H_8NO)_3 + C_{10}H_9NO + 2H_2O$$

Calculated for $Sc(C_{10}H_8NO)_3$: 8.65% Sc, 91.35% $C_{10}H_8NO^-$.

Found: 8.38% Sc, 91.4% $C_{10}H_8NO^-$, $C_{10}H_8NO^-$:Sc ratio 3.09:1.

The yellow 4-chloro-8-hydroxyquinoline complex, $Sc(C_9H_5NOCl)_3 \cdot H_2O$ (Section III.F.1.b.), was heated overnight at 165-170°C. An infrared spectrum was obtained of the bright-yellow residue.

Insufficient quantities of the 2-chloro- and 5-methyl-8-hydroxyquinoline complexes were available for thermal studies.

III.F.5. Infrared Spectra

All spectra were recorded as described in Section III.G.4.

The spectra of various 8-hydroxyquinoline complexes are given in Figure 6. The spectra of the complexes of 8-hydroxyquinoline derivatives are given in Figures 7 and 8, and those of the thermal products (Section III.F.4.b.) in Figure 9.

III.F.6. X-Ray Powder Crystallography

The d-spacings of Pokras and Bernays' compound, of $Sc(C_9H_6NO)_3 \cdot H_2O$, and of 8-hydroxyquinoline are compared in Table XXIV.

No diffraction lines were observed for the thermal product obtained by heating $Sc(C_9H_6NO)_3 \cdot H_2O$ at 180-185°C for 10 hours (Table XXII). These compounds are amorphous. Similarly, $Sc(C_9H_6NO)_{2.7}(OAc)_{0.3}$ was found to be amorphous.

The calculated d-spacings of the 2-methyl-8-hydroxyquinoline complex and its thermal products obtained at 90°C and 135-140°C (Table XXIII) are given in Table XXV.

The X-ray powder data is used in the DISCUSSION.

TABLE XXIV

d-SPACINGS (Å) OF SCANDIUM(III) COMPLEXES OF 8-HYDROXYQUINOLINE

$Sc(C_9H_6NO)_3 \cdot H_2O$	Pokras and Bernays' Compound	C_9H_7NO
12.1 ± 0.1 (m)*	14.14 (m)	9.43 (m)
10.63 ± 0.04 (s)	12.19 (w)	7.18 (w)
9.6 ± 0.1 (w)	10.72 (m)	6.25 (s)
7.81 ± 0.03 (m)	8.59 (m)	5.78 (w)
6.59 ± 0.04 (vw)	7.87 (m)	4.73 (vw)
6.23 ± 0.02 (m)	7.53 (w)	4.48 (vw)
5.51 ± 0.02 (vw)	7.00 (w)	3.77 (s)
4.91 ± 0.01 (m)	6.63 (m)	3.54 (w)
4.67 ± 0.01 (w)	6.22 (vw)	3.48 (s)
4.36 ± 0.01 (s)	5.79 (vw)	3.29 (m)
4.12 ± 0.03 (w)	5.47 (vw)	3.17 (s)
3.82 ± 0.01 (s)	5.22 (vw)	2.99 (vw)
3.73 ± 0.01 (w)	4.85 (w)	2.92 (vw)
3.51 ± 0.01 (w)	4.56 (vw)	2.87 (vw)
3.32 ± 0.01 (w)	4.23 (s)	2.80 (vw)
3.16 ± 0.04 (w)	4.01 (vw)	2.61 (vw)
3.08 ± 0.04 (w)	3.87 (s)	
2.97 ± 0.01 (vw)	3.66 (vw)	
2.85 ± 0.01 (vw)	3.45 (w)	
2.75 ± 0.01 (vw)	3.32 (vw)	
	3.19 (vw)	
	3.01 (vw)	
	2.85 (vw)	
	2.72 (vw)	

*Mean and standard deviation of five exposures.

TABLE XXV

d-SPACINGS (Å) OF SCANDIUM(III) COMPLEXES OF 2-METHYL-8-HYDROXYQUINOLINE

$Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$	Thermal Product 90°C	Thermal Product 135-140°C
10.25 (w)	8.67 (s)	12.54 (s)
9.38 (s)	8.39 (s)	10.98 (s)
8.78 (s)	7.14 (w)	9.94 (m)
7.48 (m)	6.61 (w)	8.63 (w)
5.18 (w)	5.68 (w)	7.94 (s)
4.96 (w)	5.36 (w)	7.60 (s)
4.43 (m)	4.44 (w)	7.03 (w)
4.30 (m)	4.19 (w)	6.76 (w)
4.11 (s)	3.96 (w)	6.24 (w)
3.97 (m)	3.76 (m)	5.68 (w)
3.71 (w)	3.21 (vw)	5.51 (m)
3.42 (w)	3.07 (vw)	5.08 (m)
3.33 (w)	2.97 (vw)	5.00 (m)
3.17 (w)	2.76 (vw)	4.85 (m)
2.92 (w)		4.71 (w)
		4.40 (vw)
		4.13 (vw)
		3.81 (m)
		3.72 (m)
		3.52 (s)
		3.44 (s)
		3.39 (w)
		3.29 (m)
		3.11 (w)

III.F.7. Effect of Solvents on the Complexes

The solubilities of the following 8-hydroxyquinoline complexes in dry chloroform were determined: (i) $Sc(C_9H_6NO)_3 \cdot H_2O$, (ii) the thermal product of $Sc(C_9H_6NO)_3 \cdot H_2O$ heated at 180-185°C for 10 hours, and (iii) $Sc(C_9H_6NO)_{2.7}(OAc)_{0.3}$. The procedure was as follows.

Initially, a saturated solution of the compound was made by gradually dissolving the solid in 5 ml of chloroform. The solution was then transferred to a 50-ml weighing bottle containing a further 100 mg of the compound. The bottle was stoppered and placed for 24 hours in a thermostated bath at 25.0 ± 0.1°C. Periodically, the bottle was shaken thoroughly. Next, the mixture was centrifuged and an aliquot of the supernatant liquor was analysed for scandium. The solubilities are: $Sc(C_9H_6NO)_3 \cdot H_2O$, 0.13 mg Sc/ml; thermal product, 3.0 mg Sc/ml; and $Sc(C_9H_6NO)_{2.7}(OAc)_{0.3}$, 5.7 mg Sc/ml.

The effect of 1,2-dichloroethane on Pokras and Bernays' compound was also investigated. The experiment was performed in a similar manner to that of the solubility determinations, except that residual compound was filtered through a sintered glass crucible (porosity F) and the filtrate discarded. The solid was washed with two 1-ml portions of 1,2-dichloroethane, dried <u>in vacuo</u> overnight at 40°C, and then analysed for scandium and 8-hydroxyquinoline.

Calculated for $Sc(C_9H_6NO)_3 \cdot H_2O$: 9.07% Sc, 87.29% $C_9H_6NO^-$.

Found: 8.85% Sc, 85.5% $C_9H_6NO^-$, $C_9H_6NO^-$:Sc ratio 3.01:1.

In a similar experiment, the effect of 1,2-dichloroethane on the 2-methyl-8-hydroxyquinoline complex, $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$, was investigated.

Found: 11.70% Sc, 80.3% $C_{10}H_8NO^-$, $C_{10}H_8NO^-$:Sc ratio 1.95:1.

III.F.8. Ligand Addition Reaction

An addition reaction between 4-methyl-8-hydroxyquinoline and the thermal product of its complex (Section III.F.4.b.) was attempted. The procedure was as follows.

Eighty-five milligrams of $Sc(C_{10}H_8NO)_3$ (0.16 millimoles) were ground to a fine lime-green powder and placed with 260 mg of 4-methyl-8-hydroxyquinoline (1.64 millimoles) in a 50-ml weighing bottle containing a magnetic stirring bar and 5 ml of 1,2-dichloroethane. The bottle was stoppered and placed in a thermostated bath for 24 hours at 25.0 ± 0.1°C. The mixture was stirred continuously throughout the reaction period. The resulting bright-yellow solid was filtered, washed with three 1-ml portions of 1,2-dichloroethane and dried <u>in vacuo</u> overnight at 95°C.

Calculated for $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$: 6.62% Sc, 93.23% $C_{10}H_9NO^-$.

Found: 6.53% Sc, 91.4% $C_{10}H_9NO^-$, $C_{10}H_9NO^-$:Sc ratio 3.98:1.

IV. DISCUSSION

IV.A. Characterization of 8-Hydroxyquinoline Derivatives

Elemental analysis, infrared, mass and proton magnetic resonance spectrometry were used to characterize the new ligand, 7-tert-butyl-8-hydroxyquinoline (Section III.C.). Also the PMR spectra of all ligands used in this work were recorded, mainly to confirm the structure of ligands synthesized previously in this laboratory.

Table III shows the data obtained from the PMR spectra. The three protons in the pyridine ring of 8-hydroxyquinoline exhibit an ABX system (A, Figure 1). The quartet appearing farthest downfield, centered at 8.76 ppm, is assigned to the H_2 proton. The quartet centered at 8.04 ppm is assigned to H_4 while the absorption by the H_3 quartet overlaps the spectrum of the phenol ring protons in the region 7.0 - 7.6 ppm. These results, as well as the $J_{2,3}$, $J_{3,4}$ and $J_{2,4}$ values given in Table III, agree with previous data.[72,73]

The spectra of 2-phenyl- and 2-chloro-8-hydroxyquinoline (B, Figure 1 and A, Figure 2, respectively) show the disappearance of the H_2 downfield quartet. The complicating presence of absorption by the phenyl ring protons does not allow simple interpretation of the spectrum of the 2-phenyl- derivative. The 2-chloro- derivative exhibits the H_4 doublet of the H_3 - H_4 AX system. Similar results have been published for several 2-alkyl-substituted 8-hydroxyquinolines.[59,74] The spectrum of 4-chloro-8-hydroxyquinoline (B, Figure 2) shows the disappearance of the H_4 quartet, and the presence of an H_2 doublet centered at 8.58 ppm.

5-Chloro-8-hydroxyquinoline (A, Figure 3) clearly exhibits the pyridine ring ABX system (H_2 - 8.77, H_4 - 8.49 and H_3 - 7.51 ppm) and the H_6 - H_7 AB system (H_6 - 7.47 and H_7 - 7.03 ppm), although there is an overlap of the H_3 and H_6 absorptions. This result is similar to those published for a series of 5-halo-substituted 8-hydroxyquinolines in dimethylsulfoxide-d_6.[74] The spectrum of 7-tert-butyl-8-hydroxyquinoline (Figure 5) shows the pyridine ring ABX system (H_2 - 8.64, H_4 - 7.97 and H_3 - 7.23 ppm) and the H_5 - H_6 AB system (H_5 - 7.11 and H_6 - 7.45 ppm), although there is an overlap of the H_3 and H_5 absorptions. The tert-butyl- group singlet occurs at 1.53 ppm. 5,7-Dichloro-8-hydroxyquinoline (B, Figure 3) exhibits the pyridine ring ABX system (H_2 - 8.82, H_4 - 8.48 and H_3 - 7.52 ppm) and the H_6 singlet at 7.58 ppm. Similar results for 8-hydroxyquinoline-$d_{5,7}$ are in the literature.[75] The spectrum of 2,7-dimethyl-8-hydroxyquinoline (Figure 4) shows the H_4 doublet of the H_3 - H_4 AX system and overlapping of the H_3 absorption with the H_5 - H_6 AB spectrum. The 2- and 7-methyl singlets occur at 2.53 and 2.40 ppm, respectively.

For the derivatives listed in Table III, corresponding J values lie in a fairly narrow range and agree with literature data.[74-76] The chemical shifts of the H_2 protons are in the range 8.53-8.82 ppm and are not appreciably influenced by substituents in the phenol ring. The proton is shielded the most by the 4-methyl substituent (8.53 ppm), and deshielded the most by the electron-withdrawing chloro- substituents of 5,7-dichloro-8-hydroxyquinoline (8.82 ppm). The chemical shifts of the H_4 protons are in the range 7.74 - 8.48 ppm and, as expected, are affected by 5-substituents somewhat more than are the H_2 protons. The methyl-substituents of 2,7-dimethyl-8-hydroxyquinoline shield the H_4 proton the

most (7.74 ppm), whereas chloro- substituents in the 5- and 5 and 7-positions deshield it the most (8.48 ppm). The chemical shifts of the H_3, H_5, H_6 and H_7 protons are in the range 6.93 - 7.58 ppm. The limited data for these protons was obtained from the 5- substituted and 7- substituted derivatives. The chemical shifts of the various methyl- substituents are in the range 2.40 - 2.66 ppm. As expected, the 7-methyl- substituent of 2,7-dimethyl-8-hydroxyquinoline, adjacent to the phenolic OH, is shielded the most (2.40 ppm), whereas the deshielding influence of the pyridine nitrogen affects the 4-methyl-substituent to the greatest extent (2.66 ppm).

The OH absorption is present in the spectra of all the derivatives.

IV.B. Bromination of 8-Hydroxyquinoline Derivatives

The data of Table IV show that after 5 minutes, the 5-methyl- and 7-methyl- derivatives were brominated to a greater extent than expected for simple monobromination. The high values were probably caused by the bromination of the methyl- substituents. Low values relative to those expected for the 5,7-dibromination of the 2-chloro- derivative were found for that compound, perhaps due to entrainment of some unbrominated reagent in the precipitate of 2-chloro-5,7-dibromo-8-hydroxyquinoline which formed during the titration. 4-Chloro-8-hydroxyquinoline was completely dibrominated after 3 minutes.

The data of Table IV served as the basis for the determination of the 5- and 7-methyl-, and 2- and 4-chloro-8-hydroxyquinolines that are bound in certain metal complexes described in the EXPERIMENTAL AND RESULTS. In the analysis of the complexes, bromination times of 3, 4,

5 and 5 minutes were used for 7-methyl-, 5-methyl-, 2-chloro- and 4-chloro-8-hydroxyquinoline, respectively. With the 2-chloro- derivative, an empirical factor was used to correct for the incomplete bromination of the compound. In view of the bromination experiments, the determinations of 5- and 7-methyl-, and 2-chloro-8-hydroxyquinoline are considered to be empirical.

IV.C. Protonation Constants of 8-Hydroxyquinoline Derivatives

The determination of protonation constants was necessary for the calculation of chelate formation constants and for drawing conclusions about precipitated metal complexes. Of the values listed in Table V, only those of 2-chloro-, 4-chloro- and 7-tert-butyl-8-hydroxyquinoline have not been previously reported in the literature. The unusually low $\log {}^{c}K_{NH}$ value of the 7-tert-butyl- derivative (2.50) relative to that of 8-hydroxyquinoline (4.12) is likely due to a displacement of the hydroxyl group by the tert-butyl group towards the basic nitrogen atom, thus hindering the approach of protons as has been suggested previously in the case of 7-methyl-8-hydroxyquinoline,[45] or hindering the solvation of the protonated ring nitrogen, as suggested for substituted acridines.[66] Courtauld molecular models show that the displacement is appreciable with the large tert-butyl group. The high $\log {}^{c}K_{OH}$ value of the 7-tert-butyl- derivative (13.4) relative to that of the parent compound (11.12) is due to the strong electron-donating inductive effect of the substituent. As expected, the protonation constants of the 2- and 4-chloro- derivatives are low due to the electron-withdrawing effect of the halogen.

IV.D. Uranium(VI) Complexes of 8-Hydroxyquinoline Derivatives

It has been shown that in the infrared spectra of the adduct complexes, $M(R\text{-}Q)_2 \cdot R\text{-}QH$, the broad band centered at 2650 cm^{-1} and the low intensity band at 2050 cm^{-1} are characteristic of hydrogen-bonded $>\overset{+}{N}H$.[17,32] The identification of these bands is an important diagnostic test for the adduct structure of metal 8-hydroxyquinolates.

The compounds precipitated from aqueous or aqueous acetone solution by the procedures described in Section III.G.1. are summarized in Table XXVI according to the presence or absence of the diagnostic infrared $>\overset{+}{N}H$ bands (Figures 2 and 1, respectively). Elemental analysis (Tables VIII and X) confirmed that the new complexes of 5-methyl-, 5-phenyl-, 5-chloro- and 7-phenyl-8-hydroxyquinoline are adducts. The bands are not observed in the spectra of the new complexes of 7-methyl-, 2,7-dimethyl- and 7-tert-butyl-8-hydroxyquinoline, showing that these compounds do not carry the additional ligand. The spectra do, however, suggest that other species are components of the complexes. Elemental analysis (Tables VIII, IX and X) confirmed this suggestion. If the 7-methyl-8-hydroxyquinoline complex is precipitated with dilute sodium hydroxide or ammonia solution, the composition is $UO_2(C_{10}H_8NO)_2 \cdot H_2O$; the broad OH bands centered at 3350 and 3000 cm^{-1} in spectrum B, Figure 1 show the presence of water. Spectrum A, Figure 5 was obtained after the hydrate had been heated for 3 hours at 200-210°C <u>in vacuo</u> (Section III.G.3.); the 3350 cm^{-1} band is now absent and the 3000 cm^{-1} band is reduced in intensity. The composition of the black residue was shown by analysis to be $UO_2(C_{10}H_8NO)_2$. If the pH is adjusted by urea hydrolysis, the composition is $UO_2(C_{10}H_8NO)_2 \cdot NH_3$, and NH bands are observed in the

TABLE XXVI

SUMMARY OF URANIUM(VI) COMPLEXES OF 8-HYDROXYQUINOLINE DERIVATIVES

bis Complexes*	tris Complexes†
$UO_2(7\text{-Me-Q})_2 \cdot NH_3$	$UO_2(5\text{-Me-Q})_2 \cdot 5\text{-Me-QH}$
$UO_2(7\text{-Me-Q})_2 \cdot H_2O$	$UO_2(5\text{-Ph-Q})_2 \cdot 5\text{-Ph-QH}$
$UO_2(2,7\text{-Dime-Q})_2 \cdot H_2O$	$UO_2(5\text{-Cl-Q})_2 \cdot 5\text{-Cl-QH}$
$UO_2(7\text{-t-But-Q})_2 \cdot H_2O$?	$UO_2(7\text{-Ph-Q})_2 \cdot 7\text{-Ph-QH}$
$UO_2(7\text{-t-But-Q})_2 \cdot OC(CH_3)_2$?	$UO_2(2\text{-Me-Q})_2 \cdot 2\text{-Me-QH}$

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* $^{+}_{>}$NH bands absent in the infrared spectra.

† $^{+}_{>}$NH bands present in the infrared spectra.

spectrum (A, Figure 1).

The dependence of the composition of the 7-methyl-8-hydroxyquinoline complex on the method of precipitation is interesting. The formation of the ammonia complex appears to be related to the urea hydrolysis. Since the initial urea-to-uranium molar ratio was approximately 500:1, it is likely that uranium(VI) complexes of urea were formed in solution. Such complexes have been reported in the literature,[77] with bonding to the uranium atoms through the carbonyl oxygen. Because of bonding through the carbonyl group, hydrolysis of the bound urea should be facilitated, and the proximity of the hydrolysis product, NH_3, to the uranium atom would encourage its coordination.

Sacconi et al.[78] prepared similar β-diketone complexes, $UO_2(diket)_2 \cdot NH_3$, and suggested uranium(VI)-NH_3 coordination.

The composition of the 2,7-dimethyl-8-hydroxyquinoline complex is $UO_2(C_{11}H_{10}NO)_2 \cdot H_2O$, whether precipitation is by addition of dilute sodium hydroxide or ammonia solution. The presence of water in the compound is confirmed by the broad OH band centered at 3000 cm^{-1} in the infrared spectrum (C, Figure 1). The slightly high carbon and hydrogen and low uranium determinations (Table IX) suggest the presence of a small amount of contaminating reagent in the compound.

Precipitation of the 7-tert-butyl-8-hydroxyquinoline complex from a purely aqueous solution yielded analytical data (Table IX) suggestive of an adduct compound. However, since the infrared spectrum (D, Figure 1) does not exhibit $>\overset{+}{N}H$ bands the result is most likely fortuitous and due to reagent contamination caused by the low aqueous solubility of the reagent.

After heating the compound for 3 hours at 225°C in vacuo (Section III.G.3.), the infrared spectrum (B, Figure 5) of the residue showed a reduction in intensity at 3000 cm^{-1} (in comparison with spectrum D, Figure 1) relative to other bands in the spectrum. The intensity reduction was undoubtedly caused by the loss of contaminating reagent (OH absorption) and bound water. (The remaining intensity is due to the CH stretching vibration of the tert-butyl group.) The original red-brown compound turned black on heating. Analysis showed the black compound to be $UO_2(C_{13}H_{14}NO)_2$. The colour change is likely associated with the loss of coordinated water, just as is observed when dark-brown $UO_2(7\text{-Me-Q})_2 \cdot H_2O$ is heated to yield a green-black thermal product.

From the limited evidence presented above, and in analogy with the complexes formed by 7-methyl- and 2,7-dimethyl-8-hydroxyquinoline, the formula of the 7-tert-butyl-8-hydroxyquinoline complex is likely $UO_2(C_{13}H_{14}NO)_2 \cdot H_2O$. Analysis of the pure complex is required to establish the composition with certainty.

An attempt to obtain the pure compound was made by preparing the complex from 40% v/v aqueous acetone solution. The infrared spectrum (E, Figure 1) of the resulting red-brown compound shows the stretching frequency of the carbonyl group at 1690 cm^{-1}, suggesting that the complex is an acetone adduct rather than a hydrate. The carbonyl band is not present in spectrum C, Figure 5, which was obtained after the compound had been heated for 3 hours at 225°C in vacuo (Section III.G.3.). The data of Table X clearly supports the formula $UO_2(C_{13}H_{14}NO)_2 \cdot OC(CH_3)_2$ best.

The data of Table XXVI suggests that the failure of certain reagents

to form the adduct complexes, $UO_2(R\text{-}Q)_2 \cdot R\text{-}QH$, can be correlated with the presence of a 7- substituent in those reagents (except for 7-phenyl-8-hydroxyquinoline). In view of this, the re-examination of the uranium(VI) bis and tris complexes of the 5,7-dihalo-8-hydroxyquinolines proposed by Moeller and Ramaniah[39] was undertaken (Section III.G.2.).

In general, the analytical data (Table XI) obtained for the compounds prepared following the procedures of Moeller and Ramaniah[39] are in poor agreement with the values calculated for the formulae proposed by these workers. The significant features are the tendencies to high carbon and hydrogen content and low nitrogen, halogen and uranium content. Although pure compounds are difficult to prepare without the occurrence of simultaneous and/or coprecipitation of these sparingly soluble reagents, the poor data cannot be accounted for solely in terms of contamination. Contamination would lead not only to low values for uranium and high values for carbon and hydrogen, but also to high values for nitrogen and halogen. Indeed, the high carbon and hydrogen and low nitrogen and halogen contents suggest that an additional organic moeity containing carbon and hydrogen but not nitrogen or halogen is also associated with the complexes. In view of these results, the C:X (carbon:halogen) ratio is of special significance. For all four preparations, the experimental C:X ratios are higher than the calculated ratios. Thus, the presence of an organic species other than the chelating reagents is indicated. The composition of the solvent medium suggests that this moeity is likely to be acetone. For the compounds of general formula $UO_2(C_9H_4NOX_2)_2 \cdot OC(CH_3)_2$, the C:X ratio

is 1.78:1 for X = Cℓ and 0.79:1 for X = Br. Two of the four experimental ratios are in reasonable agreement with these values. These data cast considerable doubt on the formulae proposed by Moeller and Ramaniah.

Infrared spectra provided supporting evidence for the presence of acetone in the dihalo complexes. The four infrared spectra (Figure 3) show the carbonyl group stretching frequency. In the spectra (A and B) of the 5,7-dichloro-8-hydroxyquinoline complexes, the carbonyl frequency is a single band at 1690 cm^{-1}. It occurs as a doublet centered at 1675 cm^{-1} in the spectra (C and D) of the 5,7-dibromo-8-hydroxyquinoline complexes. These frequencies are appreciably shifted from the free acetone frequency of 1720 cm^{-1}, and indicate coordinated rather than lattice-held acetone. Similar frequency shifts have been observed for the urea complexes of uranium(VI).[77]

Another important feature is the absence in spectra B and D, Figure 3, of $>\overset{+}{N}H$ bands. These spectra were taken of the compounds prepared by the method reported by Moeller and Ramaniah to yield the tris compound. Thus, it appears that in the purported tris complexes of the 5,7-dihalo-8-hydroxyquinolines, any extra reagent in the compounds is not present as a coordinated species but more likely as a contaminant. Although it is tempting to account for the intensity of the broad bands centered at 3000 cm^{-1} (spectra B and D) in terms of the OH frequency of precipitated reagent, discussion given below shows that this is not likely.

The spectra (A and C, Figure 3) of the compounds formulated as $UO_2(C_9H_4NOX_2)_2$ are identical to spectra B and D, except for moderately sharp bands at 3400 cm^{-1} exhibited in the former. Because of the reduced amount of reagent and higher pH value used in the preparation

of these compounds, the formation of partially hydrolysed uranium species is likely and may account for the 3400 cm^{-1} bands.

X-Ray powder diffraction photographs of the reported tris complexes did not reveal the presence of localized reagent crystallites, perhaps because the level of contamination was too low for this purpose and the size of the crystallites too small, or because the reagent may have coprecipitated as a solid-solution component. The diffraction patterns of the two dichloro complexes are very similar (Table XII) and do not support the conclusion that the two compounds differ in symmetry.[38] No explanation for this difference is apparent, unless the degree of contamination in each study was very different. In accord with the previous study,[38] however, the patterns of the two dibromo complexes were somewhat different (Table XII), indicating widespread incorporation of the sparingly soluble reagent in the crystals of the complex prepared using the larger amount of reagent.

The cooled filtrate from the preparation of the purported tris complex of 5,7-dibromo-8-hydroxyquinoline did not reveal crystals of the extremely insoluble reagent, suggesting that essentially total simultaneous and/or coprecipitation of the excess reagent had occurred. With the more soluble 5,7-dichloro- reagent, appreciable crystallization of the reagent was observed in the cooled filtrate. These results suggest that somewhat less contamination of the 5,7-dichloro-8-hydroxyquinoline complex could be expected. Indeed, modification of the preparative procedure to reduce the extent of reagent contamination (e.g., use of 40% v/v aqueous acetone and filtration of the mixture while warm) resulted in a 5,7-dichloro-8-hydroxyquinoline complex

relatively free of reagent. No attempt was made to prepare a purer complex of the 5,7-dibromo- derivative. The analytical data (Section III.G.2.) for the dichloro complex prepared by the modified procedure is in good agreement with the composition $UO_2(C_9H_4NOCl_2)_2 \cdot OC(CH_3)_2$, although infrared studies (vide infra) suggest that water is also present in the compound.

The infrared spectrum (A, Figure 4) of the complex prepared by the modified procedure is identical to spectrum B, Figure 3 and exhibits a broad band centered at 3050 cm^{-1}. The band is unlikely due to contaminating reagent (OH absorption) as the large amount of reagent required to give the observed intensity would have yielded analytical data quite different from the experimental values of the complex prepared by the modified procedure. In spectrum C, Figure 4, the intensity of the 3050 cm^{-1} band remains high despite the elimination of the intensity contribution of the CH vibrations of acetone by the use of acetone-d_6 in the solvent medium. Therefore it must be concluded that some other component present in the complex contributes to the intensity of the 3050 cm^{-1} band. (In the spectrum, weak bands at 3350 and 2500 cm^{-1} are probably due to absorbed deuterium oxide and water resulting from insufficient drying of the compound.)

In both the spectra of the complexes prepared from deuterium oxide/acetone-d_6 medium (C, Figure 4) and deuterium oxide/acetone (B, Figure 4) only a portion of the intensity of the 3050 cm^{-1} band is shifted to 2275 cm^{-1} ($\nu_H/\nu_D = 1.34$); the intensity of the band is still surprisingly high. A likely explanation is that the band intensity is due mainly to lattice or coordinated water which, from the position and breadth of the

band, is likely hydrogen-bonded to other atoms in the crystal. The intensity of the 3050 cm^{-1} band after precipitation from deuterium oxide medium must then be due to exchange of deuterium oxide with atmospheric moisture during the drying period and/or with traces of water present in the mulling agent, hexachloro-1,3-butadiene. (The mulls were prepared in a dry box.)*

The strong likelihood of water in the 5,7-dichloro-8-hydroxyquinoline complex leaves open the question of its composition. Analytical data from elemental analysis are not sufficiently accurate to distinguish among compositions of the type $UO_2(C_9H_4NOC\ell_2)_2 \cdot OC(CH_3)_2 \cdot H_2O$ or $UO_2(C_9H_4NOC\ell_2)_2 \cdot [OC(CH_3)_2]_{1-x} \cdot (H_2O)_x$; consequently, it appears that the question can be solved best by structure determination.

The precipitated 5,7-dihalo-8-hydroxyquinoline complexes can be converted thermally under vacuum (Section III.G.3.) to essentially black species which are likely the compounds, $UO_2(C_9H_4NOX_2)_2$, but because of their hygroscopic nature (see below), it is difficult to obtain these compounds as such. The C:X ratios of the thermal products, 1.50:1 for X = Cℓ and 0.68:1 for X = Br, are in excellent agreement with the calculated values of the bis complexes. These data strongly suggest the thermal removal of acetone from the precipitated compounds. The compounds slowly pick up moisture as evidenced by a gradual weight increase and return to the original red-brown colour after an extended period of time. Treatment with hexachloro-1,3-butadiene (in room atmosphere)

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*Similar facile exchange of deuterium for hydrogen was experienced in recording the infrared spectrum of the melt product, $Sc(C_9H_6NO)_3 \cdot C_9H_6NOD$ (Section III.F.1.g.), despite precautions taken.

causes an immediate return of the red-brown colour of the precipitated species. Apparently, the process of mulling with hexachloro-1,3-butadiene greatly accelerates the pick-up of moisture.* (Other workers have been able to convert the dibenzoylmethane complex, $UO_2(C_{15}H_{11}O_2)_2$, to $UO_2(C_{15}H_{11}O_2)\cdot H_2O$ by treatment with hexachloro-1,3-butadiene in air.[79]) In the resulting infrared spectra (D and E, Figure 5), the carbonyl bands are absent confirming the removal of acetone, and bands at 3050 (broad) and 3350 (sharp) cm^{-1} indicate the presence of water.

The behaviour of the black compounds, $UO_2(C_9H_4NOX_2)_2$, is quite different from that of the greenish-black compound, $UO_2(C_9H_6NO)_2$, obtained thermally from the uranium(VI) adduct of 8-hydroxyquinoline. The latter is stable and is not hygroscopic; the coordination number of the central uranium atom is probably satisfied by dimerization or polymerization, as suggested for bis(acetylacetonato)dioxouranium(VI).[80] It is conceivable that in the bis dihalo compounds, the presence of the relatively large halo atoms prohibits association and coordinative saturation is achieved by hydrate formation.

In view of the complexities revealed by the present work, it is not surprising that an attempt to prepare the bis complexes, $UO_2(C_9H_4NOX_2)_2$, from the tris complexes by thermal decomposition was unsuccessful.[40] Also, it would appear worthwhile to re-investigate the scandium(III) and thorium(IV) complexes of the 5,7-dihalo-8-hydroxyquinolines, which were formulated by Moeller and Ramaniah[50,81] to be $Sc(C_9H_4NOX_2)_3$, $Sc(C_9H_4NOX_2)_3\cdot C_9H_5NOX_2$, $Th(C_9H_4NOX_2)_4$ and

---

*The black compounds can be regenerated by heating again.

$Th(C_9H_4NOX_2)_4 \cdot C_9H_5NOX_2$.

The failure of 7-methyl-, 2,7-dimethyl- and 7-tert-butyl-8-hdyroxyquinoline and the 5,7-dihalo-8-hydroxyquinolines to form tris adducts is either associated with the basicity of the donor groups or steric properties of the 7-substituted ligands. Examination of the $\log {}^{c}K_{NH}$ and $\log {}^{c}K_{OH}$ values (Table V) shows that there is no relationship with the basicity of the ligands. For example, the $\log {}^{c}K_{NH}$ values of 7-methyl- and 7-tert-butyl-8-hydroxyquinoline (3.94 and 2.50, respectively) are both lower than the value of 8-hydroxyquinoline (4.12), but so is the value of 5-chloro-8-hydroxyquinoline (2.55, 60% v/v dioxane, 25°C, I = 0.1[82]) which forms a tris adduct. The $\log {}^{c}K_{OH}$ values of the 7-methyl- and 7-tert-butyl- derivatives (11.68 and 13.4, respectively) are both higher than the value of the parent derivative (11.12), yet so are the values of 5-methyl- and 2-methyl-8-hydroxyquinoline (11.44 and 11.60, respectively), which form adduct complexes.

The construction of Courtauld molecular models shows that the failure of the 7-substituted derivatives to form adducts is due to inter-ligand steric repulsions. These repulsions are demonstrated in Figure 7 for the hypothetical 7-methyl-8-hydroxyquinoline adduct. The basic structure reported by Hall et al.[15] for the 8-hydroxyquinoline was used as a model. The crosses (7-methyl groups) and short lines (α-hydrogens) have been drawn to scale. The heavy dots represent the centres of the hydrogen atoms. The repulsions occur between (i) the hydrogen-bonded proton and the 7-methyl group of the neighbouring bidentate ligand, (ii) the α-hydrogen of the monodentate ligand and the 7-methyl group of the neighbouring ligand, and (iii) the 7-methyl

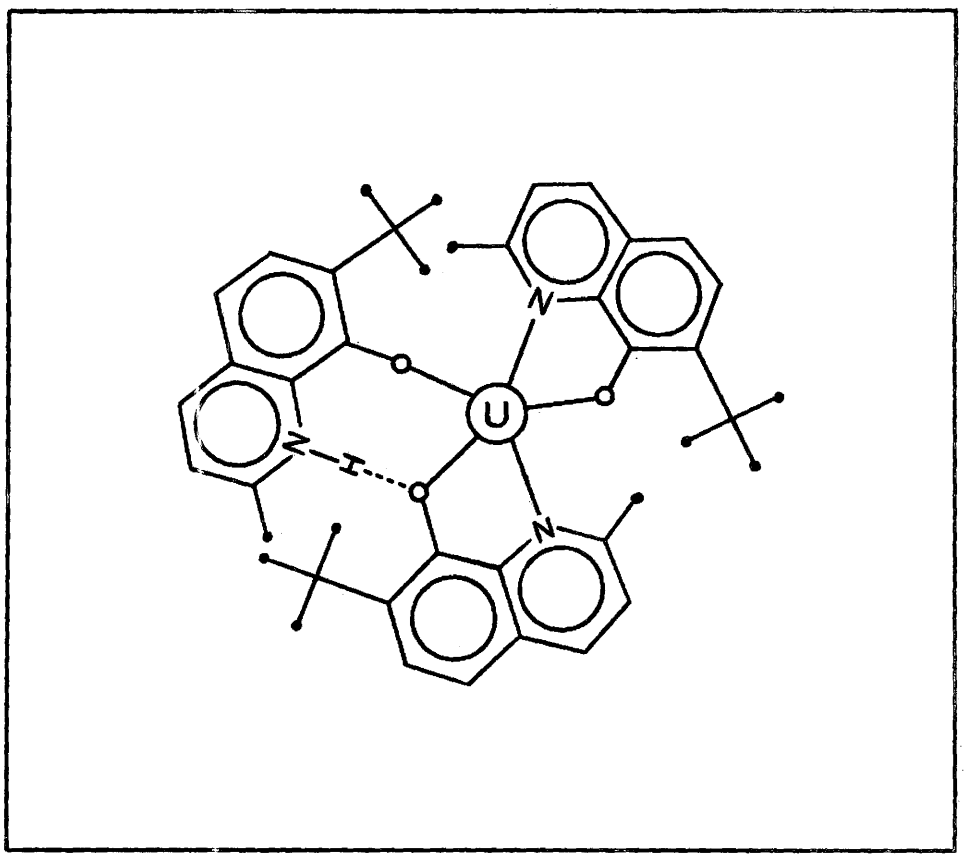


Figure 7. Steric interactions in hypothetical tris U(VI) complex of 7-methyl-8-hydroxyquinoline.

group of the monodentate ligand and the α-hydrogen of the neighbouring ligand. As a result of these repulsions, smaller coordinating species such as water, ammonia and acetone replace the monodentate reagent molecule.

The formation of an adduct with 7-phenyl-8-hydroxyquinoline, although initially surprising, is also explicable on the basis of molecular models. In the ligand, the phenyl group is twisted out of plane of the quinoline ring because of steric hindrance between (i) the 6-hydrogen (quinoline ring) and the 2'-hydrogen (phenyl ring), and (ii) the quinoline oxygen and the 6'-hydrogen. Because of this effect, three such twisted ligands can be arranged equatorially around the uranyl-ion and hydrogen-bond formation allowed, provided small deviations from coplanarity around the uranyl-ion are made. An X-ray structure of this compound is required to verify these interactions and would be of considerable interest.

The models also reveal that although considerable crowding exists in the adduct of 2-methyl-8-hydroxyquinoline, it is not quite as severe as in the 7-methyl-8-hydroxyquinoline adduct, and adduct formation should occur, as is observed. The infrared spectrum (F, Figure 2) of the adduct clearly shows the $>\overset{+}{N}H$ bands. As with the adduct of 8-hydroxyquinoline, the proton is likely hydrogen-bonded to an oxygen atom. It is obvious from models that substituents of larger size than the methyl group will prevent adduct formation. Thus, attempts to prepare the adduct with 2-n-butyl-, 2-phenyl- and 2-(2'-thienyl)-8-hydroxyquinoline (Section III.G.1.d.) failed. Indeed, these ligands did not yield even the $UO_2(R\text{-}Q)_2 \cdot Y$ compounds (Y = H_2O, NH_3, acetone),

as are normally obtained with the 7-substituted 8-hydroxyquinolines. No well-defined chelates were obtained; the precipitate was largely hydrolysed uranium and precipitated reagent (even in acetone solution).

The failure to precipitate complexes of the type $UO_2(R\text{-}Q)_2 \cdot Y$ is not due to inter-ligand repulsions but to steric interactions between the 2-substituent and one or more water molecules remaining in the coordination plane of the uranium atom. This effect has been previously described for the complexes of 2-substituted 8-hydroxyquinolines and transition metal-ions and results in reduced values for $\log {}^{c}K_1$.[83] Even though the $\log {}^{c}K_{NH}$ and $\log {}^{c}K_{OH}$ values for 2-methyl- and 2-n-butyl-8-hydroxyquinoline are larger than the corresponding values for 8-hydroxyquinoline (Table V), the values of the first step-wise formation constant, $\log {}^{c}K_1$, (Table VI), are lower by more than one log unit. With 2-phenyl- and 2-(2'-thienyl)-8-hydroxyquinoline, the combination of a larger substituent and a greatly reduced $\log {}^{c}K_{NH}$ value (Table V) results in hydrolysis during addition of the first ligand. Curve D, Figure 2, for the 2-phenyl-8-hydroxyquinoline system shows hydrolysis at ∿pH 4; at ∿pH 5.7, a significant amount of solid hydrolysis products is present. Values of $\bar{n}$ did not exceed 0.1 (Appendix E, Table 1). The behaviour of the 2-(2'-thienyl)-8-hydroxyquinoline system was similar ($\bar{n} < 0.2$).

With the transition metal-ions, the occurrence of distortion towards a tetrahedral configuration on addition of the first ligand relieves the steric interactions and permits substitution of the second ligand without a serious decrease in stability, such that $\log {}^{c}K_2 > \log {}^{c}K_1$.[83] In the present study, hydrolysis prevented the determination of $\log {}^{c}K_2$ values for the 2-methyl- and 2-n-butyl-8-hydroxyquinoline systems (Table VI;

curve C, Figure 2). This result likely arises from the fact that the essentially linear uranyl-ion is not readily distorted, thus allowing hydroxyl-ion to successfully compete for the remaining coordination sites.

Indirect evidence of the steric interactions with coordinated water is provided by the 7-tert-butyl-8-hydroxyquinoline system (curve D, Figure 1). Because the oxygen donor atom, unlike the nitrogen donor, is not heterocyclic, the 7-position is not sterically equivalent to the 2-position and, as suggested by molecular models, intereference with coordinated water should not occur. This is verified experimentally by the $\log {}^{c}K_1$ and $\log {}^{c}K_2$ values (Table VI), which are normal in all respects. The high values (13.39 and 11.58, respectively), relative to those of the 8-hydroxyquinoline system (11.42 and 9.67), reflect the high $\log {}^{c}K_{OH}$ value of 7-tert-butyl-8-hydroxyquinoline (Table V) relative to that for the parent ligand. Other workers have suggested that a 7-methyl-substituent sterically hinders the formation of the uranium(VI) complex, resulting in a reduced $\log {}^{c}K_1$ value.[45] In view of the present work with the large 7-tert-butyl group, this suggestion is likely incorrect.

IV.E. Scandium(III) Complexes of 8-Hydroxyquinoline and Derivatives

As stated earlier (Section II.B.), Pokras and Bernays[47] were first to precipitate the scandium(III) complex of 8-hydroxyquinoline (from an aqueous medium at about pH 8.5), but their procedure was not described clearly. For example, although the weight of Sc_2O_3 taken, about 0.024 g (0.35 millimoles Sc), is mentioned twice in their study,

the procedure states that approximately 0.03 millimoles of scandium were taken. Depending on which figure is used for scandium, the ratio of C_9H_7NO:Sc taken was either 99:1 or 9.9:1. Since the ratio of 9.9:1 is considered the more likely, it was assumed in the present work that the value of 0.03 millimoles of scandium was an error. Finally, it is not clear whether the precipitate was filtered hot or cold.

In the present work (Section III.F.2.), the compound was precipitated according to Pokras and Bernays' procedure (3.45 millimoles reagent, 0.35 millimoles Sc) and the precipitate was filtered hot to avoid or reduce reagent coprecipitation (procedure (i)). The product was dried at 40°C in vacuo to avoid any loss of contaminating reagent by sublimation under more stringent drying conditions. Pokras and Bernays suggested that contaminating reagent could be eliminated by heating the precipitate from 2-5 hours to constant weight at 100-110°C at atmospheric pressure. Table XV shows the results of heating the compound for an extended period of time (688 hours). After 5 hours, constant weight was not achieved. Indeed, Pokras and Bernays' own data (at 110°C) confirmed this:

Time (hrs)	Weight (g)
3.3	0.1545
5.3	0.1543
7.3	0.1538

These results demonstrate that the compound either slowly decomposes or slowly loses contaminating 8-hydroxyquinoline at 100-110°C.

Table XIII shows the effect of reagent concentration and solvent

on the composition of the 8-hydroxyquinoline complex precipitated from aqueous solution at about pH 8. The calculated elemental and 8-hydroxyquinoline contents for several possible complexes are collected in Table XIV. As Petronio and Ohnesorge[52] pointed out, little information can be obtained from hydrogen and nitrogen determinations. However, there are appreciable differences in the carbon, 8-hydroxyquinoline and scandium percentages and in view of this, the results of Table XIII reveal three significant features.

(i) An average value for 4.05:1 for the $C_9H_6NO^-$:Sc ratio was found for Pokras and Bernays' compound, although the 8-hydroxyquinoline determination (90.0%) is 2.6% (absolute) low for $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$. (The carbon content (67.00%) is 2.45% low for the same compound.)

(ii) The presence of 10% v/v aqueous acetone in the precipitation medium reduced the $C_9H_6NO^-$:Sc ratio of Pokras and Bernays' compound to an average value of 3.4:1.

(iii) In all cases, the sum of the reagent and scandium contents are 3-4% lower than 100%.

Although the ratio 4.05:1 supports the adduct formula proposed by Pokras and Bernays, the ratio 3.4:1 obtained when the medium contains 10% v/v acetone to increase the solubility of the reagent, suggests that the fourth molecule of reagent in the compound obtained from a purely aqueous medium is due to contamination. Furthermore, the low result for the $C_9H_6NO^-$ content in Pokras and Bernays' compound and the failure of the reagent and scandium contents in all the preparations to total better than 97% are significant, since the errors involved are well within the error limits of the methods of analysis, and suggest

the presence of another species in the scandium compound. These observations place considerable doubt on the adduct formula proposed by Pokras and Bernays.

Compounds with a $C_9H_6NO^-$:Sc ratio of 3.00:1 were prepared by reducing the amount of scandium taken for precipitation (procedure (iii), Section III.F.2.; Table XVI). The effect of progressive drying on the compounds (Table XVI) increased the sum of the reagent and scandium contents slightly from 95.6 to 96.5% with no change in $C_9H_6NO^-$:Sc ratio indicating that the compound dried at 40°C in vacuo tends to retain a small amount of moisture. After heating at 105°C for 161 hours (Table XVII) the small amount of moisture (∿1 mg) was removed from the compound (∿108 mg). As expected, the weight losses of Table XVII are much less than those of Pokras and Bernays' compound (Table XV). The analytical data (C, Table XVI) obtained for the dried compound (100°C/14 hrs in vacuo) are clearly in much closer agreement with the composition $Sc(C_9H_6NO)_3 \cdot H_2O$ than the composition $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ advanced by Pokras and Bernays. The 3:1 $C_9H_6NO^-$:Sc ratio found in the present work is in agreement with the composition $Sc(C_9H_6NO)_3$ proposed recently by Petronio and Ohnesorge,[52] but these workers did not identify the additional species, water, in the compound.

The infrared spectra of Pokras and Bernays' compound, the compound prepared from 10% v/v aqueous acetone, and the proposed complex, $Sc(C_9H_6NO)_3 \cdot H_2O$, are shown in A, B and C, Figure 6, respectively. Two significant features are apparent. Firstly, the three spectra are very similar except that the three bands at 3330, 1410 and 710 cm^{-1} in spectrum A are reduced in intensity in spectrum B (relative to other

bands in the spectrum), and are absent in spectrum C. The bands at 1410 and 710 cm^{-1} are present in the spectrum of 8-hydroxyquinoline (not shown). The band at 3330 cm^{-1} (ν_{OH}) shifted from the center (3100 cm^{-1}) of the very broad OH band in the spectrum of pure 8-hydroxyquinoline, probably because of a lower order of intermolecular hydrogen-bonding. The decrease in intensity of the three bands is consistent with the decrease in the $C_9H_6NO^-$:Sc ratio from 4.05:1 to 3.4:1 to 3.00:1. Thus, the bands are likely due to contaminating reagent. Secondly, a broad band centered at 2900 cm^{-1} is present in all three spectra. The spectrum (D, Figure 6) of the complex prepared from deuterium oxide solution (Section III.F.1.e.) shows the 2900 cm^{-1} band shifted to 2150 cm^{-1}, proving that the absorption is protonic (ν_H/ν_D = 1.34). This band is assigned to the stretching vibrations of the hydrate water present in the complex. As shown below, the band is absent (E, Figure 6) after the compound has been heated in the range 160-240°C to remove the water.

Similar broad bands have been found in the infrared spectra of the hydrated 8-hydroxyquinoline complexes, $Mg(C_9H_6NO)_2 \cdot 2H_2O$ and $Bi(C_9H_6NO)_3 \cdot H_2O$,[84] $Zn(C_9H_6NO)_2 \cdot 2H_2O$ and $Ni(C_9H_6NO)_2 \cdot 2H_2O$,[85] and $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$.[86] The OH stretching modes of these compounds occur in the range 3300-3600 cm^{-1}. The 2900 cm^{-1} frequency is unusually low compared to other hydrated metal 8-hydroxyquinolates, but this may be due to both stronger hydrogen-bonding[87,88] and stronger coordination of the water molecule to the scandium atom. With respect to the latter effect, Sartori et al.[89] used an electrostatic model to calculate that the stretching frequencies of water are lowered 400-500 cm^{-1} relative to "free" water on coordination of the molecule to a metal-ion. Also,

it was shown that the bending fundamental of water is raised ~50 cm^{-1} and that the new modes associated with water coordination, rocking, wagging and metal-oxygen stretching, appear at 900, 768 and 673 cm^{-1}, respectively. The latter three frequencies have been characterized by deuterium isotope shifts and have been used to confirm the coordinate nature of water in aquo complexes.[90,91] Unfortunately, isotopic shifts and an increase in the bending fundamental could not be detected in the present study. Spectra C and D, Figure 6 of $Sc(C_9H_6NO)_3 \cdot H_2O$ and $Sc(C_9H_6NO)_3 \cdot D_2O$ are identical in the range 2000 - 630 cm^{-1}. Either the water molecule is not coordinated or the relevant bands in the spectra are masked by bands due to the complex and mulling agent.

The results of this work suggest that the extra reagent in Pokras and Bernays' compound is due to contamination by coprecipitation. The data of Table XXIV show that the powder diffraction lines of the compound do not contain lines due to 8-hydroxyquinoline or $Sc(C_9H_6NO)_3 \cdot H_2O$. Therefore, the compound prepared by Pokras and Bernays is not a bi-crystalline mixture of the latter two components, and the extra reagent is likely incorporated into the crystal of $Sc(C_9H_6NO)_3 \cdot H_2O$ where it is held by lattice forces. The coprecipitation is likely of the occlusion type.[92] The reagent is very easily removed by stirring in a solvent such as 1,2-dichloroethane (Section III.F.7.) to yield $Sc(C_9H_6NO)_3 \cdot H_2O$ and a 1,2-dichloroethane solution of 8-hydroxyquinoline.

The thermogram (A, Figure 5) of $Sc(C_9H_6NO)_3 \cdot H_2O$ shows that loss of the water molecule occurs over the temperature range 120 - 160°C. The constant-weight level associated with the compound $Sc(C_9H_6NO)_3$ occurs in the range 160-240°C. As shown below, this compound is slightly non-

stoichiometric. Ultimately, it decomposes to Sc_2O_3 at ~600°C. The compound prepared by the procedure of Pokras and Bernays (curve B, Figure 5) loses both the hydrating water and extra reagent in the temperature range 75 - 160°C to yield $Sc(C_9H_6NO)_3$.

The thermogravimetric data served as the basis for selecting conditions for studying the thermal reaction of $Sc(C_9H_6NO)_3 \cdot H_2O$ (Section III.F.4.b.). The compound was heated for various times and temperatures in vacuo. The analytical data (Table XXII) show that removal of the hydrate molecule results in the formation of a non-stoichiometric compound. In all experiments, a small amount of 8-hydroxyquinoline (1.4 - 3.5 mg) was evolved, and a residue slightly deficient in 8-hydroxyquinoline ($C_9H_6NO^-$:Sc ratios in the range 2.86 - 2.92) remained. The ligand deficiency can be explained by the solid-phase hydrolysis of the hydrate according to the following thermal reactions:

$$Sc(C_9H_6NO)_3 \cdot H_2O = Sc(C_9H_6NO)_2 \cdot OH + C_9H_7NO$$

$$Sc(C_9H_6NO)_2 \cdot OH = Sc(C_9H_6NO) \cdot O + C_9H_7NO$$

The reaction occurs only to a small extent, the major process being the total removal of water from the hydrate. Similar behaviour has been observed for other 8-hydroxyquinoline complexes such as $Mg(C_9H_6NO)_2 \cdot 2H_2O$ and $Ba(C_9H_6NO)_2 \cdot 4H_2O$,[93] and $Be_2O(C_9H_6NO)_2 \cdot 2H_2O$,[86] and for the rare earth acetylacetonates, $Ln(C_5H_7O_2)_3 \cdot nH_2O$,[94] and dibenzoylmethides, $Ln(C_{15}H_{11}O_2)_2 \cdot H_2O$.[95] Muetterties and Wright[96] have suggested that the hydrolysis of the rare earth complexes indicates a significant bonding interaction between the metal atoms and the donor atom of the solvent. The monosolvate phases may well

contain hepta-coordinate metal atoms. Therefore, in $Sc(C_9H_6NO)_3 \cdot H_2O$, the water molecule is likely coordinated to the scandium atom, but an X-ray structural determination is required to decide this point.

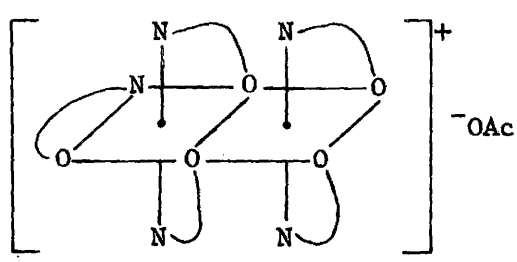
The infrared spectra of the thermal products listed in Table XXII, of which spectrum E, Figure 6 is typical, show the removal of the water molecule by the absence of the 2900 cm^{-1} band. The spectrum is similar to that of the hydrate (C, Figure 6), although there are minor differences in the 1000-630 cm^{-1} region. It was not possible to detect the OH frequency of the proposed hydrolysis product, $Sc(C_9H_6NO)_2 \cdot OH$, because of its expected small concentration.

According to X-ray powder crystallography (Section III.F.6.), the anhydrous thermal products are amorphous; consequently, the removal of the water molecule destroys the crystal structure of the hydrate. Because of reduced crystal forces and reduced polarity due to the removal of water, the solubility of the thermal products in organic solvents is much greater than that of $Sc(C_9H_6NO)_3 \cdot H_2O$. For example, in chloroform the solubility is increased thirty-fold (Section III.F.7.).

The precipitation of scandium(III) by 8-hydroxyquinoline was also investigated at pH values below 8. The data of Table XVIII demonstrate that the complexes precipitated from aqueous media at pH 5.0 - 6.8 do not contain sufficient reagent-anion to neutralize the positive charge of scandium(III). Therefore, anionic species such as chloride, hydroxide or acetate must be present in the compounds to preserve charge neutrality. In order to identify the anion, the compound precipitated at pH 6.2 ($C_9H_6NO^-$:Sc ratio, 2.7) was studied and taken to be representative of the compounds obtained in the pH range 5.0 - 6.8. The silver nitrate

test showed that chloride was not present in the compound. Proton magnetic resonance identified the anion to be acetate. The PMR spectrum (B, Figure 4) exhibits a sharp singlet at 1.72 ppm that is not present in the spectrum (A, Figure 4) of $Sc(C_9H_6NO)_3 \cdot H_2O$, and is consistent with the resonance expected for the acetate methyl group. Integration of the spectrum demonstrates that the 8-hydroxyquinoline-anion and acetate-anion protons are in the ratio 17:1. This ratio compares favourably with the ratio (18:1) for the formula, $Sc(C_9H_6NO)_{2.7}(OAc)_{0.3}$, arrived at from the analytical data and acetate identification. The infrared spectrum (E, Figure 6) is almost identical to that of the thermal product, $Sc(C_9H_6NO)_3$, and confirms the absence of water. The spectrum, however, does not indicate the presence of the carbonyl group stretching frequency, likely because of the small amount of acetate present in the compound. These studies show that the compounds of Table XVIII have the general formula, $Sc(C_9H_6NO)_{3-x}(OAc)_x$, where x = 0.4 at pH 5.0 and x = 0.2 at pH 6.8. The formation of these acetate complexes arises from the decreased concentration of the 8-hydroxyquinoline-anion below pH 7.

Similar non-stoichiometric rare earth complexes of 8-hydroxyquinoline, $Ln(C_9H_6NO)_{3-x}(OAc)_x$, have been reported by Charles and Perrotto.[97] These workers suggested that the precipitation of the rare earth complexes may involve the formation of polymeric species such as



It is possible that the scandium acetate complexes are also polymerized rather than mixtures of $Sc(C_9H_6NO)_3$ and $Sc(C_9H_6NO)_2(OAc)$. Polymerization of scandium involving oxygen bridging exists in such species as $[Sc(H_2O)_5OH]_2^{4+}$ [98] and $Sc_4O_5(NO_3)_2$.[99] A molecular weight determination of $Sc(C_9H_6NO)_{2.7}(OAc)_{0.3}$ (calculated molecular weight, 452) by vapour-phase osmometry gave a value 760, suggestive of some degree of association in benzene solution. The properties of the acetate complexes are similar to the thermal product $Sc(C_9H_6NO)_3$, in that they are amorphous (Section III.F.6.) and soluble in chloroform (Section III.F.7.).

In summary, a brief appraisal of the investigations of previous workers is considered appropriate. The adduct formula proposed by Pokras and Bernays[46,47] was based on contaminated $Sc(C_9H_6NO)_3 \cdot H_2O$. Insufficient investigation by these workers did not reveal the water molecule in the compound. Analytically, the poor reproducibility yielded by Pokras and Bernays' gravimetric procedure for scandium[100] can be reconciled with variation in reagent coprecipitation within a series of determinations. There is no objection to the continued use of 8-hydroxyquinoline as a gravimetric reagent for scandium provided that the correct hydrate formula is used, and precautions are taken to avoid reagent contamination. However, it should be stated that the importance of the procedure is diminished by the facility of alternative methods, such as the EDTA titrimetric determination.[57]

The poor reproducibility experienced by Petronio and Ohnesorge[52] for the elemental analyses of the compound was probably caused by variation in the amount of unsublimed reagent contaminant at 110-120°C. Likely, attempts to achieve constant weight resulted in analytical data

much closer to the values calculated for the normal rather than the adduct complex. The average %C (65.63) and %H (4.16) values found by Petronio and Ohnesorge compare favourably with the values (65.46%C, 4.07%H) calculated for $Sc(C_9H_6NO)_3 \cdot H_2O$ and the values (65.24%C, 4.17%H) found in this work.

In view of the complexities revealed by the present work, it is not surprising that other workers[37,40,51] have been unable to convert the adduct complex to the normal tris complex by thermal decomposition. The broad ill-defined endothermic peak obtained in a differential thermal analysis study[38] is probably associated with the removal of contaminating reagent and/or the water molecule from the compound.

The complexes $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ and $[Sc(C_9H_6NO)_3]_2 \cdot C_9H_7NO$ precipitated from homogeneous solution by Cardwell and Magee[49] may also be the result of reagent contamination. It is noticeable that the infrared spectra of the two compounds in the region 3700-2500 cm^{-1} are complicated by the presence of bands caused by moisture in the potassium bromide. Therefore, the identification of reagent contamination and/or other species such as hydrating water that absorb in this region of the spectra is impossible.

The product $[Sc(C_9H_6NO)_3]_2 \cdot 3C_9H_7NO$ from the "solid-phase" reaction between $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ and 8-hydroxyquinoline described by Cardwell and Magee was re-examined in this work. It was presumed that the contaminated complex $Sc(C_9H_6NO)_3 \cdot H_2O$ was the reactant rather than $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ since the latter compound cannot be prepared by precipitation from aqueous solution. Careful observation of the melt

reaction between $Sc(C_9H_6NO)_3 \cdot H_2O$ and 8-hydroxyquinoline (Section III.F.1.f.) was made. Below the melting point of 8-hydroxyquinoline, there was no change in the original lemon-yellow colour of the reaction mixture. Upon melting of the reagent (∿73°C), a bright-orange liquid formed. The colour change upon formation of the liquid suggests that the reaction does not occur in the solid phase but in molten 8-hydroxyquinoline in which $Sc(C_9H_6NO)_3 \cdot H_2O$ dissolves. As described in Section III.F.1.f., a bright-orange solid was isolated from the solidified mass which analysis showed to be $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$, replacement of hydrate water by C_9H_7NO having occurred.

The infrared spectrum (C, Figure 8) of the tetrakis adduct shows bands centered at 2600 and 2100 cm^{-1} that are characteristic of hydrogen-bonded $>\overset{+}{N}H$; furthermore, the water band at 2900 cm^{-1} is absent. The spectrum (D, Figure 8) of the product obtained from molten 8-deuteroxy-quinoline (Section III.F.1.g.) shows a significant reduction in intensity at 2600 cm^{-1} (broad) and a broadening of intensity at 2100 cm^{-1} (ν_H/ν_D = 1.25). Although complete deuteration of the product was not achieved, the result confirms that the vibrations are protonic and are associated with the hydrogen-bonded $>\overset{+}{N}H$ system.

As with the uranium(VI) and thorium(IV) adducts, the additional molecule of 8-hydroxyquinoline in the scandium adduct is likely mono-dentate and bound to the metal atom through the phenolic oxygen. If it is assumed that the complex exists as a monomer in the solid-phase, this result strongly suggests that the scandium is hepta-coordinate in the complex. No examples of hepta-coordinate scandium have been reported in the literature, although several examples of hexa-coordination

$([Sc(P)_2 \cdot nH_2O](C\ell)_3$,[101] $[Sc(P)_3](CNS)_3$,[102] $Sc(NCS)_3(D)_3$[103] and $[Sc(D)_6](C\ell O_4)_3$,[104] where P represents 1,10-phenanthroline and D represents dimethylsulfoxide) have been well documented. It is conceivable that hepta-coordinate scandium exists in the tropolone complex $Sc(C_7H_5O_2)_3 \cdot C_7H_6O_2$; however, Muetterties and Wright[55] were only able to isolate the anion, $Sc(C_7H_5O_2)_4^-$, in which octa-coordinate scandium was proposed.* In view of this result, an attempt to prepare $Sc(C_9H_6NO)_4^-$ would be of interest.

The thermogram (C, Figure 5) of $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ shows the loss of the additional 8-hydroxyquinoline molecule over the temperature range 130-240°C. The constant-weight level associated with $Sc(C_9H_6NO)_3$ occurs in the range 240-280°C. The bright-orange adduct was converted to the lime-green tris complex by heating at 200°C in vacuo (Section III.F.4.). Similar marked changes in physical appearance have been observed for the thermal decomposition of the uranium(VI) and thorium(IV) adducts.[56] As expected, the infrared spectrum (E, Figure 9) of the thermal product shows the disappearance of the $>\overset{+}{N}H$ bands at 2600 and 2100 cm^{-1}.

The effect of reagent concentration and solvent on the composition of the 2-methyl-8-hydroxyquinoline complex precipitated from aqueous solution (∿pH 8.5) is given in Table XIX. The calculated compositions of several possible complexes are collected in Table XX. The data of Table XIX show three significant features.

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*It is interesting to note that the compact and small "bite" ligands, tropolone and 8-hydroxyquinoline, are capable of generating high coordination-numbers of scandium. The rigorous establishment of hepta-coordinate scandium in the 8-hydroxyquinoline adduct (and in the hydrate complex), however, awaits an X-ray structural determination.

(i) The presence of 10% v/v aqueous acetone reduced the average $C_{10}H_8NO^-$:Sc ratio from 4.17:1 to 4.00:1.

(ii) The $C_{10}H_8NO^-$:Sc ratio decreases with decreasing amount of reagent taken.

(iii) The sum of the $C_{10}H_8NO^-$ and Sc percentages is 4-5% lower than 100%.

The results suggest that an adduct complex is formed and that the presence of acetone is necessary (when large amounts of reagent are used) for the preparation of a compound free of contaminating reagent. In addition, the summation of % $C_{10}H_8NO^-$ and % Sc to 95-96% indicates that another species is present in the compound. The analysis of the pure adduct compares favourably with that of $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$ (Table XX). The data of Table XXI show the adduct species can be precipitated consistently over the pH range 5.5-8.5.

The infrared spectrum (A, Figure 8) of the compound shows two significant features. Firstly, an intense broad band is observed at 3200 cm^{-1}. This band confirms the presence of water in the compound. The breadth and position of the band indicate water of hydration rather than contaminating moisture. The infrared bands of complexes contaminated with a small amount of moisture usually occur at a higher frequency ($\sim$3400 cm^{-1}) and are considerably less broad and intense. Secondly, the spectrum shows broad bands centered at 2650 and 2070 cm^{-1} characteristic of hydrogen-bonded $>\overset{+}{N}H$, although the band at 2650 cm^{-1} is somewhat overlapped with the broad water band at 3200 cm^{-1}.

If the water molecules are coordinated, nona-coordination of scandium is implied. Although nona-coordinate scandium has not been

previously reported, its possibility cannot be discounted.

The thermogram (B, Figure 6) of $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$ shows a weight loss at 70°C and then a constant-weight level over the range 80-100°C. This level corresponds closely to the composition $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$. A further weight loss occurs at 105°C followed by a constant-weight level over the range 150-240°C. This level is associated with the composition $Sc(C_{10}H_8NO)_3$. Finally, the compound decomposes to Sc_2O_3 at 560°C. The thermogram supports the composition $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$.

The data of Table XXIII also show that water is removed from the complex after heating at temperatures of 75 and 90°C in vacuo. Also, a small amount of decomposition of the adduct at these temperatures was indicated by the experimental $C_{10}H_8NO^-$:Sc ratio of 3.93:1. The results suggest that complete removal of the water was not achieved and that partial hydrolysis of the complex occurs. The small amount of water that remains could not be detected in infrared spectra (A, Figure 9). On heating at 135-140°C and 165-170°C in vacuo, the complex was converted essentially to the tris complex, although analysis of the residue and of the sublimed $C_{10}H_9NO$ indicates that the conversion was not quite complete. A marked colour change accompanied the loss of the additional reagent from the complex (bright-yellow to lime-green). The infrared spectra (B, Figure 9) of the thermal products show the disappearance of the $>\overset{+}{N}H$ bands.

X-Ray powder diffraction studies indicate that the water in the complex is not likely present as a contaminant. The results of Table XXV show that the compound obtained by heating at 75°C in vacuo has a

different powder pattern, and therefore crystal structure, than the original compound. The removal of contaminating moisture would not affect the powder pattern in this manner. Unfortunately, the interpretation is clouded by the fact that the adduct was also slightly decomposed by the heating process. As expected, the results of Table XXV also show that the removal of the additional ligand causes a further change in crystal structure.

The 2-methyl-8-hydroxyquinoline complex is somewhat less stable than $Sc(C_9H_6NO)_3 \cdot H_2O$. For example, when the complex was placed in a dry organic solvent such as 1,2-dichloroethane, extensive hydrolysis occurred (Section III.F.7.); no such hydrolysis of the 8-hydroxyquinoline hydrate was observed. (Similar facile hydrolysis of the rare earth acetylacetone complexes, $Ln(C_5H_7O_2)_3 \cdot nH_2O$, has also been reported.[94]) Furthermore, continual washing of the complex with hot water caused extensive hydrolysis but no such effect was observed for the 8-hydroxyquinoline complex.

Unfortunately, the relative instability of the 2-methyl-8-hydroxyquinoline complex could not be detected by the determination of chelate formation constants (Table VII). The $\log {}^{c}K_1$ values for complexation of the 2-methyl-derivative and the parent ligand are about the same (11.18 and 11.26, respectively). In addition, the $\log {}^{c}K_2$ and $\log {}^{c}K_3$ values for the complexation of the two ligands cannot be compared due to the uncertainty in the values for the 2-methyl-8-hydroxyquinoline system.

Some conclusions in the present work regarding the 2-methyl-8-hydroxyquinoline complex do not agree with conclusions drawn by Phillips

et al.[34] These workers reported the composition $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$, but the drying conditions used (100-110°C) were adequate for the removal of the water from the complex. The loss of the additional ligand at 80°C reported by Wendlandt et al.[36] is incorrect; more likely a loss of hydrating water was observed.

The composition of the new 4-methyl-8-hydroxyquinoline adduct is $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$ (Section III.F.1.d.). The infrared spectrum (B, Figure 8) confirms the absence of water. The $>\overset{+}{N}H$ bands are observed at 2650, 2150 and 2050 cm^{-1}. The scandium is likely hepta-coordinate.

The thermogram (A, Figure 6) of the adduct shows a gradual weight loss occurring initially at 190°C, with a discontinuity at 270°C corresponding to the composition $Sc(C_{10}H_8NO)_3$. Thermal removal of the neutral ligand is accompanied by a change in colour from yellow to lime-green (Section III.F.4.b.). The bands at 2600, 2150 and 2050 cm^{-1} are not present in the infrared spectrum (D, Figure 9) of $Sc(C_{10}H_8NO)_3$.

The yellow adduct can be regenerated by reaction between the thermal product and 4-methyl-8-hydroxyquinoline in 1,2-dichloroethane (Section III.F.8.). This reaction is consistent with the well-established reactions between the thermal products, $UO_2(C_9H_6NO)_2$ and $Th(C_9H_6NO)_4$, and 8-hydroxyquinoline in 1,2-dichloroethane.[21,25,32]

The infrared spectra of the 2-chloro-, 4-chloro- and 5-methyl-8-hydroxyquinoline complexes (Figure 7, A, B and C, respectively) do not show the presence of $>\overset{+}{N}H$ bands. Broad bands in the region 2900-3200 cm^{-1} indicate the presence of water. The amount of water in the complexes is uncertain since detailed chemical analysis was restricted by the small amount of reagents available. The limited analytical data do

indicate, however, the compositions $Sc(2\text{-}C\ell\text{-}Q)_3 \cdot H_2O$, $Sc(4\text{-}C\ell\text{-}Q)_3 \cdot H_2O$ and $Sc(5\text{-}Me\text{-}Q)_3 \cdot H_2O$.

The thermal behaviour of only the 4-chloro-8-hydroxyquinoline complex was examined. The water could be readily removed by heating at 165-170°C in vacuo (Section III.F.4.b.) to give $Sc(4\text{-}C\ell\text{-}Q)_3$. The infrared spectrum (C, Figure 9) shows the disappearance of the water band. Presumably, the other complexes behave similarly.

A summary of the scandium(III) complexes precipitated from aqueous solution (above pH 7) is given in Table XXVII. 8-Hydroxyquinoline and its derivatives precipitate scandium(III) as either tris chelate hydrates or adduct complexes. It appears that there is a competition between the monodentate ligand and water for an "extra" scandium coordination site (assuming the water molecules of $Sc(2\text{-}Me\text{-}Q)_2 \cdot 2\text{-}Me\text{-}QH \cdot 2H_2O$ are waters of crystallization and not coordinated). The competition is well illustrated by the displacement of water in $Sc(C_9H_6NO)_3 \cdot H_2O$ on dissolution of the compound in molten 8-hydroxyquinoline.

The failure of 8-hydroxyquinoline and its 2-chloro-, 4-chloro- and 5-methyl- derivatives to form adducts from aqueous solution must be due to a property of these ligands that is different from the 2- and 4-methyl- derivatives. Of the properties considered (solubility of the reagents, steric properties of the substituents, and basicity of the ligand nitrogen and oxygen atoms), the only apparent correlation is with the nitrogen basicity (Table XXVII). The $\log {}^{c}K_{NH}$ values of 2- and 4-methyl-8-hydroxyquinoline (4.75 and 4.85, respectively) are for the most part appreciably higher than those of the ligands forming tris complexes (<2.0, 2.83, 4.12 and 4.27). Previous studies[15,17,22] on the adducts

TABLE XXVII

SUMMARY OF SCANDIUM(III) COMPLEXES OF 8-HYDROXYQUINOLINE DERIVATIVES

tris Complexes	Protonation Constants		tetrakis Complexes	Protonation Constants	
	$Log\ ^cK_{NH}$	$Log\ ^cK_{OH}$		$Log\ ^cK_{NH}$	$Log\ ^cK_{OH}$
$Sc(Q)_3 \cdot H_2O$	4.12	11.12	$Sc(4\text{-Me-Q})_3 \cdot 4\text{-Me-QH}$	4.85	11.25
$Sc(2\text{-C}\ell\text{-Q})_3 \cdot H_2O$	$< 2.0^*$	10.65	$Sc(2\text{-Me-Q})_3 \cdot 2\text{-Me-QH} \cdot 2H_2O$	4.75	11.60
$Sc(4\text{-C}\ell\text{-Q})_3 \cdot H_2O$	2.83	10.38			
$Sc(5\text{-Me-Q})_3 \cdot H_2O$	4.27	11.44			

* This value is below the limit of determination by potentiometric titration.

of uranium(VI) and thorium(IV) with 8-hydroxyquinoline ligands have demonstrated that the adduct ligand is coordinated as a zwitterion. The infrared spectra presented in this thesis clearly show that the adduct ligand in the scandium complexes is also zwitterionic. Since the stability of the zwitterion is increased with increased nitrogen basicity, some dependance of adduct formation on $\log^{c}K_{NH}$ is not surprising. A possible mechanism is one in which the OH proton of the reacting neutral ligand is displaced to the nitrogen atom of the ligand where it is stabilized by hydrogen-bonding. Additional experiments with derivatives having $\log^{c}K_{NH}$ values greater than 4.8 are required to substantiate the above proposal. In addition, it would be interesting to determine if derivatives with $\log^{c}K_{NH}$ values in the range 4.3-4.7 would yield a mixture of the hydrate and adduct complexes.

The formation constants for the scandium(III) complexes of 8-hydroxyquinoline and its derivatives have not been reported previously. In the present work, such constants were determined (Table VII). The $\log^{c}K_{1}$, $\log^{c}K_{2}$ and $\log^{c}K_{3}$ values for the complexes of 8-hydroxyquinoline (11.26, 9.61 and 8.05, respectively) and its 4-methyl- derivative (11.78, 10.28 and 8.82, respectively) are normal in all respects. The high values for the 4-methyl-8-hydroxyquinoline system reflect the higher $\log^{c}K_{NH}$ and $\log^{c}K_{OH}$ values (4.85 and 11.23, respectively) of the derivative with respect to those of the parent ligand (4.12 and 11.12, respectively). Although the $\log^{c}K_{NH}$ and $\log^{c}K_{OH}$ values of 2-methyl-8-hydroxyquinoline (4.75 and 11.60, respectively) also are higher than those of the parent ligand, the chelate formation constants do not reflect these values. This result is suggestive of steric effects

involving the 2-substituent.

IV.F. Factors Governing Formation of the Complexes $M(R\text{-}Q)_z \cdot R\text{-}QH$

In view of the results of this work, some general comments on the chemistry of the 8-hydroxyquinoline adducts are appropriate.

The factors governing the formation of these complexes appear to be the coordination number of the metal-ion (which is some function of the size and charge of the ion and availability of suitably hybridized orbitals), the "bite" of the ligand, and steric and basicity properties associated with the ligand. Known adducts of 8-hydroxyquinoline ligands are mainly restricted to the area of relatively large metal-ions of high charge. For example, solid adducts have been obtained with scandium(III), yttrium(III), zirconium(IV), thorium(IV), uranium(IV), uranium(VI) and plutonium(VI) from aqueous solution. It is also apparent that the compact nature and small "bite" of 8-hydroxyquinoline and its derivatives are capable of generating high coordinate-structures. For example, with these ligands the coordination numbers seven and nine for uranium(VI)[15,17] and thorium(IV),[22,105] respectively, have been rigorously established, and the high coordination-number of seven for scandium(III) is strongly suggested in this work. 8-Hydroxyquinoline behaves similarly to tropolone, which as mentioned above, generates high coordination-numbers in metal-ions.

In the present work, the formation of uranium(VI) adducts is prevented by suitable substituents in the 7-position of the ligand. This effect is almost certainly due to inter-ligand steric interactions and to interference with the formation of the $\overset{+}{N}$—H--O system. There

appears to be no correlation with the basicity of the nitrogen atom. On the other hand, formation of the scandium adducts appears to be dependant on nitrogen basicity (although additional data is required to substantiate this finding). Perhaps the apparent difference in behaviour between uranium(VI) and scandium(III) may be due to a sensitive balance of factors such as metal-ion charge, size and coordination geometry. The result of these factors may be that the coordination of a seventh donor to the scandium atom lies in the balance. An effect such as a decrease in nitrogen atom basicity which would hinder the formation of the zwitterion may be sufficient to allow coordination of water in its place.

Although no evidence of steric effects was found in the study of precipitated scandium complexes, this must be due to the fact that only ligands with small 2-substituents were studied, and that no attempts were made to prepare complexes with 7-substituted ligands.

Finally, it is interesting to note that 8-hydroxyquinoline precipitates zinc(II) from aqueous solution as the dihydrate, $Zn(C_9H_6NO)_2 \cdot 2H_2O$, in which the water molecules are coordinated.[106] However, in the solvent extraction of zinc(II) by 8-hydroxyquinoline into chloroform, the species extracted has been identified to be either $Zn(C_9H_6NO)_2 \cdot C_9H_7NO$[107] or $Zn(C_9H_6NO)_2 \cdot 2C_9H_7NO$.[108] Perhaps, in analogy with the scandium(III) complexes of this work, the precipitation of zinc(II) from aqueous solution with an appropriate 8-hydroxyquinoline derivative may result in adduct formation.

IV.G. Discussion of Errors

(i) The determination of equilibrium constants is subject to

errors in precision and accuracy. The factors contributing to these errors have been discussed elsewhere.[82] In summary, the largest source of error arises from the measurement of pH, essentially resulting from the uncertainty in the pH values of standard buffer solution used to calibrate the pH meter.

Errors in accuracy affect the absolute value of equilibrium constants. In general, however, errors in accuracy are minimized by using the same conditions for a series of potentiometric titrations. Therefore, protonation and formation constants resulting from such titrations can be compared with some certainty.

The protonation constants reported in the present study were calculated by a linear least-squares analysis. The parameter, σ, associated with this calculation is a measure of the fit of a series of data points within a titration to the calculated constants.

The computer program SCOGS[68,69] uses a non-linear least-squares analysis to calculate formation constants. Estimated input constants are refined in an iterative procedure via the difference between the experimental base titre and calculated (using refined constants) base titre for each titration point. The final constants correspond to a minimum in this difference. The SCOGS standard deviation, σ, is a measure of the fit of the data points within a titration to the calculated overall constants.

(ii) Conclusions concerning the compositions of scandium(III) complexes described in this thesis depend heavily on the ligand and scandium determinations. The absolute accuracy of the bromometric titration of 8-hydroxyquinoline and its 2-methyl- derivative is ±0.1

mg. The precision of ±0.1% for the determination of the two ligands (Tables XIII and XIX) was based on the analysis of at least five samples. The accuracy of the scandium determination is ±0.01 mg; the precision (Tables XIII and XIX) was ±0.02%. Therefore, the precision expected for the ligand:scandium molar ratios of the complexes containing the above two reagents is ±0.01:1.

The applicability of the bromometric titration to the determination of 2-chloro-, 4-chloro- and 5-methyl-8-hydroxyquinoline was described in Section IV.B. The accuracy and precision of the determination of 4-methyl-8-hydroxyquinoline have been given as ±0.1 mg and ±0.2%, respectively.[64]

IV.H. Suggestions for Further Work

(i) The structure of $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ and other scandium(III) and uranium(VI) complexes reported in this work should be examined by three-dimensional X-ray analysis.

(ii) In view of errors in the literature concerning the 5,7-dihalo-8-hydroxyquinoline complexes of uranium(VI), work describing the corresponding thorium(IV) and scandium(III) complexes should be re-examined.

(iii) The nitrogen basicity effect which appears to determine the formation of $Sc(4\text{-Me-Q})_3 \cdot 4\text{-Me-QH}$ and $Sc(2\text{-Me-Q})_3 \cdot 2\text{-Me-QH} \cdot 2H_2O$ should be further examined with other 8-hydroxyquinoline derivatives, and with other metal-ions.

(iv) Scandium(III) should be precipitated with 2- (groups larger than methyl) and 7-substituted 8-hydroxyquinolines to study possible steric effects.

(v) Attempts should be made to prepare the anion, $Sc(C_9H_6NO)_4^-$,

perhaps by careful neutralization of the protonated complex. The determination of the coordination number of scandium in the anion would be of interest.

(vi) The techniques described in this work should be extended to the 8-hydroxyquinoline adducts of other metal-ions (e.g., yttrium(III), zirconium(IV) and antimony(III)) reported in the literature.

V. SUMMARY

(i) The new uranium(VI) complexes of 5-methyl-, 5-chloro-, 5-phenyl- and 7-phenyl-8-hydroxyquinoline have been prepared and shown by elemental and infrared analysis to have formulae of the type $UO_2(R\text{-}Q)_2 \cdot R\text{-}QH$. The infrared spectra exhibit bands characteristic of the $\overset{+}{N}\text{—}H\text{--}O$ hydrogen-bonded system found in the 8-hydroxyquinoline adducts of uranium(VI) and thorium(IV). This strongly suggests that the additional ligands are coordinated as zwitterions.

(ii) The new complexes of the 7-methyl-, 2,7-dimethyl- and 7-tert-butyl- derivatives have been prepared and shown by similar techniques to have the formulae $UO_2(R\text{-}Q)_2 \cdot Y$, where Y = NH_3, H_2O or acetone.

(iii) The present study shows that the complexes, $UO_2(C_9H_4NOX_2)_2$ and $UO_2(C_9H_4NOX_2)_2 \cdot C_9H_5NOX_2$, where X = Cℓ or Br, cannot be precipitated from aqueous acetone solution as proposed by Moeller and Ramaniah. As demonstrated for the 5,7-dichloro- derivative, one compound is precipitated, with the formula $UO_2(C_9H_4NOC\ell_2)_2 \cdot OC(CH_3)_2$. Because of the insolubility of 5,7-dibromo-8-hydroxyquinoline, the composition of its uranium(VI) complex could not be established with certainty but the similarity of its infrared spectrum with that of the dichloro complex suggests a corresponding composition.

(iv) The failure of certain 7-substituted derivatives to form complexes of the type $UO_2(R\text{-}Q)_2 \cdot R\text{-}QH$ has been attributed to inter-ligand steric interactions.

(v) The thermal products of the general reaction,

$$UO_2(R\text{-}Q)_2 \cdot Y(solid) \overset{\Delta}{\rightleftharpoons} UO_2(R\text{-}Q)_2(solid) + Y(gas)$$

have been prepared and characterized.

(vi) The acidic proton of the previously known complex of 2-methyl-8-hydroxyquinoline, $UO_2(C_{10}H_8NO)_2 \cdot C_{10}H_9NO$, has been located on the ring nitrogen atom of the monodentate ligand, and is likely bonded in a similar manner to the additional ligand in $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$. Attempts to prepare complexes of other 2-substituted derivatives such as 2-n-butyl-, 2-phenyl- and 2-(2'-thienyl)-8-hydroxyquinoline were unsuccessful. The failure of these derivatives to form even complexes of the type $UO_2(R\text{-}Q)_2 \cdot Y$ has been attributed to steric interactions between the 2-substituent and water molecules coordinated to the uranium atom. This effect was substantiated by chelate-formation data.

(vii) The composition of the 8-hydroxyquinoline complex of scandium(III) precipitated from aqueous solution has been re-examined and shown by chemical analysis, infrared spectroscopy, X-ray powder crystallography and thermogravimetric analysis to have the formula $Sc(C_9H_6NO)_3 \cdot H_2O$ rather than the formulae $Sc(C_9H_6NO)_3$ and $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ proposed by other workers. The erroneous "adduct" formula resulted from reagent contamination. The continued use of the complex as an analytical compound is possible but other existing methods of determination for scandium appear to be more convenient.

(viii) The scandium(III) complex of the 2-methyl- derivative precipitated from aqueous solution has been demonstrated by similar techniques to have the formula $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$ (when dried

at low temperature) rather than $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$ proposed previously.

(ix) The new scandium(III) complexes of 2- and 4-chloro- and 5-methyl-8-hydroxyquinoline have been prepared from aqueous solution and shown to have formulae of the type $Sc(R\text{-}Q)_3 \cdot H_2O$. The new complex of the 4-methyl- derivative has the formula $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO$.

(x) Precipitation of the complexes $Sc(R\text{-}Q)_3 \cdot R\text{-}QH$ from aqueous solution appears to depend on the $\log {}^{c}K_{NH}$ value of the ligands. For ligands with $\log {}^{c}K_{NH}$ values that are too low, a water molecule can successfully compete for a scandium coordination site, and complexes of the type $Sc(R\text{-}Q)_3 \cdot H_2O$ are formed. The 8-hydroxyquinoline adduct, $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$, can be prepared in the absence of water.

(xi) The scandium(III) complex of 8-hydroxyquinoline obtained from the reagent melt has been shown to be $Sc(C_9H_6NO)_3 \cdot C_9H_7NO$ rather than $[Sc(C_9H_6NO)_3]_2 \cdot 3C_9H_7NO$ proposed by other workers.

(xii) The thermal products of the general reaction,

$$Sc(R\text{-}Q)_3 \cdot Z(\text{solid}) \overset{\Delta}{=} Sc(R\text{-}Q)_3(\text{solid}) + Z(\text{gas})$$

have been prepared and characterized (Z = H_2O or R-QH).

(xiii) Formation constants of the scandium(III) complexes of 8-hydroxyquinoline and its 2- and 4-methyl- derivatives have been determined by potentiometric titration.

(xiv) The major factors that govern the formation of the complexes $M(R\text{-}Q)_z \cdot R\text{-}QH$ (where, for example, M = U(VI), Th(IV) and Sc(III)) are metal-ion coordination number, and ligand basicity and steric effects.

(xv) It is the recommendation of this thesis that the terms

"addition" or "adduct" complex be discontinued because the compounds are clearly not precipitated from solution by an addition reaction in the strictest sense of term. Use of the IUPAC convention[109] is suggested; for example, this nomeclature designates $UO_2(C_9H_6NO)_2 \cdot C_9H_7NO$ as bis(8-hydroxyquinolato)(8-hydroxyquinoline)uranyl(VI) and $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_9NO \cdot 2H_2O$ as tris(2-methyl-8-hydroxyquinolato)(2-methyl-8-hydroxyquinoline)scandium(III) dihydrate.

VI. APPENDICES

APPENDIX A

PROTON MAGNETIC RESONANCE SPECTRA OF 8-HYDROXYQUINOLINE DERIVATIVES

All spectra were recorded with carbon tetrachloride as solvent and tetramethylsilane as internal reference.

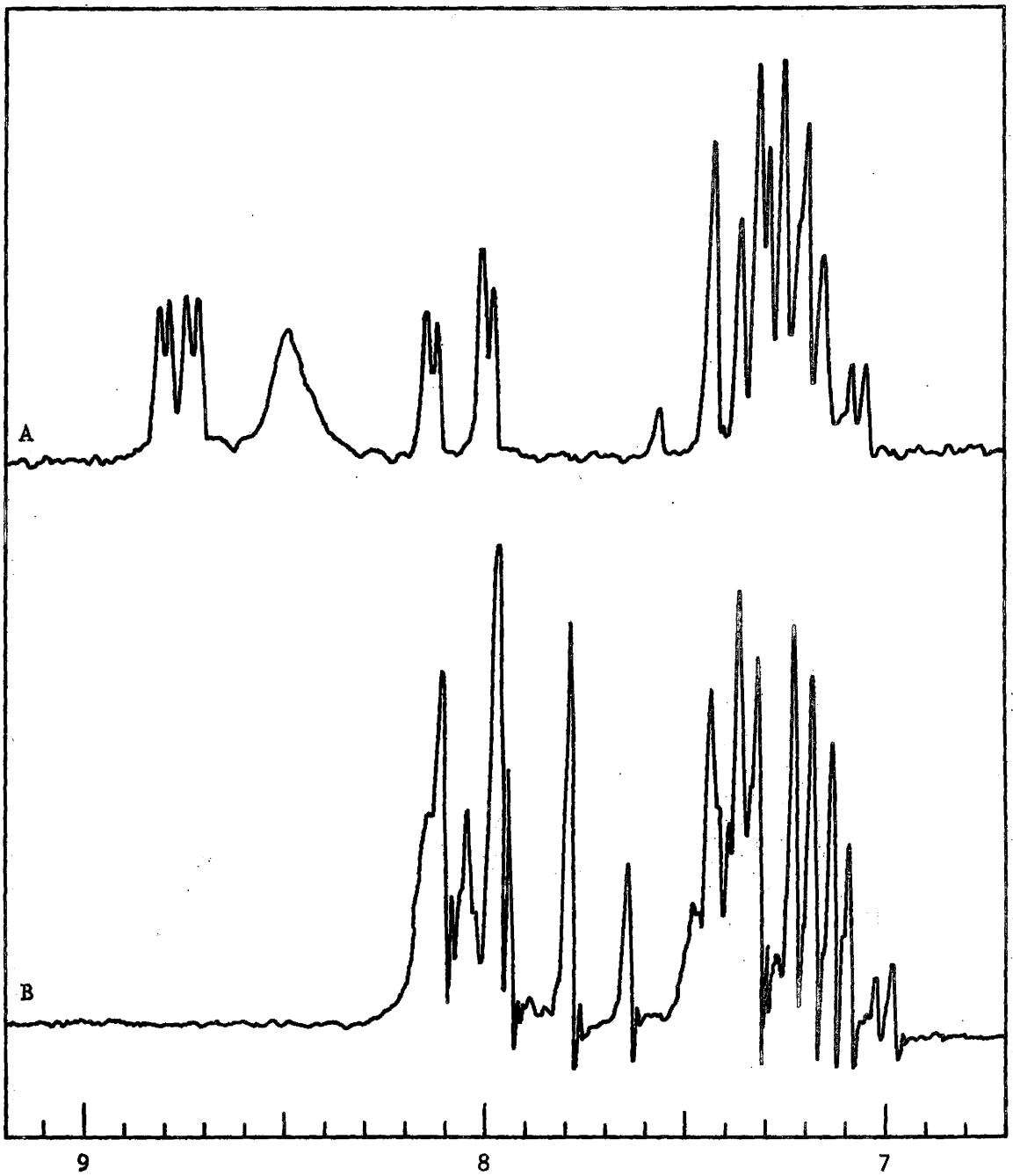

Figure 1. Proton magnetic resonance spectra.

A. 8-Hydroxyquinoline; B. 2-Phenyl-8-hydroxyquinoline.

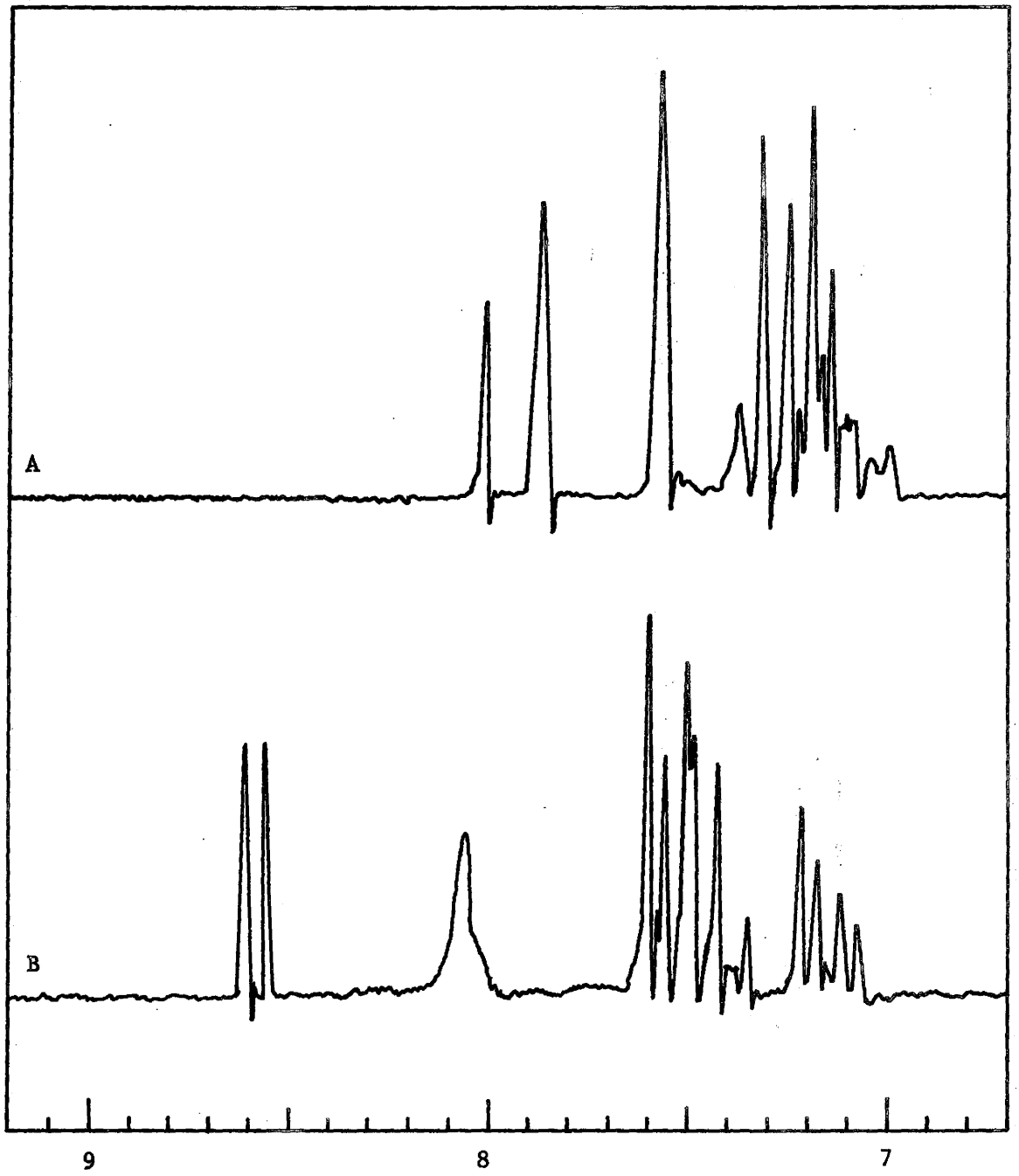

Figure 2. Proton magnetic resonance spectra.

A. 2-Chloro-8-hydroxyquinoline;

B. 4-Chloro-8-hydroxyquinoline.

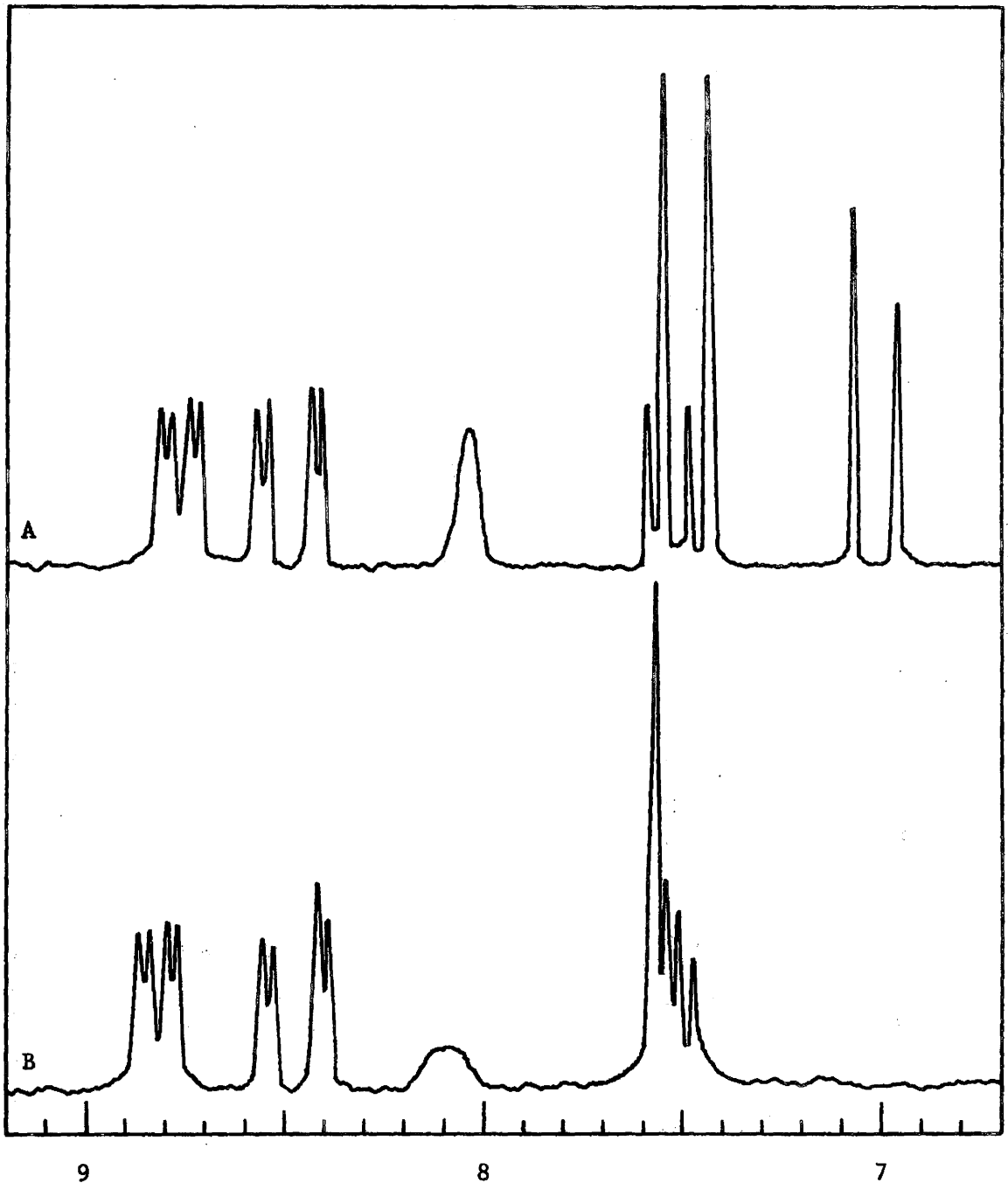

Figure 3. Proton magnetic resonance spectra.

A. 5-Chloro-8-hydroxyquinoline;

B. 5,7-Dichloro-8-hydroxyquinoline.

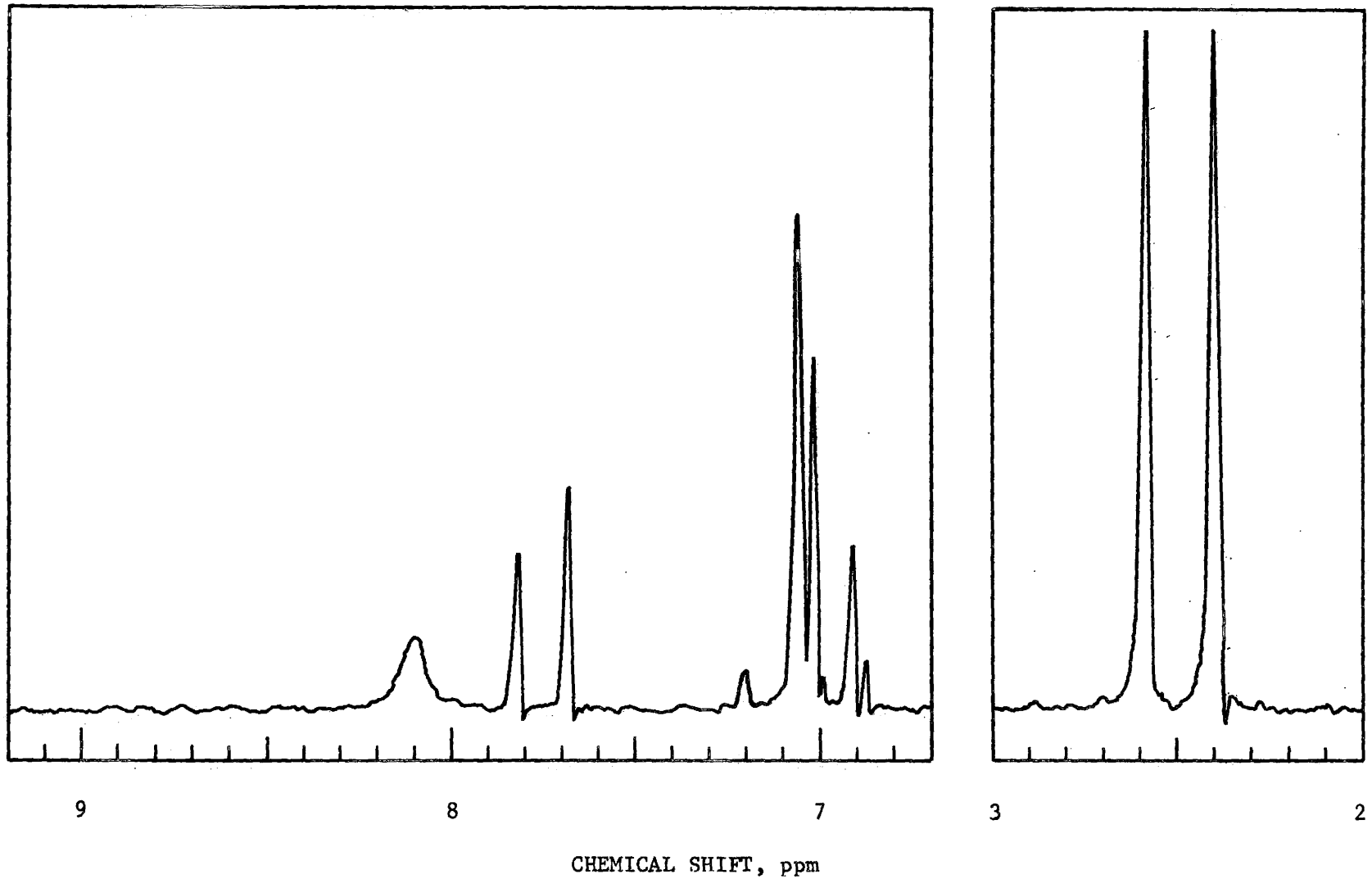

Figure 4. Proton magnetic resonance spectrum of 2,7-dimethyl-8-hydroxyquinoline.

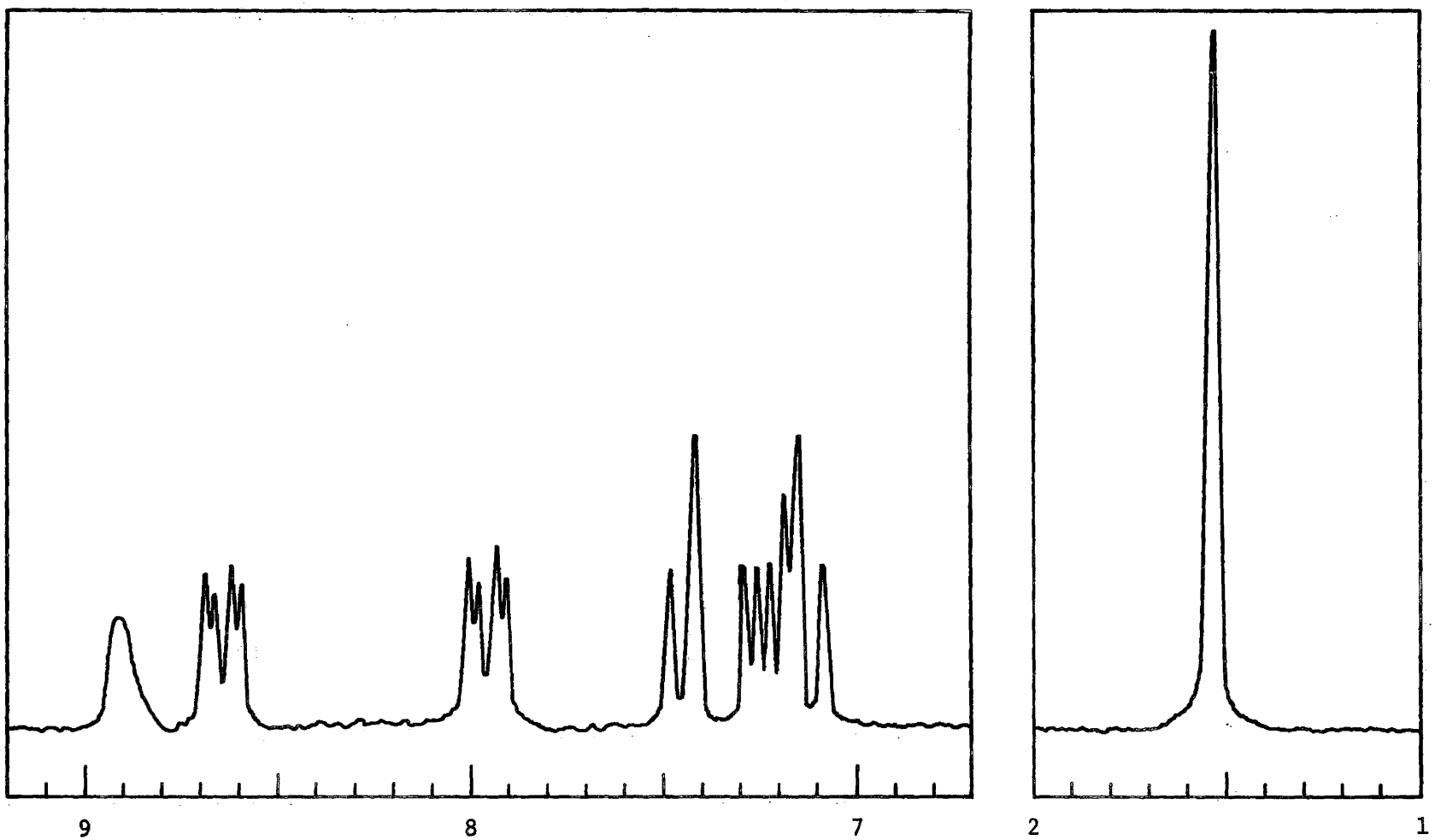

Figure 5. Proton magnetic resonance spectrum of 7-tert -butyl-8-hydroxyquinoline. (Note: 1.53 ppm peak is not at the same spectrum amplitude as the peaks in the region 7-9 ppm.)

APPENDIX B

FORTRAN IV COMPUTER PROGRAM FOR EVALUATION OF PROTONATION CONSTANTS

```
C     EVALUATION  OF  REAGENT  DISSØCIATIØN  CØNSTANTS
C     PØTENTIØMETRIC  TITRATIØN  DATA
C
      DIMENSIØN   TITLE(12), VNAØH(48), B(48), P(48), TH(48),A(10)
      READ(5,100)M
  100 FØRMAT(I4)
      DØ 10  L = 1,M
      READ(5,101) TITLE
  101 FØRMAT(12A6)
      READ(5,500) TNAØH, THCLØ, TØR, RMW
  500 FØRMAT(4E11.5)
      WRITE(6,103) TITLE
  103 FØRMAT(1H1,12A6)
      WRITE(6,107)
  107 FØRMAT(8OH- NØ.       VØL. NAØH       PH(CØRR.)            P
     1CØRRECT N       PK(CALC)/)
      READ(5,108) VNAØH, B
  108 FØRMAT(16F5.3)
      JJ  =  48
      DØ 60 J = 1,48
      IF(B(J).NE.0.000) GØ TØ 1400
 1401 NF  =  J - 1
      GØ  TØ  1402
 1400 IF(J.NE.JJ)  GØ  TØ  1404
 1403 NF  =  J
      GØ TØ 1402
 1404 CØNTINUE
   60 JD = J+1
 1402 N  =  NF
      PRDX  =  50.00
      PKW=15.37
      CF=-0.08
      Ø = PRDX/(100.0-PRDX)
      DØ  11  J = 1,N
      VØLA=110.00
      VDIØX = Ø*VNAØH(J)
      VØL = VØLA + VNAØH(J) + VDIØX
      THR  =  (TØR*0.1EO4)/(RMW*VØL)
      TCLØ  =  (50.00*THCLØ)VØL
      TNA  =  (VNAØH(J)*TNAØH)/VØL
      IF(B(J)-9.6)  70,71,71
   70 C = 0.0
      GØ  TØ  400
   71 CY  =  (0.438*B(J)) - 7.2
      C  =  10.0**CY
  400 BA  =  B(J) + CF + C
      TH(J) = 10.0**(-BA)
      TØH = (10.0**(-PKW))/TH(J)
      P(J)  =  ((1.000*THR) + TCLØ + TØH - TH(J) - TNA)/THR
      IF(P(J).GT.2.900) GØ TØ 1100
 1109 IF(P(J).LT.1.900) GØ TØ 1101
 1102 IF(P(J).LT.2.100) GØ TØ 1100
```

```
 1103 YM = P(J) - 2.000
      YN = 3.000 - P(J)
      GØ TØ 1200
 1101 IF(P(J).LT.0.900) GØ TØ 1104
 1105 IF(P(J).LT.1.100) GØ TØ 1100
 1106 YM = P(J) - 1.000
      YN = 2.000 - P(J)
      GØ TØ 1200
 1104 IF(P(J).LT.0.100) GØ TØ 1100
 1107 YM = P(J)
      YN = 1.000 - P(J)
      GØ TØ 1200
 1100 WRITE(6,117) J, VNAØH(J), BA, P(J)
  117 FØRMAT(1H+, I4,3(6X, F9.3))
      GØ TØ 1300
 1200 YP  =  ALØG10(YM/YN)
      PKC  =  BA + YP
      WRITE(6,111) J, VNAØH(J), BA, P(J), YP, PKC
  111 FØRMAT(1H+, I4,5(6X, F9.3))
 1300 CØNTINUE
   11 JA = J + 1
C
C       SØRTING  ØF  HALF-P VALUES
C       DETERMINATIØN  ØF  LLSFTD PARAMETERS
C
      DØ 40 J = 1,N
      IF(P(J).GT.1.800) GØ TØ 40
 2001 IF(P(J).LE.1.200.AND.P(J).GE.0.800)  GØ  TØ  40
 6000 IF(J.EQ.1)  GØ  TØ  2020
 2021 NNN  =  J - 1
      GØ TØ 2002
 2020 NNN  =  1
      GØ  TØ  2002
   40 JC = J+1
 2002 DØ 41 J = 16,N
      IF(P(J).GE.0.200) GØ TØ 41
 2004 NNS = J-1
      GØ TØ 2005
   41 JD = J+1
      NNS  =  N
 2005 DØ 42 J = 1,10
      K = NNN + J
   42 A(J) = P(K+1) - P(K)
      DØ 43 J = 1,10
      IF(A(J).LT.0.000) GØ TØ 43
 2007 MT = NNN + J
      GØ TØ 2008
   43 JE = J + 1
      JA = NNN
      GØ TØ 2009
 2008 JA = MT
 2009 NA = NNS - JA
```

```
      SUMV = 0.0
      DØ 44 J = 1,N
      IF(P(J).LE.1.200.AND.P(J).GE.0.800) GØ TØ 2010
 2011 GØ TØ 44
 2010 AX  =  J
      SUMV  =  SUMV + (AX/AX)
   44 JF = J + 1
      NF = INT(SUMV)
      IF(P(JA).LE.1.200.AND.P(JA).GE.0.800)  GØ  TØ  7011
 7010 NB  =  NA - NF
      GØ TØ 7012
 7011 NB  =  NA
 7012 WRITE(6,5010) JA, NA, NB
 5010 FØRMAT(1HO, 3I4)
C
C     REAGENT  DISSØCIATIØN  CØNSTANT  REFINEMENT
C     LINEAR  LEAST  SQUARE  FIT  TØ  DATA  TREATMENT
C
      SUMX = 0.0
      SUMY = 0.0
      SUMXY = 0.0
      SUMX2 = 0.0
      DØ  12   J = 1,NA
      K  =  JA + J
C
C     ELIMINATIØN  ØF  P  VALUES  WITHIN  1.2  AND  0.8
C
      IF(P(K).LE.1.200.AND.P(K).GE.0.800)  GØ  TØ  31
   30 X = ((2.0 - P(K))*TH(K))/(P(K) - 1.0)
      Y = P(K)/((P(K) - 1.0)*TH(K))
      GØ  TØ  800
   31 X = 0.0
      Y = 0.0
  800 SUMX = SUMX + X
      SUMY = SUMY + Y
      SUMXY = SUMXY + (X*Y)
   12 SUMX2 = SUMX2 + (X*X)
      AN = NB
      YIN = (SUMX*SUMXY) - (SUMY*SUMX2)
      SLØ = (SUMX*SUMY) - (AN*SUMXY)
      DEN = (SUMX*SUMX) - (AN*SUMX2)
      YINT = YIN/DEN
      SLØPE = SLØ/DEN
      AK1 = -YINT
      DK1 = ABS((1.0/AK1))
      AK2 = SLØPE/AK1
      DK2 = ABS((1.0/AK2))
      PK2 = -ALØG10(DK1)
      PK1 = -ALØG10(DK2)
      WRITE(6,122)PK1,PK2
  122 FØRMAT(7HO PK1 =,F8.4,7H  PK2 =,F8.4)
```

```
      ALK2  =  10.00**(-PK2)
      ALK1  =  10.00**(-PK1)
      ZI  =  FLØAT(NA)
      SIGMA  =  0.000
      DØ  23  J = 1,NA
      K  =  JA + J
      AX  =  (ALK1*TH(K)) + (2.000*TH(K)*TH(K))
      AY  =  (ALK1*ALK2) + (ALK1*TH(K)) + (TH(K)*TH(K))
      PT  =  AX/AY
      DELP  =  P(K) - PT
   23 SIGMA  =  SIGMA + (DELP*DELP)
      SIGMA  =  SQRT(SIGMA/ZI)
      WRITE(6,7253) SIGMA
 7253 FØRMAT(44HO EVALUATIØN  ØF  DATA  PRECISIØN,  SIGMA  =, E11.41
   10 LA = L + 1
      STØP
      END
```

APPENDIX C

POTENTIOMETRIC DETERMINATION OF PROTONATION CONSTANTS

TABLE I

PROTONATION CONSTANTS OF 8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

HL = 0.707 millimoles

$HC\ell O_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\overline{P}$	$Log^{C}K$
0.00	3.803	1.671	4.113
0.20	3.869	1.641	4.120
0.30	3.901	1.625	4.123
0.40	3.928	1.609	4.121
0.50	3.958	1.593	4.122
0.60	3.987	1.578	4.123
0.70	4.018	1.562	4.126
0.80	4.046	1.546	4.125
0.90	4.072	1.529	4.123
1.00	4.103	1.513	4.126
1.10	4.130	1.497	4.125
1.20	4.159	1.481	4.126
1.50	4.246	1.432	4.127
1.70	4.302	1.399	4.124
1.90	4.364	1.366	4.125

Table I (cont'd.)

Vol. Base (ml)	pH	$\bar{P}$	$\text{Log}^{C}K$
2.10	4.426	1.333	4.124
2.30	4.494	1.300	4.125
2.50	4.570	1.266	4.130
2.70	4.649	1.233	4.132
5.30	10.542	0.797	11.137
5.40	10.584	0.781	11.135
5.50	10.624	0.764	11.134
5.60	10.662	0.747	11.133
5.70	10.697	0.731	11.130
5.80	10.733	0.714	11.130
6.00	10.801	0.681	11.129
6.20	10.863	0.647	11.127
6.40	10.923	0.614	11.125
6.70	11.011	0.565	11.123
7.00	11.096	0.515	11.122
7.20	11.152	0.483	11.122
7.40	11.204	0.450	11.117
7.70	11.288	0.402	11.115
8.00	11.373	0.354	11.111
8.30	11.461	0.307	11.108
8.60	11.554	0.261	11.103
9.00	11.685	0.203	11.092

$\text{Log}^{C}K_{NH} = 4.12$ $\text{Log}^{C}K_{OH} = 11.12$ $\sigma = 0.01$

TABLE II

PROTONATION CONSTANTS OF 2-METHYL-8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

HL = 0.558 millimoles

$HClO_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\bar{P}$	$Log^{C}K$
0.40	4.179	1.782	4.734
0.60	4.280	1.742	4.738
1.30	4.574	1.596	4.743
1.40	4.611	1.575	4.742
1.50	4.650	1.554	4.744
1.60	4.685	1.533	4.742
1.80	4.761	1.490	4.744
2.00	4.836	1.448	4.745
2.40	4.912	1.405	4.745
2.60	4.994	1.362	4.749
2.80	5.078	1.320	4.750
3.00	5.173	1.277	4.756
5.20	11.083	0.773	11.615
5.40	11.174	0.732	11.612
5.60	11.255	0.692	11.607
5.80	11.333	0.653	11.607

Table II (cont'd.)

Vol. Base (ml)	pH	$\bar{P}$	$\text{Log}^{c}K$
6.00	11.404	0.613	11.604
6.20	11.473	0.574	11.603
6.40	11.539	0.536	11.601
6.60	11.604	0.498	11.601
6.80	11.670	0.461	11.603
7.00	11.730	0.425	11.599
7.20	11.794	0.390	11.600
7.40	11.856	0.356	11.599
7.60	11.919	0.324	11.601
7.80	11.981	0.294	11.600
8.00	12.043	0.265	11.600

$\text{Log}^{c}K_{NH} = 4.75$ $\text{Log}^{c}K_{OH} = 11.60$ $\sigma = 0.001$

TABLE III

PROTONATION CONSTANTS OF 4-METHYL-8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

HL = 0.422 millimoles

$HC\ell O_4$ = 0.00984 M

NaOH = 0.1250 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\overline{P}$	Log^cK
1.20	4.222	1.795	4.810
1.40	4.372	1.740	4.826
1.60	4.502	1.684	4.837
1.80	4.625	1.626	4.850
2.00	4.732	1.569	4.852
2.20	4.841	1.510	4.859
2.40	4.948	1.452	4.864
2.60	5.060	1.393	4.872
2.80	5.177	1.335	4.879
3.00	5.301	1.276	4.882
3.20	5.451	1.217	4.894
4.80	10.777	0.751	11.257
5.00	10.896	0.694	11.252
5.20	11.010	0.638	11.256
5.40	11.111	0.582	11.255
5.62	11.212	0.521	11.248

Table III (cont'd.)

Vol. Base (ml)	pH	$\overline{P}$	$Log^{C}K$
5.80	11.294	0.472	11.245
6.00	11.376	0.418	11.231
6.20	11.465	0.365	11.225
6.40	11.549	0.314	11.209
6.60	11.638	0.265	11.195
6.80	11.730	0.219	11.177

$Log^{C}K_{NH} = 4.85$ $Log^{C}K_{OH} = 11.23$ $\sigma = 0.01$

TABLE IV

PROTONATION CONSTANTS OF 5-METHYL-8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

HL = 0.481 millimoles

$HC\ell O_4$ = 0.00984 M

NaOH = 0.1250 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\overline{P}$	$Log^{c}K$
0.80	3.710	1.770	4.234
1.00	3.825	1.728	4.253
1.20	3.925	1.683	4.259
1.40	4.024	1.637	4.268
1.60	4.119	1.589	4.276
1.80	4.209	1.541	4.280
2.00	4.299	1.491	4.284
2.20	4.389	1.441	4.287
2.40	4.480	1.391	4.288
2.60	4.576	1.341	4.290
2.80	4.681	1.290	4.293
3.00	4.799	1.239	4.297
4.80	10.914	0.784	11.474
5.00	11.036	0.735	11.479
5.20	11.142	0.686	11.482
5.40	11.230	0.638	11.475

Table IV (cont'd.)

Vol. Base (ml)	pH	$\bar{P}$	$Log^{c}K$
5.60	11.314	0.590	11.472
5.80	11.394	0.542	11.467
6.00	11.467	0.495	11.459
6.20	11.542	0.449	11.453
6.40	11.612	0.404	11.444
6.60	11.680	0.360	11.430
6.80	11.754	0.318	11.422
7.00	11.820	0.276	11.402
7.20	11.892	0.238	11.386
7.40	11.962	0.201	11.362

$Log^{c}K_{NH} = 4.27$ $Log^{c}K_{OH} = 11.44$ $\sigma = 0.01$

TABLE V

PROTONATION CONSTANTS OF 7-METHYL-8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

HL = 0.462 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1250 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\bar{p}$	$Log^{c}K$
0.60	3.325	1.788	3.896
0.80	3.418	1.756	3.909
1.00	3.510	1.719	3.918
1.20	3.600	1.679	3.925
1.40	3.692	1.636	3.935
1.60	3.781	1.591	3.941
1.80	3.869	1.544	3.946
2.00	3.960	1.497	3.954
2.20	4.049	1.447	3.957
2.40	4.138	1.397	3.957
2.60	4.232	1.347	3.957
2.80	4.336	1.296	3.959
3.00	4.449	1.244	3.958
4.80	11.164	0.782	11.720
5.00	11.282	0.733	11.722
5.20	11.386	0.685	11.723

Table V (cont'd.)

Vol. Base (ml)	pH	$\bar{p}$	$Log^{c}K$
5.40	11.476	0.637	11.721
5.60	11.559	0.590	11.718
5.80	11.635	0.544	11.713
6.00	11.707	0.499	11.706
6.20	11.774	0.455	11.695
6.40	11.838	0.412	11.683
6.60	11.901	0.370	11.670
6.80	11.962	0.330	11.654
7.00	12.021	0.292	11.636
7.20	12.079	0.255	11.614
7.40	12.134	0.220	11.584

$Log^{c}K_{NH} = 3.94$ $Log^{c}K_{OH} = 11.68$ $\sigma = 0.02$

TABLE VI

PROTONATION CONSTANTS OF 2-CHLORO-8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

HL = 0.267 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1250 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\bar{p}$	$Log^{C}K$
4.40	10.097	0.785	10.660
4.60	10.322	0.693	10.677
4.80	10.502	0.602	10.681
5.00	10.654	0.511	10.673
5.20	10.804	0.421	10.665
5.40	10.946	0.332	10.643
5.60	11.095	0.246	10.608

$Log^{C}K_{OH}$ = 10.65

TABLE VII

PROTONATION CONSTANTS OF 4-CHLORO-8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

HL = 0.358 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1250 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\bar{p}$	$Log^{c}K$
0.00	2.602	1.606	2.788
0.20	2.638	1.594	2.804
0.42	2.676	1.574	2.806
0.60	2.710	1.559	2.812
0.80	2.749	1.539	2.817
1.00	2.790	1.517	2.820
1.20	2.832	1.493	2.819
1.40	2.879	1.469	2.825
1.60	2.930	1.444	2.832
1.80	2.981	1.414	2.830
2.00	3.039	1.385	2.835
2.20	3.102	1.353	2.839
2.40	3.170	1.319	2.841
2.60	3.242	1.282	2.836
2.80	3.332	1.246	2.846
3.00	3.430	1.206	2.845

Table VII (cont'd.)

Vol. Base (ml)	pH	$\bar{p}$	$Log^{C}K$
4.60	9.872	0.769	10.396
4.80	10.036	0.700	10.404
5.00	10.177	0.631	10.410
5.20	10.297	0.562	10.405
5.40	10.412	0.493	10.400
5.60	10.522	0.424	10.389
5.80	10.629	0.356	10.371
6.00	10.740	0.288	10.347
6.20	10.853	0.220	10.304

$Log^{C}K_{NH} = 2.83$ $Log^{C}K_{OH} = 10.38$ $\sigma = 0.01$

TABLE VIII

PROTONATION CONSTANTS OF 2-N-BUTYL-8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

H_2L^+ = 0.572 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\bar{p}$	Log ^cK
5.10	4.038	1.769	4.561
5.30	4.126	1.731	4.559
5.50	4.209	1.691	4.559
5.70	4.287	1.651	4.559
6.00	4.399	1.591	4.559
6.20	4.472	1.550	4.559
6.40	4.549	1.509	4.565
6.60	4.624	1.468	4.569
6.80	4.703	1.427	4.575
7.00	4.783	1.386	4.581
7.20	4.871	1.344	4.591
7.40	4.969	1.303	4.607
7.60	5.074	1.261	4.623
7.80	5.200	1.220	4.650
10.00	11.396	0.783	11.953
10.20	11.476	0.746	11.944

Table VIII (cont'd.)

Vol. Base (ml)	pH	$\bar{p}$	$\text{Log}^{c}K$
10.40	11.548	0.709	11.935
10.60	11.617	0.673	11.931
10.80	11.681	0.638	11.926
11.00	11.740	0.603	11.921
11.20	11.794	0.568	11.913
11.40	11.852	0.535	11.912
11.60	11.908	0.503	11.913
11.80	11.963	0.472	11.914
12.00	12.015	0.442	11.914
12.20	12.071	0.414	11.921
12.40	12.122	0.387	11.923
12.60	12.168	0.361	11.920
12.80	12.218	0.337	11.925
13.00	12.267	0.316	11.931
13.20	12.313	0.295	11.935
13.40	12.355	0.275	11.935
13.60	12.398	0.258	11.939

$\text{Log}^{c}K_{NH} = 4.58$ $\text{Log}^{c}K_{OH} = 11.93$ $\sigma = 0.02$

TABLE IX

PROTONATION CONSTANTS OF 2-(2'-THIENYL)-8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

HL = 0.370 millimoles

$HCl\ell O_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\bar{p}$	$Log^{C}K$
4.80	11.113	0.788	11.684
5.00	11.237	0.729	11.667
5.20	11.352	0.672	11.663
5.40	11.456	0.615	11.660
5.60	11.551	0.560	11.656
5.80	11.639	0.507	11.651
6.00	11.725	0.455	11.647
6.20	11.811	0.407	11.647
6.40	11.891	0.361	11.642
6.60	11.972	0.319	11.642
6.80	12.051	0.281	11.642
7.00	12.124	0.246	11.636
7.20	12.195	0.215	11.633

$Log^{C}K_{OH}$ = 11.64

TABLE X

PROTONATION CONSTANTS OF 2-PHENYL-8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

HL = 0.367 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\bar{p}$	$Log^{C}K$
0.00	2.510	1.414	2.360
0.20	2.536	1.399	2.359
0.50	2.578	1.378	2.361
0.80	2.624	1.356	2.366
1.10	2.672	1.330	2.364
1.40	2.724	1.302	2.360
1.90	2.827	1.256	2.365
2.20	2.898	1.226	2.363
2.40	2.954	1.207	2.370
4.80	11.206	0.791	11.783
5.00	11.339	0.734	11.779
5.20	11.455	0.677	11.777
5.40	11.558	0.623	11.776
5.60	11.650	0.569	11.771
5.80	11.737	0.518	11.769
6.00	11.818	0.469	11.765

Table X (cont'd.)

Vol. Base (ml)	pH	$\bar{p}$	$Log^{c}K$
6.20	11.899	0.423	11.764
6.40	11.975	0.379	11.761
6.60	12.050	0.340	11.761
6.80	12.119	0.302	11.756
7.00	12.186	0.269	11.752
7.20	12.250	0.240	11.748

$Log^{c}K_{NH} = 2.36$ $Log^{c}K_{OH} = 11.77$ $\sigma = 0.01$

TABLE XI

PROTONATION CONSTANTS OF 7-TERT -BUTYL-8-HYDROXYQUINOLINE IN 50% v/v DIOXANE

HL = 0.522 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

Vol. Base (ml)	pH	$\bar{p}$	Log ^{c}K
0.00	2.468	1.512	2.488
0.20	2.498	1.510	2.516
0.40	2.525	1.492	2.512
0.60	2.556	1.482	2.525
1.00	2.619	1.446	2.525
1.20	2.653	1.426	2.523
1.40	2.690	1.407	2.526
1.60	2.731	1.389	2.535
1.80	2.773	1.366	2.534
2.00	2.819	1.342	2.536
2.20	2.870	1.319	2.540
2.40	2.923	1.289	2.533
2.60	2.993	1.272	2.565
2.80	3.068	1.246	2.582
3.00	3.151	1.215	2.589
6.30	12.652	0.868	13.468

Table XI (cont'd.)

Vol. Base (ml)	pH	$\bar{p}$	$\text{Log}^{c}K$
6.60	12.704	0.847	13.447
6.90	12.749	0.820	13.407
7.20	12.791	0.801	13.395

$\text{Log}^{c}K_{NH} = 2.50$ $\text{Log}^{c}K_{OH} = 13.4$ $\sigma = 0.03$

(By extrapolation)

APPENDIX D

FORTRAN IV COMPUTER PROGRAM FOR EVALUATION OF $\bar{\pi}$ AND [L] PARAMETERS

```
C       EVALUATION  OF  STABILITY  CONSTANTS  OF  METAL  CHELATES
C       N BAR  CALCULATIONS
C       POTENTIOMETRIC  TITRATION  DATA
C
      DIMENSION VNAOH(32), B(32), EN(32), R(32), ENN(32), RR(32),
     1ENNN(32), RRR(32), TITLE(3), PKNH(4), PKOH(4), DOT(44), TTLA(3)
      READ(5,100) MN
  100 FORMAT(I4)
      DO  47   MP = 1,MN
      READ(5,65) TTLA
   65 FORMAT(3A6)
      READ(5,206) PKNH(1), PKOH(1)
  206 FORMAT(2F5.3)
      READ(5,102) TITLE,THM
  102 FORMAT(3A6,E11.4)
      WRITE(6,64) (TTLA(J), J = 1,3)
   64 FORMAT(1H1,20HMETAL  CHELATES  OF ,3A6)
      READ(5,311) TNAOH, THCLO, TOHR, TOR, TOM
  311 FORMAT(5E11.5)
      WRITE(6,211) PKNH(1), PKOH(1)
  211 FORMAT( 14HO PK   VALUES,2(6X,F7.3))
      READ(5,106) VNAOH, B
  106 FORMAT(16F5.3)
      JJ  =  32
      DO  60  J = 1,32
      IF(B(J).NE.0.000) GO TO 1400
 1401 NF  =  J - 1
      GO  TO  1402
 1400 IF(J.NE.JJ)  GO  TO  1404
 1403 NF  =  J
      GO TO 1402
 1404 CONTINUE
   60 JD = J+1
 1402 N  =  NF
      VOLCU=5.00
      PKW=15.37
      PRDX  =  50.00
      CF=-0.08
  280 O = PRDX/(100.0-PRDX)
      AKNH  =  10.00**(-PKNH(1))
      AKOH  =  10.00**(-PKOH(1))
      WRITE(6,109) TITLE, PRDX
  109 FORMAT(1HO,3A6,41H  STABILITY  CONSTANT, PERCENT  DIOXANE =,F6.1)
  992 WRITE(6,110)
  110 FORMAT( 99HO              CALVIN-WILSON                          GIL
     1BERT-HEARON                          ROSSOTTI)
  993 WRITE(6,111)
  111 FORMAT(108HO NO.          N-BAR             PR                   N-B
     1AR            PR                N-BAR           PR  /)
      DO 11   J = 1,N
      VOLA=110.00
```

```
      VDIOX = O*VNAOH(J)
      VOL = VOLA + VDIOX + VNAOH(J)
      IF(B(J)-9.6)  70,71,71
   70 C = 0.0
      GO  TO  400
   71 CY  = (0.438*B(J)) - 7.2
      C  =  10.0**CY
  400 BA  =  B(J) + CF + C
      TH = 10.0**(-BA)
      TM  =  (TOM*VOLCU)/VOL
      THR  =  (TOHR*O.1E04)/(TOR*VOL)
      TOH = (10.0**(-PKW))/TH
      EA  =  (VOLCU*THM)/VOL
  295  TCLO  =  ((50.00*THCLO)/VOL) + EA
      TNA  =  (V AOH(J)*TNAOH)/VOL
C
C     CALVIN  WILSON  METHOD
C
      S = THR + TCLO + TOH - TNA - TH
      RAT = (AKNH + TH)/(AKNH + (2.0*TH))
      EN(J) = (THR - (S*RAT))/TM
      R(J) = (S*AKNH*AKOH)/(TH*(AKNH + (2.0*TH)))
      PR  =  -ALOG10(ABS(R(J)))
C
C     GILBERT  HEARON  METHOD
C
      BETA1  =  1.000/AKOH
      BETA2  =  1.000/(AKNH*AKOH)
      RATA  =  (BETA1*TH) + (2.000*BETA2*TH*TH)
      TCL  =  TCLO + (2.000*TM)
      RR(J)  =  (THR - (2.000*TM) - TNA - TH + TCL  + TOH)/RATA
      REGA  =  1.000 + (BETA1*TH) + (BETA2*TH*TH)
      ENN(J)  =  (THR - (RR(J)*REGA))/TM
      PRA  =  -ALOG10(ABS(RR(J)))
C
C     ROSSOTTI  ROSSOTTI  METHOD
C
      ENH  =  RATA/REGA
      RRR(J)  =  (THR - (ENH*TM))/REGA
      STS  =  (TCLO + THR - TNA - TH + TOH)/ENH
      ENNN(J)  =  (THR - STS)/TM
      PRB  =  -ALOG10(ABS(RRR(J)))
   11 WRITE(6,112) J, EN(J), PR, ENN(J), PRA, ENNN(J), PRB
  112 FORMAT(1H ,I4,2(6X,F9.3),6X,2(6X,F9.3),6X,2(6X,F9.3))
   47 MPA  =  MP + 1
      STOP
      END
```

APPENDIX E

POTENTIOMETRIC DETERMINATION OF CHELATE FORMATION CONSTANTS

TABLE I

CHELATES OF URANIUM(VI) IN 50% v/v DIOXANE

8-HYDROXYQUINOLINE FORMATION CONSTANTS

HL = 0.319 millimoles

M^{2+} = 0.050 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

$\bar{n}$	pL^*
0.368	11.674
0.436	11.545
0.512	11.410
0.594	11.272
0.687	11.134
0.775	10.985
0.859	10.829
0.945	10.673
1.027	10.515
1.107	10.357
1.189	10.203
1.272	10.052
1.345	9.892

* $pL = -Log[L^-]$.

Table I (cont'd.)

$\bar{n}$	pL^*
1.430	9.736
1.506	9.565

$Log^C K_1 = 11.42$ $Log^C K_2 = 9.67$

2-METHYL-8-HYDROXYQUINOLINE FORMATION CONSTANTS

HL = 0.367 millimoles

M^{2+} = 0.050 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

$\bar{n}$	pL
0.307	10.684
0.380	10.487
0.455	10.313
0.523	10.147
0.583	9.987
0.646	9.837
0.708	9.694

$Log^C K_1 = 10.28$

2-n-BUTYL-8-HYDROXYQUINOLINE FORMATION CONSTANTS

H_2L^+ = 0.259 millimoles

M^{2+} = 0.050 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1202 M

Table I (cont'd.)

Ionic strength = 0.1

Temperature = 25°C

$\bar{n}$	pL
0.253	10.863
0.331	10.667
0.410	10.481
0.487	10.298
0.574	10.122

$\text{Log}^{C}K_1 = 10.39$

7-TERT -BUTYL-8-HYDROXYQUINOLINE FORMATION CONSTANTS

HL = 0.375 millimoles

M^{2+} = 0.050 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

$\bar{n}$	pL
0.412	13.606
0.442	13.573
0.438	13.582
0.461	13.494
0.478	13.454
0.500	13.414
0.551	13.377
0.550	13.328
0.590	13.284

Table I (cont'd.)

$\bar{n}$	pL
0.616	13.235
0.633	13.182
0.662	13.127
0.685	13.066
0.702	12.999
0.745	12.933
0.786	12.858
0.817	12.770
0.866	12.674
0.934	12.565
1.008	12.431
1.105	12.262
1.249	12.042
1.453	11.713

$Log^{c}K_1 = 13.39$ $Log^{c}K_2 = 11.58$

2-PHENYL-8-HYDROXYQUINOLINE FORMATION CONSTANTS

HL = 0.243 millimoles

M^{2+} = 0.050 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

$\bar{n}^{*}$	pL
0.107	12.137
0.096	12.095

Table I (cont'd.)

$\bar{n}$*	pL
0.094	12.054
0.068	12.005
0.098	11.967

2-(2'-THIENYL)-8-HYDROXYQUINOLINE FORMATION CONSTANTS

HL = 0.324 millimoles

M^{2+} = 0.050 millimoles

$HClO_4$ = 0.00984 M

NaOH = 0.1202 M

Ionic strength = 0.1

Temperature = 25°C

$\bar{n}$*	pL
0.076	11.732
0.098	11.705
0.145	11.680
0.161	11.648
0.193	11.616
0.219	11.581
0.223	11.539

*The $\bar{n}$ values represent the maximum chelation obtained with the 2-phenyl-, and 2-(2'-thienyl)- substituted ligands.

TABLE II

CHELATES OF SCANDIUM(III) IN 50% v/v DIOXANE

8-HYDROXYQUINOLINE FORMATION CONSTANTS

HL = 0.512 millimoles

M^{3+} = 0.050 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1250 M

Ionic strength = 0.1

Temperature = 25°C

$\bar{n}$	pL
0.538	11.306
0.595	11.171
0.650	11.031
0.682	10.962
0.799	10.770
0.869	10.639
0.947	10.515
1.016	10.390
1.085	10.269
1.156	10.153
1.228	10.042
1.292	9.930
1.363	9.824
1.425	9.716
1.497	9.614
1.574	9.513

Table II (cont'd.)

$\bar{n}$	pL
1.639	9.404
1.718	9.299
1.791	9.185
1.871	9.065
1.950	8.931
2.042	8.782
2.140	8.599
2.278	8.378
2.358	8.231
2.464	8.064
2.580	7.823

$Log^{c}K_1 = 11.26$ $Log^{c}K_2 = 9.61$ $Log^{c}K_3 = 8.05$

2-METHYL-8-HYDROXYQUINOLINE FORMATION CONSTANTS

HL = 0.505 millimoles

M^{3+} = 0.050 millimoles

$HC\ell O_4$ = 0.00984 M

NaOH = 0.1250 M

Ionic strength = 0.1

Temperature = 25°C

$\bar{n}$	pL
0.327	11.878
0.379	11.600
0.455	11.351
0.530	11.110
0.613	10.899

Table II (cont'd.)

$\bar{n}$	pL
0.675	10.689
0.749	10.515
0.810	10.347
0.864	10.191
0.923	10.051
0.965	9.911
0.997	9.775
1.057	9.659
1.091	9.534
1.157	9.426
1.206	9.309
1.279	9.200
1.354	9.087
1.446	8.974
1.538	8.849
1.710	8.747
1.853	8.608

$Log^{c}K_1 = 11.18$ $Log^{c}K_2 = 8.6$ $Log^{c}K_3 = 8.5$

4-METHYL-8-HYDROXYQUINOLINE FORMATION CONSTANTS

HL = 0.505 millimoles

M^{3+} = 0.050 millimoles

$HCl O_4$ = 0.00984 M

NaOH = 0.1250 M

Ionic strength = 0.1

Temperature = 25°C

Table II (cont'd.)

$\bar{n}$	pL
0.534	11.834
0.629	11.621
0.746	11.418
0.870	11.211
0.995	11.004
1.135	10.784
1.250	10.619
1.373	10.441
1.494	10.277
1.613	10.126
1.726	9.981
1.830	9.841
1.928	9.707
2.013	9.572
2.092	9.441
2.165	9.313
2.233	9.186
2.292	9.057
2.342	8.923

$\text{Log}^{C}K_1 = 11.78$ $\text{Log}^{C}K_2 = 10.28$ $\text{Log}^{C}K_3 = 8.82$

APPENDIX F

INFRARED SPECTRA OF URANIUM(VI) AND SCANDIUM(III) COMPLEXES OF 8-HYDROXYQUINOLINE AND DERIVATIVES

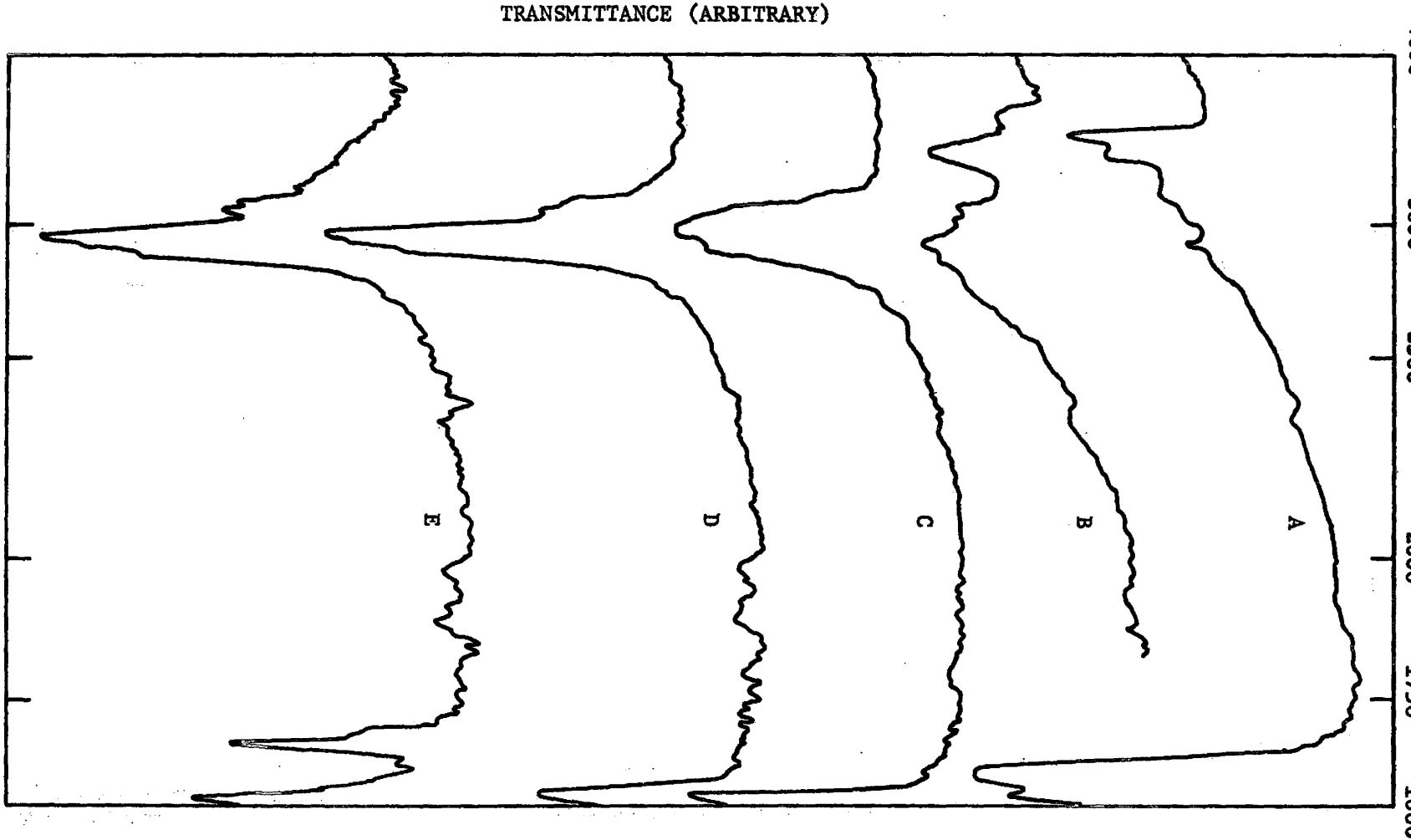

Figure 1. Infrared spectra of bis U(VI) complexes of 8-hydroxyquinoline derivatives. A. $UO_2(7\text{-Me-Q})_2 \cdot NH_3$; B. $UO_2(7\text{-Me-Q})_2 \cdot H_2O$; C. $UO_2(2,7\text{-Dime-Q})_2 \cdot H_2O$; D. U(VI)—7-t-But-QH compound, aqueous precipitation; E. U(VI)—7-t-But-QH compound, aqueous acetone precipitation.

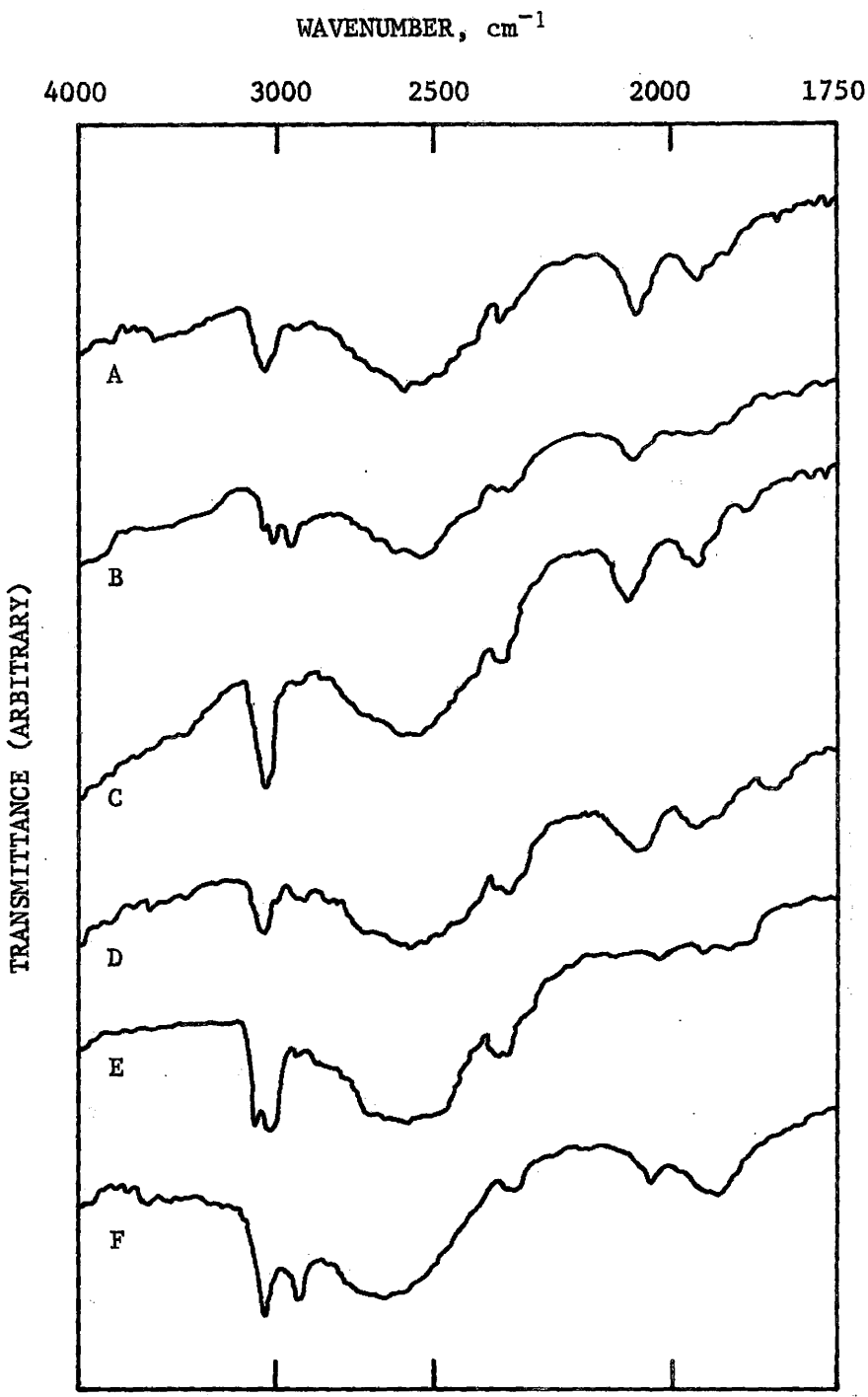

Figure 2. Infrared spectra of tris U(VI) complexes of 8-hydroxyquinoline derivatives.

A. $UO_2(Q)_2 \cdot QH$[17]; B. $UO_2(5\text{-Me-Q})_2 \cdot 5\text{-Me-QH}$;

C. $UO_2(5\text{-Ph-Q})_2 \cdot 5\text{-Ph-QH}$; D. $UO_2(5\text{-C}\ell\text{-Q})_2 \cdot 5\text{-C}\ell\text{-QH}$;

E. $UO_2(7\text{-Ph-Q})_2 \cdot 7\text{-Ph-QH}$; F. $UO_2(2\text{-Me-Q})_2 \cdot 2\text{-Me-QH}$.

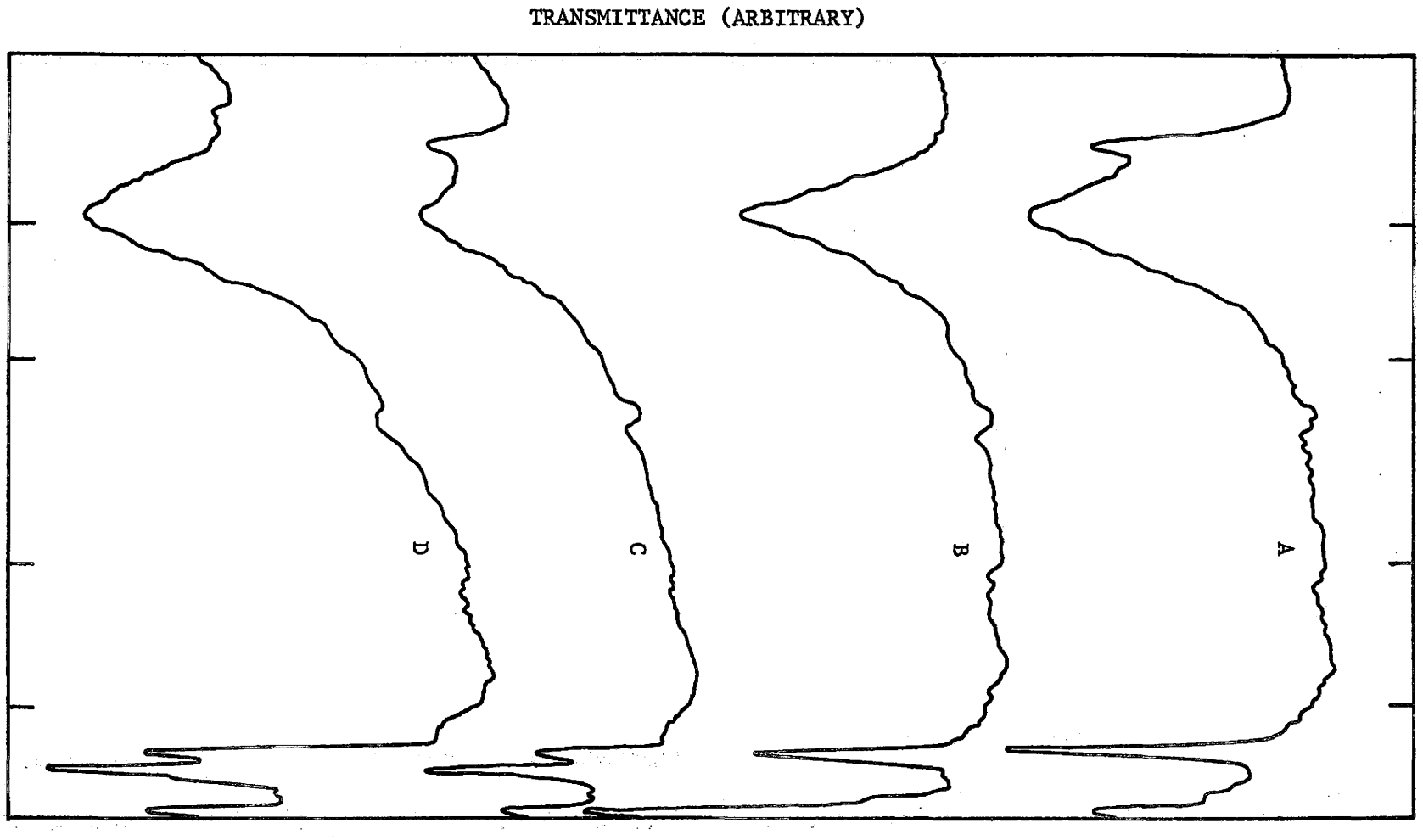

Figure 3. Infrared spectra of U(VI) complexes of 5,7-dihalo-8-hydroxyquinolines prepared by the literature method.

A. $UO_2(5,7\text{-DiC}\ell\text{-Q})_2$; B. $UO_2(5,7\text{-DiC}\ell\text{-Q})_2 \cdot 5,7\text{-DiC}\ell\text{-QH}$; C. $UO_2(5,7\text{-DiBr-Q})_2$;

D. $UO_2(5,7\text{-DiBr-Q})_2 \cdot 5,7\text{-DiBr-QH}$.

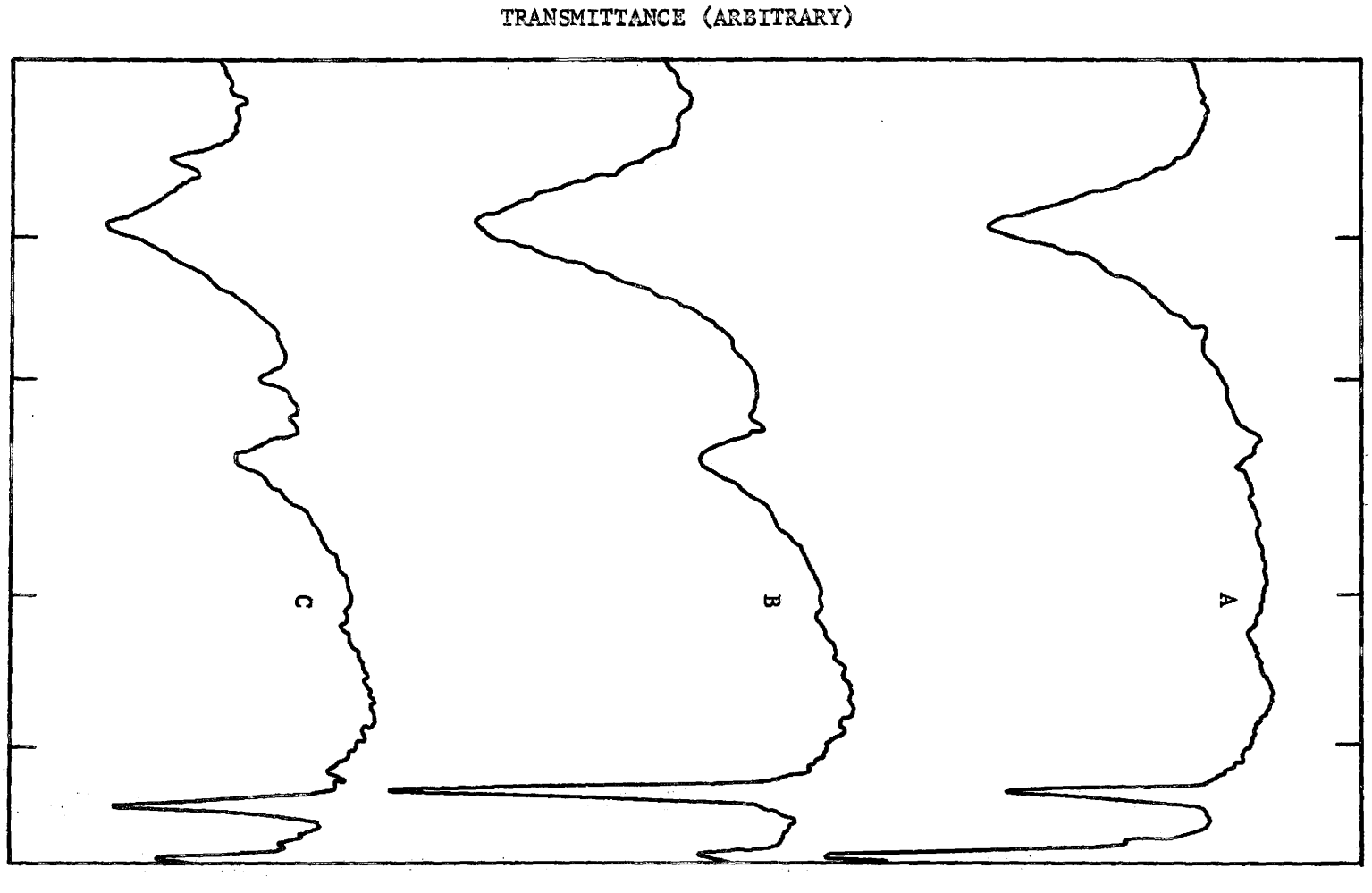

Figure 4. Infrared spectra of U(VI) complexes of 5,7-dichloro-8-hydroxyquinoline. A. U(VI)—5,7-DiCℓ-QH complex by modified procedure; B. A from D_2O/CH_3COCH_3 medium; C. A from D_2O/CD_3COCD_3 medium.

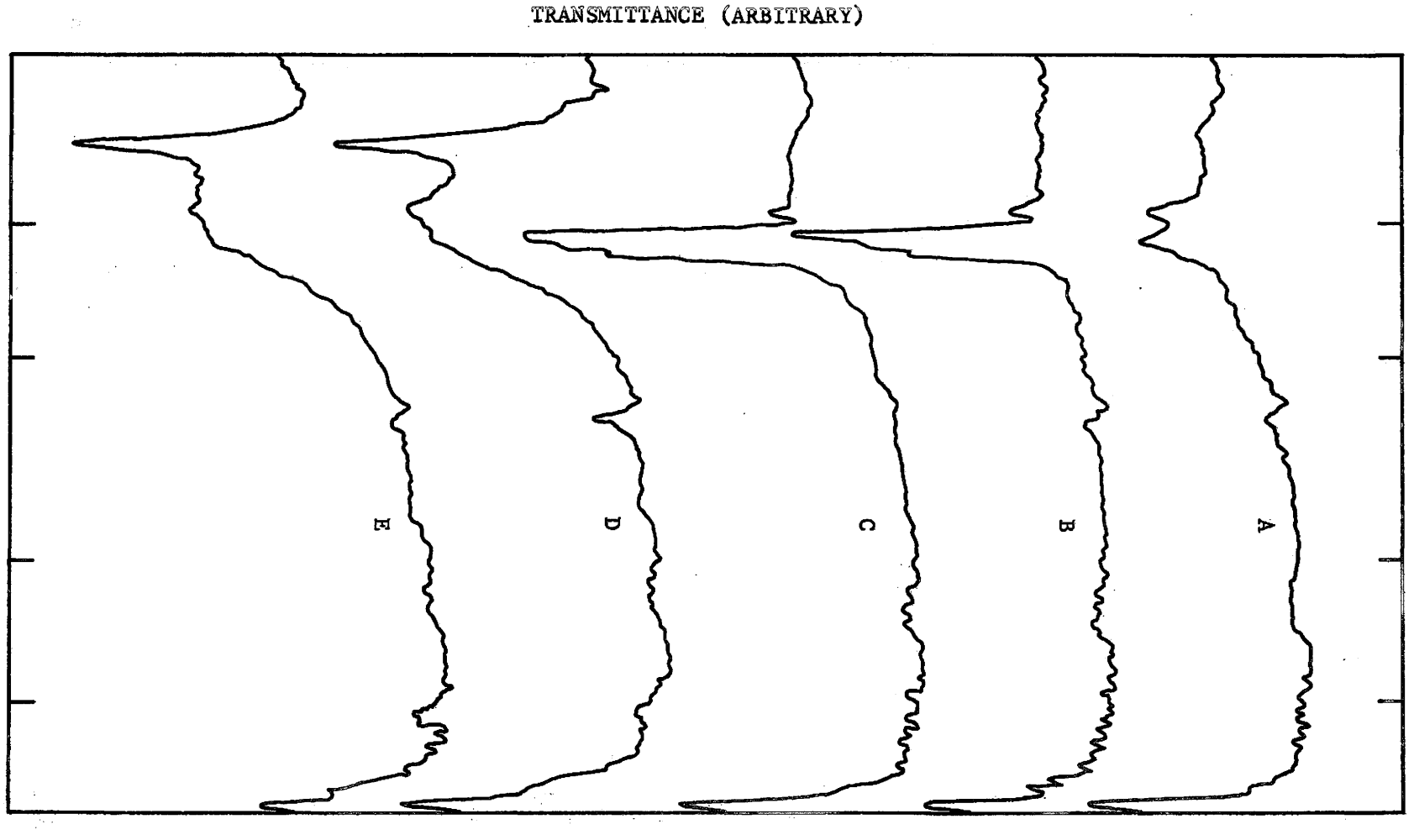

Figure 5. Infrared spectra of thermal products of bis U(VI) complexes of 8-hydroxyquinoline derivatives. A. $UO_2(7\text{-Me-Q})_2$; B. $UO_2(7\text{-t-But-Q})_2$ from aqueous precipitated compound; C. $UO_2(7\text{-t-But-Q})_2$ from aqueous acetone precipitated compound; D. $UO_2(5,7\text{-DiCl-Q})_2$; E. $UO_2(5,7\text{-DiBr-Q})_2$.

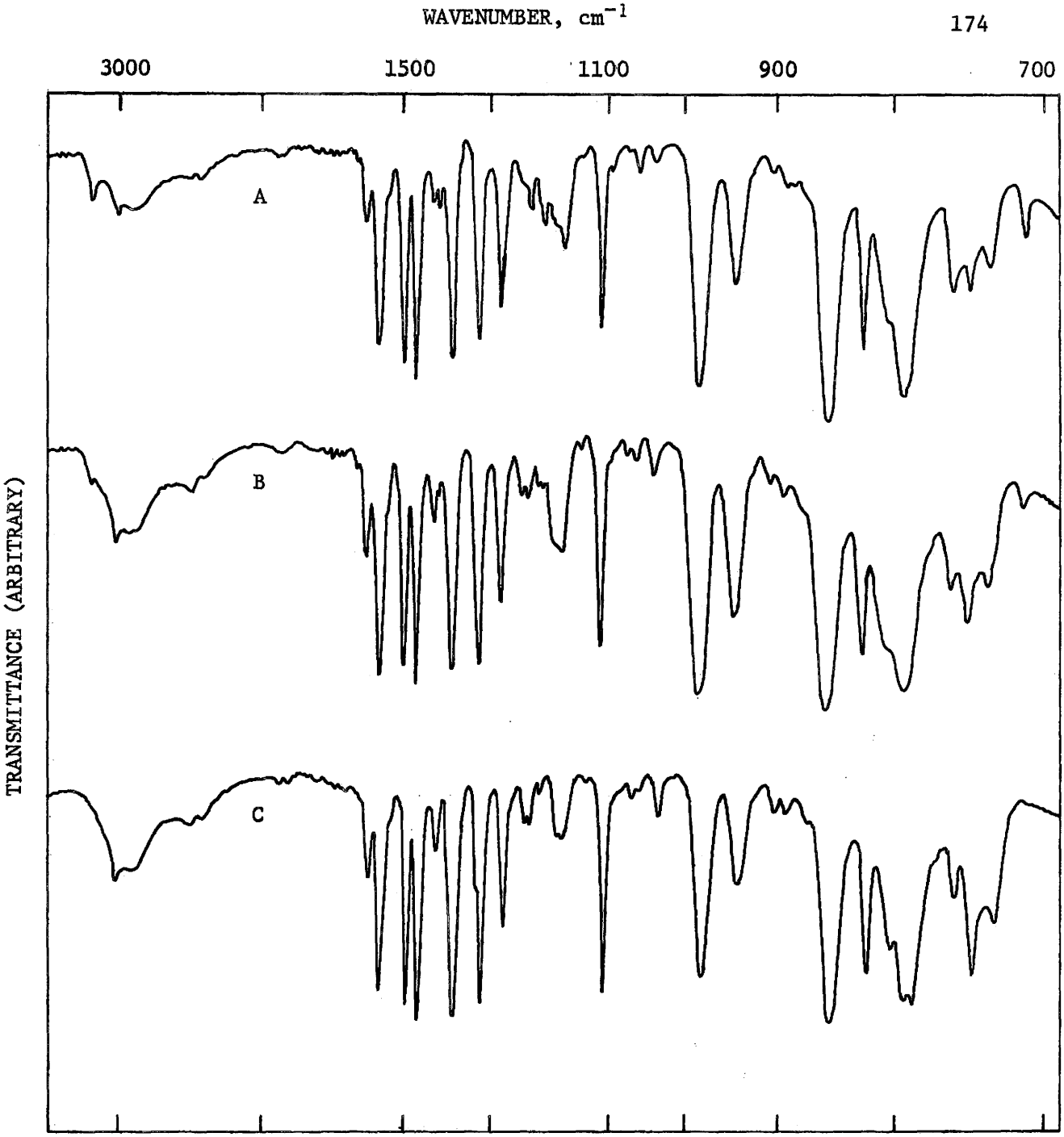

Figure 6. Infrared spectra of Sc(III) complexes of 8-hydroxyquinoline. A. Pokras and Bernays' compound; B. Compound precipitated from 10% v/v aqueous acetone; C. $Sc(Q)_3 \cdot H_2O$.

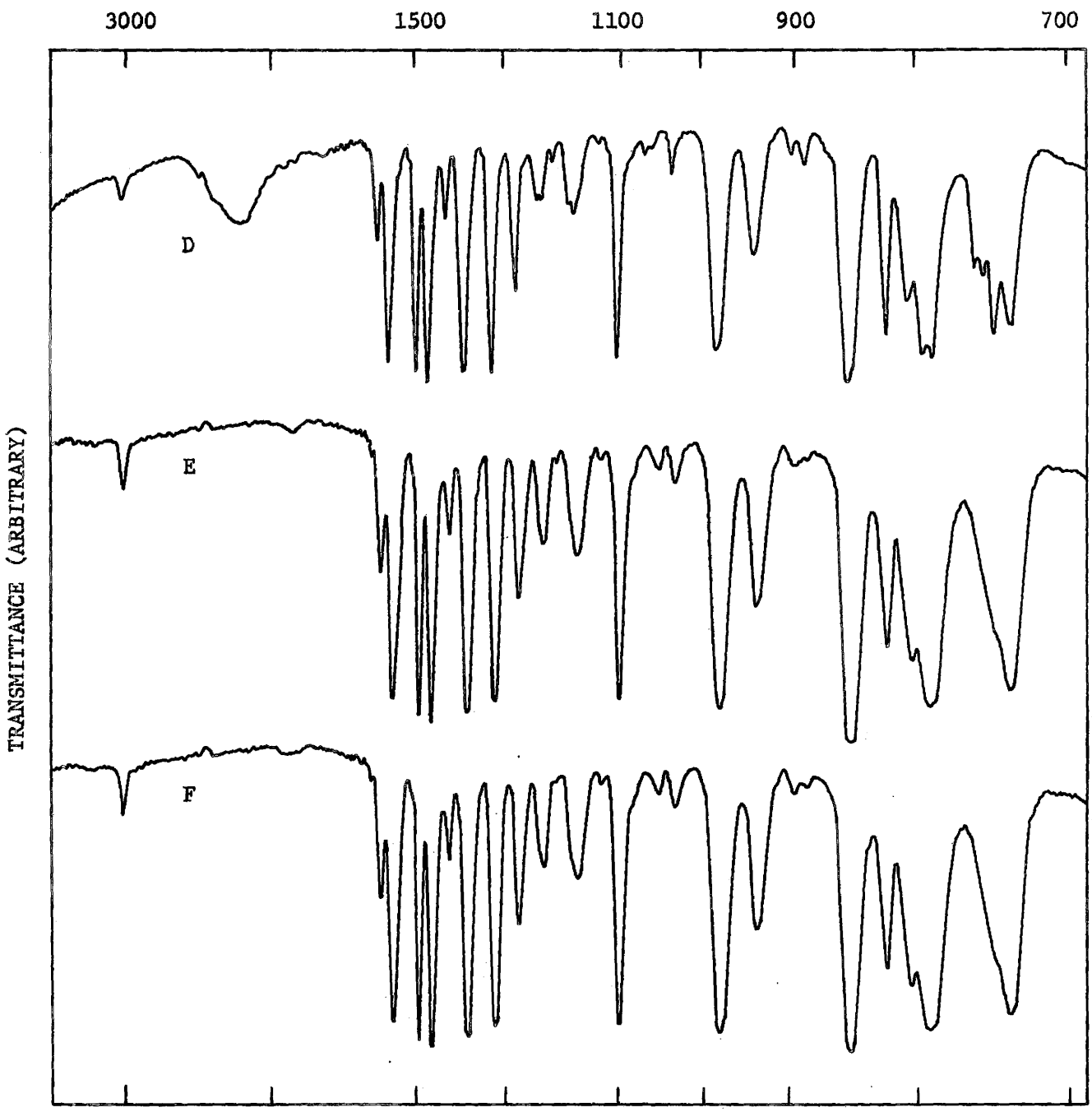

Figure 6 (cont'd.) Infrared spectra of Sc(III) complexes of 8-hydroxyquinoline.

D. $Sc(Q)_3 \cdot D_2O$; E. $Sc(Q)_{2.7}(OAc)_{0.3}$; F. Thermal product, $Sc(Q)_3$.

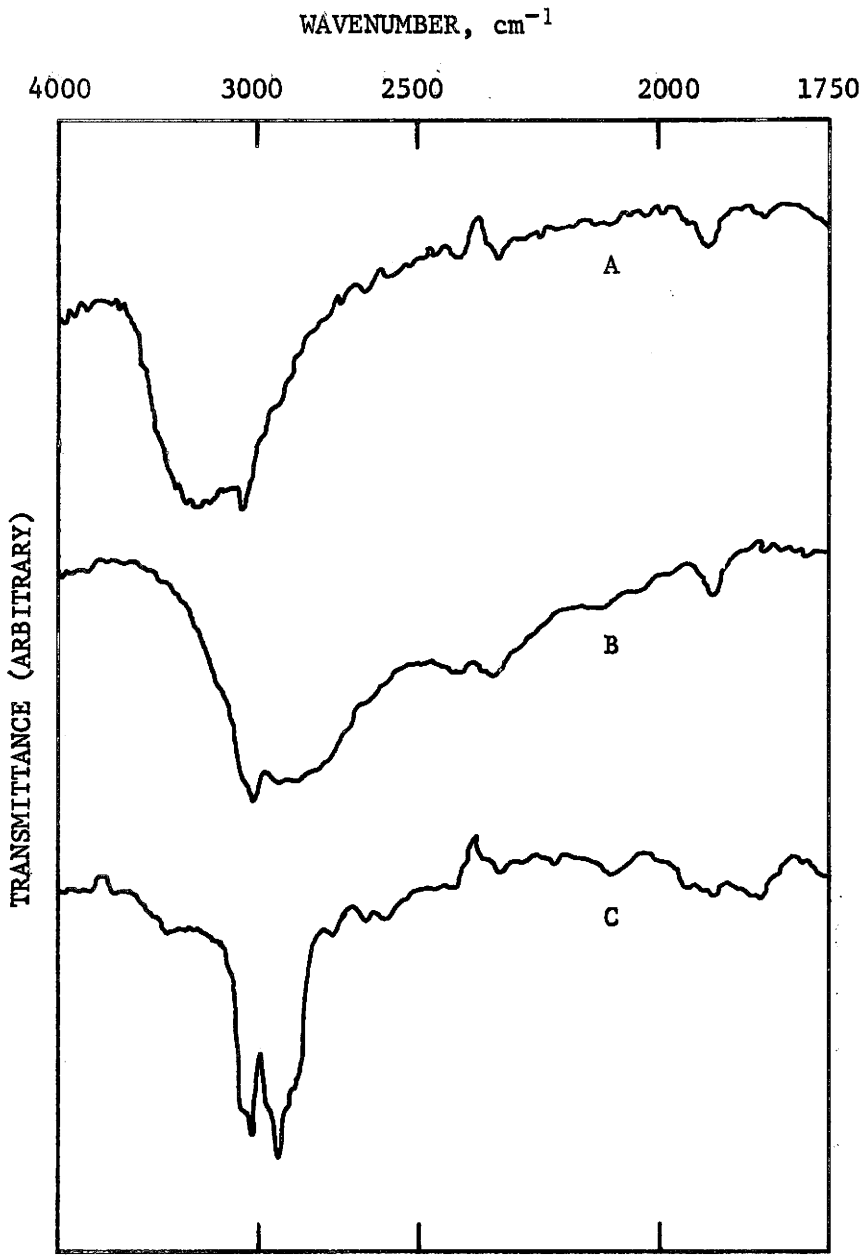

Figure 7. Infrared spectra of tris Sc(III) complexes of 8-hydroxyquinoline derivatives.

A. $Sc(2\text{-}C\ell\text{-}Q)_2 \cdot H_2O$; B. $Sc(4\text{-}C\ell\text{-}Q)_2 \cdot H_2O$;

C. $Sc(5\text{-}Me\text{-}Q)_2 \cdot H_2O$.

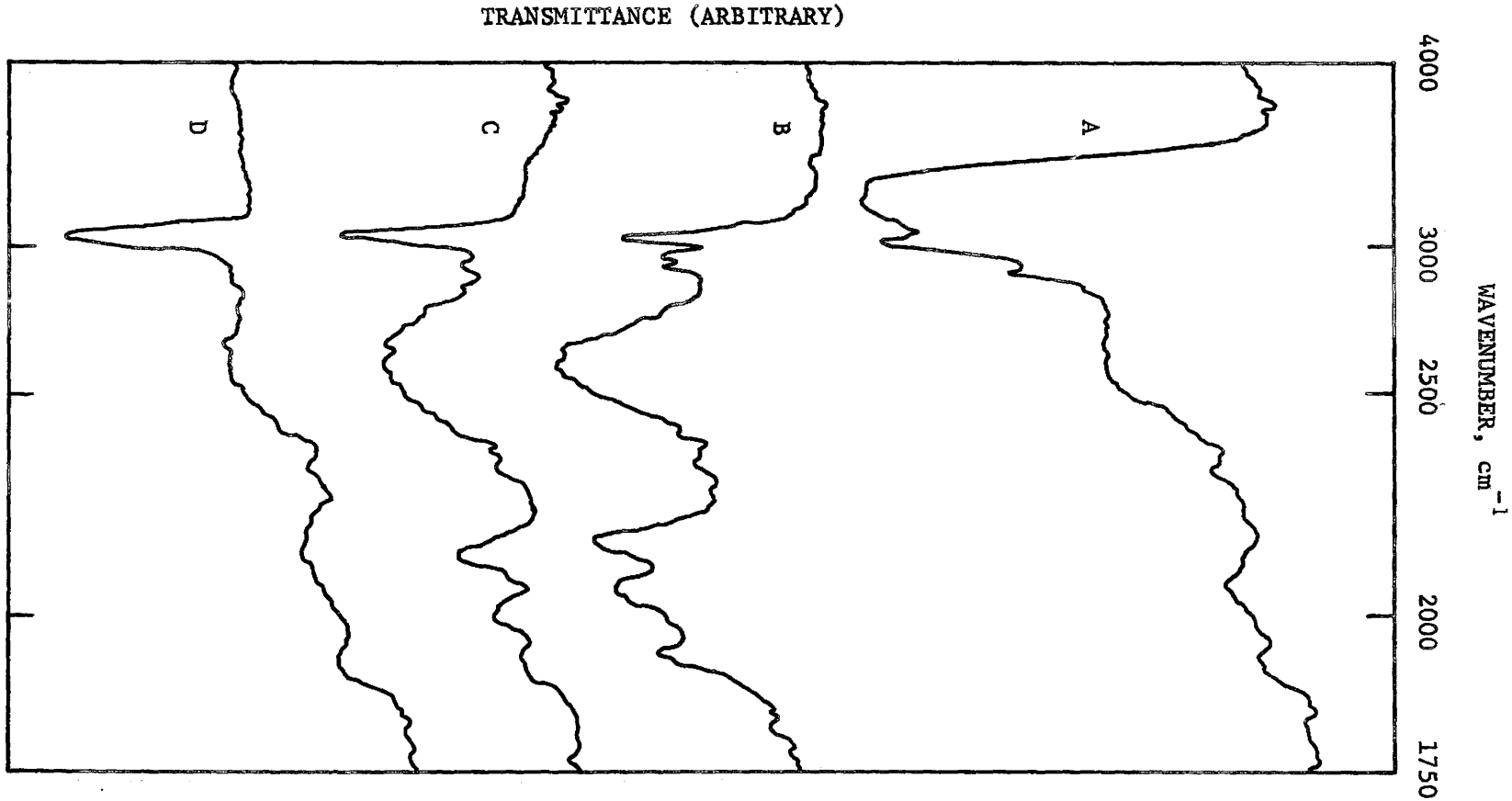

Figure 8. Infrared spectra of tetrakis Sc(III) complexes of 8-hydroxyquinoline and derivatives. A. $Sc(2\text{-Me-Q})_3 \cdot 2\text{-Me-QH} \cdot 2H_2O$; B. $Sc(4\text{-Me-Q})_3 \cdot 4\text{-Me-QH}$; C. Melt product, $Sc(Q)_3 \cdot QH$; D. Melt product, $Sc(Q)_3 \cdot QD$.

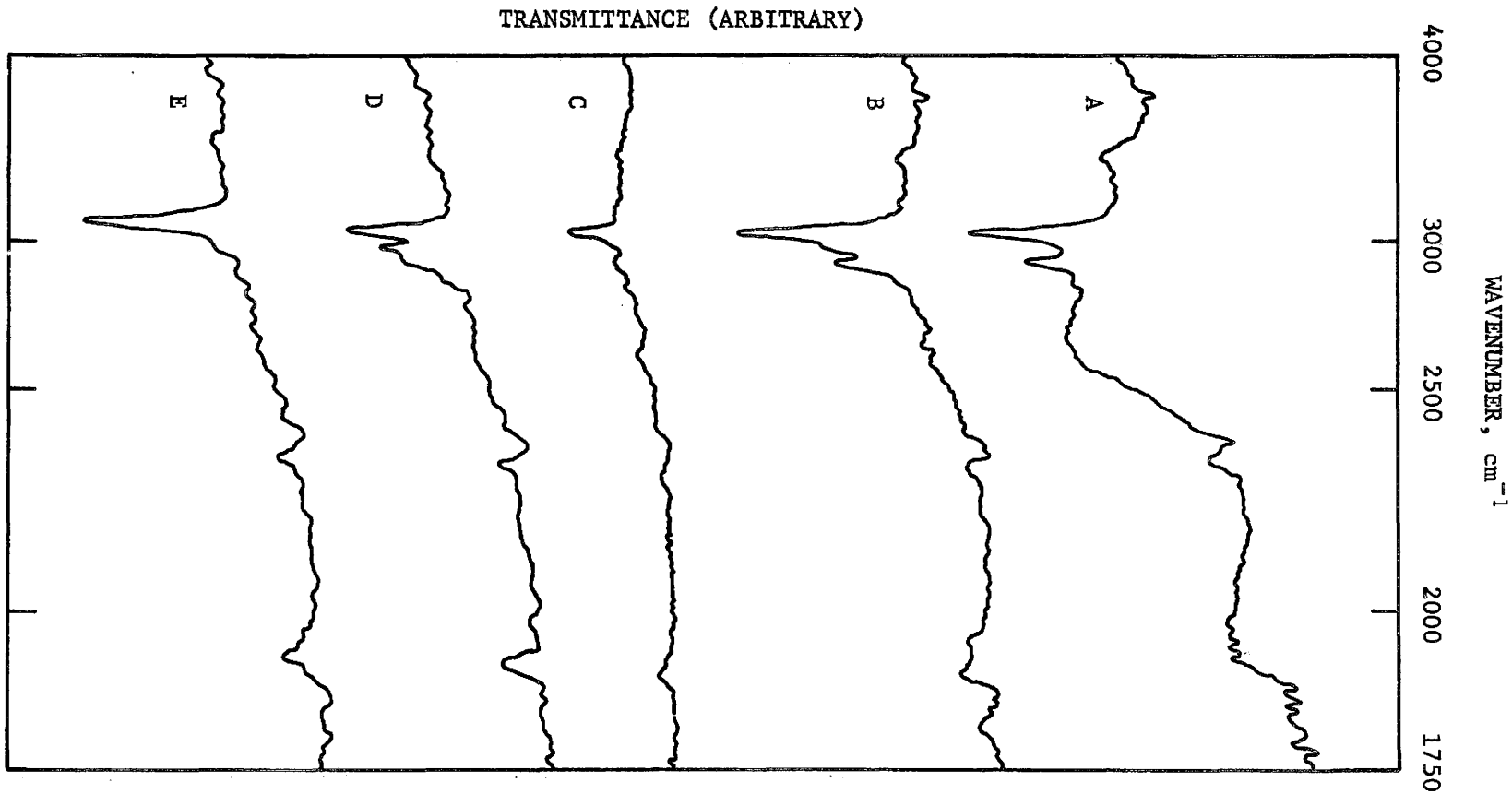

Figure 9. Infrared spectra of thermal products of Sc(III) complexes of 8-hydroxyquinoline and derivatives.

A. $Sc(2\text{-Me-Q})_3 \cdot 2\text{-Me-QH}$; B. $Sc(2\text{-Me-Q})_3$; C. $Sc(4\text{-C}\ell\text{-Q})_3$; D. $Sc(4\text{-Me-Q})_3$; E. $Sc(Q)_3$ from melt product.

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