

tainties for K_2 and K'_2 are much larger than for K_1 and K'_1 , the observed rather large difference in the second hydrolysis constants may not be real. However, the ion exchange experiments were also consistent with a difference in the extent of the second hydrolysis.

A comparison of the $[\text{PtCl}_4]^-$ and $[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]^-$ hydrolysis systems shows some very interesting similarities and differences. The $[\text{PtCl}_3(\text{NH}_3)]^-$ system was described in an earlier paper.⁴ K'_1 for the two systems are equal within experimental uncertainties. The presence of the NH_3 -ligand therefore cancels any electrostatic effect due to the differences in charge of the ions. However, for $[\text{PtCl}_4]^-$ the K_2 is at least ten times larger than for $[\text{PtCl}_3(\text{NH}_3)]^-$. For the latter system, the second hydrolysis reaction was not detectable by the dilution method which has been used in the present work.

The present experiments are in substantial agreement with the titrations which were performed only for aged 0.0166 M $K_2[\text{PtCl}_4]$ solutions in the original studies.^{2a} The analysis of the exchange kinetics is not changed significantly. However, in view of the extensive hydrolysis of the $[\text{PtCl}_3(\text{H}_2\text{O})]^-$, it appears that reaction 2 can account for the exchange of the chloride ligand of this complex with free chloride and that no additional process need be postulated.

An attempt has been made to estimate the dissociation constants for the three acids which were titrated in these experiments. A titration for solutions in NaNO_3 at $\mu = 0.318$ (substantially constant) was considered for which dissociation equilibrium constants were defined

$$[\text{PtCl}_3(\text{H}_2\text{O})]^-: K'_{11} = a_{\text{H}^+}[\text{PtCl}_3(\text{OH})^-]/[\text{PtCl}_3(\text{H}_2\text{O})^-] \quad (12)$$

$$[\text{PtCl}_2(\text{H}_2\text{O})_2]: K'_{21} = a_{\text{H}^+}[\text{PtCl}_2(\text{H}_2\text{O})(\text{OH})^-]/[\text{PtCl}_2(\text{H}_2\text{O})_2] \quad (13)$$

(4) T. S. Elleman, J. W. Reishus and D. S. Martin, Jr., *THIS JOURNAL*, **80**, 56 (1958).

$$[\text{PtCl}_2(\text{H}_2\text{O})(\text{OH})]^-: K'_{22} = a_{\text{H}^+}[\text{PtCl}_2(\text{OH})_2^-]/[\text{PtCl}_2(\text{H}_2\text{O})(\text{OH})^-] \quad (14)$$

a_{H^+} represents the hydrogen ion activity indicated by the pH meter. For a titration the starting concentrations of $[\text{PtCl}_3(\text{H}_2\text{O})]^-$ and $[\text{PtCl}_2(\text{H}_2\text{O})_2]$ were calculated from K'_1 , K'_2 and Pt-total. $E_{i\text{-obsd.}}$ were the equivalents of NaOH added to give pH_{*i*} for the *i*-th point on the titration curve. $E_{i\text{-calcd.}}$ can be computed from the concentrations of the two acids and a set of equilibrium constants K'_{11} , K'_{21} and K'_{22} . A program was processed on an IBM-650 computer to find the values of K'_{11} , K'_{21} and K'_{22} which minimized the sum of squares, $[(E_{i\text{-calcd.}} - E_{i\text{-obsd.}})/E_{i\text{-obsd.}}]^2$, for the titration points taken before the end-point. The computer was unable to select a set of constants satisfactorily for a high concentration solution, *i.e.*, $a = 0.0163$, in which the fraction y/a was only 0.03. However, for a solution of $a = 4.83 \times 10^{-3}$ for which $y/a = 0.09$ it selected values of $pK'_{11} = 7.0$, $pK'_{21} = 5.2$ and $pK'_{22} = 8.3$. From the results of different computations it is estimated that the uncertainty in pK'_{11} is less than 0.1 unit, but the uncertainty in pK'_{21} and pK'_{22} may be as high as 0.8 unit. These values for the dissociation constants appear reasonable in that the ionization constant of the neutral species $[\text{PtCl}_2(\text{H}_2\text{O})_2]$ is higher than that of the anion $[\text{PtCl}_3(\text{H}_2\text{O})]^-$. Also, there is a satisfactory, even if rather small, difference between the first and second ionization constants of $[\text{PtCl}_2(\text{H}_2\text{O})_2]$. The values of these dissociation constants are offered as tentative ones, however, until the computation method has been subjected to much more rigorous testing.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEXAS TECHNOLOGICAL COLLEGE, LUBBOCK, TEXAS]

The Chemistry of the Solvated Metal Chelates. IV. 8-Quinolinol Chelates of Scandium (III), Thorium (IV) and Uranium(VI)¹⁻³

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The 8-quinolinol metal chelates of scandium, thorium and uranium (VI) were studied by X-ray powder diagrams and non-aqueous titrations. X-Ray data showed that the solvated chelates were triclinic in structure while the unsolvated chelates were of monoclinic symmetry. The non-aqueous titrations of the solvated metal chelates with potassium methoxide in acetonitrile showed that the scandium and thorium compounds behaved in a different manner than the uranium compound. It was not possible to prepare "mixed chelates," where the solvate molecule was different than the coordinated groups.

Introduction

Of the many metals ions that form chelates with 8-quinolinol and its derivatives, only scandium (III), thorium (IV), uranium (VI) and plutonium

(VI) ions are known to form complexes of the type, $\text{M}(\text{C}_9\text{H}_6\text{NO})_n \cdot \text{C}_9\text{H}_6\text{NOH}$.⁴⁻⁷ All of these compounds contain an extra mole of chelating agent which is retained in the crystal, and in some

(1) Taken in part from the Ph.D. thesis of J. H. Van Tassel, Texas Technological College, August, 1959.

(2) Presented at the 15th Southwest Regional Meeting of the American Chemical Society, Baton Rouge, Louisiana, December 3-5, 1959.

(3) For part III see *J. Phys. Chem.*, **64**, 1289 (1960).

(4) L. Pokras and P. M. Bernays, *THIS JOURNAL*, **73**, 7 (1951).

(5) F. J. Prere, *ibid.*, **55**, 4362 (1933).

(6) F. Hecht and W. Reich-Rohrwig, *Monatsh. Chem.*, **53-54**, 596 (1929).

(7) R. G. Harvey, H. G. Heal, A. G. Maddock and E. L. Rowley, *J. Chem. Soc.*, 1010 (1947).

cases in solution, by bonding forces of an unknown magnitude.

The composition of the normal and solvated metal chelates of the above metal ions has been the subject of a number of investigations.⁹⁻¹⁴ The structure of the solvated uranium 8-quinolinol chelate was shown to contain the complex anion,¹² $[\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_3]^{-1}$; however, the structures for the solvated thorium and scandium analogs remain unknown. The heats of solvation of the normal thorium and uranium (VI) 8-quinolinol chelates in the solid state are similar; values found were -4.9 and -6.5 kcal. mole⁻¹, respectively.¹³ No such data are available for the scandium complex since the normal metal chelate cannot be prepared.

It is the object of this investigation to further characterize these metal chelates by X-ray powder studies, non-aqueous titrations and chemical studies.

Experimental

Reagents.—8-Quinolinol, m.p. 74–76°, was obtained from the Matheson, Coleman and Bell Co., Norwood, Ohio; 2-methyl-8-quinolinol, m.p. 72–73.5°, from the Aldrich Chemical Co., Milwaukee, Wisc.; scandium oxide, 99.8% purity, from A. D. Mackay, Inc., New York, N.Y.; thorium nitrate 4-hydrate from the Lindsay Chemical Co., West Chicago, Ill.; and uranium (VI) nitrate 6-hydrate from Merck and Co., Rahway, N. J.

All other chemicals were of C.p. quality.

The acetonitrile was dried over P_2O_5 and the fraction distilling at 81–81.5° was collected and stored in sealed glass containers.

The 0.1 *M* potassium methoxide solution in benzene was prepared as previously described.¹⁵

Preparation of Metal Chelates.—The solvated scandium chelate was prepared according to the method of Pokras and Bernays.⁴ Attempts to prepare the unsolvated scandium chelate by subjecting the solvated form to sublimation at a pressure of 1×10^{-3} mm. of Hg and temperatures up to 180° were unsuccessful.

The solvated thorium chelate was prepared and converted to the normal chelate as previously described.⁹

The solvated uranium chelate was prepared using an acetone solution of chelating agent¹³ and converted to the normal chelate by heating.¹⁶

X-ray Studies.—X-ray powder photographs were taken on a Norelco diffraction unit produced by Phillips Electronics Inc., using Ni filtered $\text{Cu K}\alpha$ radiation. A 114.6 mm. powder camera was used employing Kodak Industrial X-ray film, Type KK. Powder samples were mounted on collodion coated glass filaments. Exposure times varied from 3 to 3.5 hr. The unit cell parameters were calculated using Ito's method.¹⁷

Non-aqueous Titration.—An apparatus similar to that previously described¹² was used to carry out the titrations of the solvated metal chelates. Samples of approximately 0.2 mmoles of chelate were dissolved in 40–60 ml. of acetonitrile in a 150 ml. high form beaker. The beaker was fitted with a rubber stopper which was bored to admixt two burets, stirrer, nitrogen flush tube and a glass-calomel electrode

combination. The volume of the titration solution was kept constant by the periodic addition of acetonitrile from a protected buret. Potassium methoxide titrant solution was added in 0.1 ml. increments and the electromotive force read from a Beckman Model H pH meter. The solution required from 2–5 minutes to attain equilibrium after each addition of titrant.

Mixed Chelates.—The reactions attempted were: $\text{M}(\text{C}_9\text{H}_6\text{NO})_n(\text{s}) + \text{CH}_3\text{C}_9\text{H}_6\text{NOH}(\text{soln.}) \rightarrow \text{M}(\text{C}_9\text{H}_6\text{NO})_n \cdot \text{CH}_3\text{C}_9\text{H}_6\text{NOH}(\text{s})$; $\text{M}(\text{CH}_3\text{C}_9\text{H}_6\text{NO})_n(\text{s}) + \text{C}_9\text{H}_6\text{NOH}(\text{soln.}) \rightarrow \text{M}(\text{CH}_3\text{C}_9\text{H}_6\text{NO})_n \cdot \text{C}_9\text{H}_6\text{NOH}(\text{s})$ where M is thorium (IV) or uranium (VI) ion, in various concentrations of aqueous acetic acid (2–4%) and sodium hydroxide (0.1 *N*) as well as in ethanol, ethanol-water mixtures and benzene. In most cases, the exchange reactions were followed by the change in color of the solutions and residues obtained as the various reagents and metal chelates were contacted with each other in a specific solvent. In other cases, the residual solids were recovered by filtration, washed repeatedly with the pure solvent and dried in the desiccator over anhydrous calcium chloride. The resultant solids were then subjected to sublimation and the identity of the solvate molecule determined from the melting point of the sublimate and also by elemental analysis.

Experimental Results

X-ray Studies.—The *d* spacings for the solvated and normal thorium chelates were in fair agreement with those previously reported.⁹ However, more diffraction lines were found in this study.

It was not possible to apply Ito's method¹⁶ to the powder data obtained on $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_9\text{H}_6\text{NOH}$. Evidently, the sample used was nearly amorphous. The crystal lattices of the solvated chelates were triclinic, while the normal chelates were of monoclinic symmetry. Because of the small amount of the scandium chelate available, the density was calculated from the X-ray data assuming one molecule per unit cell. All of the other densities were determined by a pycnometer method. The unit cell dimensions and densities of the metal chelates are given in Tables I and II.

TABLE I
UNIT CELL DIMENSIONS OF METAL CHELATES

Compound	<i>a</i> ^a	<i>b</i>	<i>c</i>	α	β	γ
$\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_6\text{NOH}$	11.60	8.21	7.94	76° 31'	98° 42'	107° 25'
$\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2$	12.07	8.26	9.14	90°	101° 48'	90°
$\text{Sc}(\text{C}_9\text{H}_6\text{NO})_3 \cdot \text{C}_9\text{H}_6\text{NOH}$	9.30	10.06	7.83	89° 51'	92° 30'	93° 5'
$\text{Th}(\text{C}_9\text{H}_6\text{NO})_4$	11.74	7.42	10.77	90°	96° 27'	90°

^a Ångström units.

TABLE II
DENSITIES OF METAL CHELATES AT 25°

Compound	Particles per unit cell	Volume, Å ³	Density, g. cm. ⁻³
$\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_6\text{NOH}$	0.95	699	1.543 ± 0.003
$\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2$	2.09	936	2.071 ± .003
$\text{Sc}(\text{C}_9\text{H}_6\text{NO})_3 \cdot \text{C}_9\text{H}_6\text{NOH}$	1	731	1.414
$\text{Th}(\text{C}_9\text{H}_6\text{NO})_4$	1.04	932	1.509 ± .003

Non-aqueous Titrations.—In agreement with the studies of Bullwinkel and Noble,¹² the titration curve of $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_6\text{NOH}$ gave an inflection point at a slightly more positive electromotive force value than either benzoic acid or 8-quinolinol. The inflection points, in millivolts, so obtained were: 8-quinolinol, -148 ; benzoic acid, 60 ; and $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_6\text{NOH}$, 87 . The more positive value of the latter indicates that it is a stronger acid than the other two compounds. When the unsolvated complex, $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2$, was titrated in a similar manner, the curve ob-

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(9) T. Moeller and M. V. Ramaniah, *ibid.*, **75**, 3946 (1953).

(10) N. Eswaranarayana and Bh. S. V. Raghava Rao, *Anal. Chim. Acta*, **11**, 339 (1954).

(11) K. S. Venkateswarlu and Bh. S. V. Raghava Rao, *ibid.*, **12**, 554 (1955).

(12) E. P. Bullwinkel and P. Noble, Jr., *THIS JOURNAL*, **80**, 2955 (1958).

(13) J. H. Van Tassel and W. W. Wendlandt, *ibid.*, **81**, 813 (1959).

(14) J. H. Van Tassel and W. W. Wendlandt, *ibid.*, **82**, 4821 (1960).

(15) J. S. Fritz and R. T. Keen, *Anal. Chem.*, **25**, 179 (1953).

(16) T. Moeller and D. H. Wilkins, "Inorganic Syntheses," Vol. IV, McGraw-Hill Book Co., New York, N. Y., 1953, p. 101.

(17) T. Ito, "X-ray Studies on Polymorphism," Maruzen Co. Ltd., Tokyo, 1949, pp. 187–228.

tained did not show an inflection point, indicating little, if any, acid character. There was evidence, on the basis of a color change from green to red-orange, of the disproportionation into $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2 \cdot \text{C}_9\text{H}_6\text{NOH}$ and UO_2^{++} . The complexes, $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_9\text{H}_6\text{NOH}$ and $\text{Sc}(\text{C}_9\text{H}_6\text{NO})_3 \cdot \text{C}_9\text{H}_6\text{NOH}$, gave such broad titration curves that it was not possible to assign an inflection point value to them.

Mixed Chelates.—In all of the solvents used, it was not possible to prepare any of the mixed chelates, *i.e.*, complexes containing a solvate molecule of a different species than the coordinated groups. In most cases, the $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2$ disproportionated as was evidenced by the change in color of the solution from green to red-orange.¹² This was similar to the behavior of $\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_2$ when titrated with potassium methoxide.

The unsolvated thorium complex, $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4$, reacted in a different manner than the unsolvated uranium chelate. When it was digested in a dilute sodium hydroxide solution of 2-methyl-8-quinolinol, no reaction was observed. When the solution was made neutral, an immediate color change from yellow to orange occurred. In weakly acidic solutions, the thorium chelate showed no tendency to disproportionate, but the addition of 2-methyl-8-quinolinol caused an immediate change to the solvated form. Despite the fact that the thorium chelate did not appear to disproportionate, some interchange reaction the solvate position and the normal chelate position was in evidence. The resulting sublimates all proved to be mixtures of the two chelating agents present.

Discussion

It appears that the solvated 8-quinolinol chelates of scandium and thorium are not analogous to the uranium (VI) compound. Using substituted 8-quinolinols with a large group at the 2- or 7-position, it is possible to prepare the unsolvated chelates of scandium and thorium directly from solution while only the solvated uranium chelate is precipitated. With 2-methyl-8-quinolinol, thorium forms $\text{Th}(\text{CH}_3\text{C}_9\text{H}_5\text{NO})_4$ ¹⁸ as well as $\text{Th}(\text{CH}_3\text{C}_9\text{H}_5\text{NO})_4 \cdot \text{CH}_3\text{C}_9\text{H}_5\text{NOH}$,¹⁴ while uranium gives only the solvated chelate. Scandium reacts with 7-[α -anilinobenzyl]-8-quinolinol¹⁹ to give the unsolvated chelate while again, uranium gives only the solvated compound. These reactions suggest that perhaps the solvate molecule in the scandium and thorium chelates is held in a different manner than in the uranium chelate. In basic solution, the normal uranium chelate could easily form a complex anion with 8-quinolinol having the formula, $[\text{UO}_2(\text{C}_9\text{H}_6\text{NO})_3]^{-1,12}$ giving uranium a coordination number of eight. To form a similar complex anion with the scandium and thorium chelates would require the unlikely cation coordination numbers of eight and ten, respectively.

Acknowledgment.—The financial assistance of grants from the Research Corporation and the U. S. Atomic Energy Commission through Contract No. AT-(40-1)-2482 is gratefully acknowledged.

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(19) J. P. Phillips and A. L. Duckwall, *THIS JOURNAL*, **77**, 5504 (1955).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, RIVERSIDE, CALIFORNIA, AND THE W. A. NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

Stereochemistry of Inorganic Complexes. XXVI.¹ The Ammoniation of Two Optically Active Cobalt(III) Complexes^{2,3}

BY RONALD D. ARCHER AND JOHN C. BAILAR, JR.

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The stereochemical changes involved in the reaction of ammonia with optically active *cis*-dichlorobis-(ethylenediamine)-cobalt(III) chloride and optically active *cis*-chloroamminebis-(ethylenediamine)-cobalt(III) chloride have been investigated. It has been found that the "Walden ($D^* \rightarrow L^*$)" inversion of the two step ammoniation of the dichloro complex⁵ occurs in the first step of the ammoniation of the dichloro complex at low (liquid ammonia) temperatures. The relative configurations are based on the rotatory dispersion curves and the absorption spectra of the complexes. The ammoniation of racemic and D^* -*cis*-chloroamminebis-(ethylenediamine)-cobalt(III) chloride to the corresponding diammine complex occurs with almost complete retention of configuration under a variety of conditions. The ammoniation of D^* -*cis*-dichlorobis-(ethylenediamine)-cobalt(III) chloride gives considerable *trans*-diammine as well as the *cis*-diammine. Possible reaction intermediates are discussed for the inversion, which requires an S_N2 reaction.

Introduction

A previous study⁵ has shown that either of two optically active forms of *cis*-diamminebis-(ethyl-

enediamine)-cobalt(III) chloride can be formed in excess of the other by varying the temperature at which ammonia reacts with optically active *cis*-dichlorobis-(ethylenediamine)-cobalt(III) chloride. This inversion is complicated by the stereochemical changes possible during the reaction

- (1) Number XXV of this series, *THIS JOURNAL*, **82**, 1524 (1960).
- (2) Presented in part at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April, 1960.
- (3) In part from the Doctoral Dissertation of R. D. Archer, in partial fulfillment for the Ph.D., University of Illinois, Urbana, Illinois, 1959.
- (4) D^* and L^* refer to absolute configurations, whereas *d*, *l*, D and L are designations given to optically active substances by other investigators but have not always implied absolute or even relative configurations.
- (5) J. C. Bailar, Jr., J. H. Haslam and E. M. Jones, *THIS JOURNAL*, **58**, 2226 (1936).

