curves. Another run in this region, with $\beta = 0.0150$ also gave an observed $\alpha(0.177 \times 10^{-3} < \alpha < 0.181 \times 10^{-3})$ about midway between the curves, but this value was not reported above because equilibrium was not approached from both sides. These points are shown in Fig. 3 and indicate that both UF_2^{++} and UF_3^+ are present.

It may well be that other ionic species such as UF^{+3} and U^{+4} also exist in these solutions. However, if they do exist, they are present in quantities so small as to be undetected by the methods of this investigation, and postulating their existence is not necessary to fit the observed data to a smooth curve.

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The Chemistry of the Solvated Metal Chelates. II. The Uranium(VI), Thorium(IV) and Scandium(III) 2-Methyl-8-quinolinol Metal Chelates[1,2]

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The 2-methyl-8-quinolinol chelates of thorium(IV), scandium(III) and uranium(VI) were studied by chemical, thermogravimetric and calorimetric methods and infrared spectroscopy. The heat of solvation, ΔH_4, for the reaction

$$M(C_{10}H_8NO)_n(s) + C_{10}H_8NOH(s) = M(C_{10}H_8NO)_n \cdot C_{10}H_8NOH(s)$$

was determined for the thorium and uranium chelates and found to be 2.5 ± 0.5 and −2.9 ± 0.5 kcal. mole^{-1}, respectively. It was possible to prepare the unsolvated scandium and uranium chelates by vacuum sublimation techniques and also the previously unreported solvated thorium chelate. There was little difference between the infrared spectra of the solvated and unsolvated metal chelates.

Introduction

2-Methyl-8-quinolinol (2-methyloxine) forms five membered ring metal chelates with a number of metal ions which are quite similar in properties to the chelates formed by 8-quinolinol.[3] The normal formula for the metal chelates is $M(C_{10}H_8NO)_n$, where M is a metal ion of oxidation number n. However, with uranium (VI) and scandium (III), complexes having the formulas, $UO_2(C_{10}H_8NO)_2 \cdot C_{10}H_8NOH$ and $Sc(C_{10}H_8NO)_3 \cdot C_{10}H_8NOH$, are obtained.[4] The extra molecule of chelating agent is held in the crystal lattice by forces of an unknown magnitude. The 2-methyl-8-quinolinol chelate with thorium(IV) does not contain an extra solvate molecule; this is in contrast to the corresponding metal chelate with 8-quinolinol.[5] Because of the excellent thermal properties of the 4:1 thorium 2-methyl-8-quinolinol chelate, it has been recommended as an organic precipitant for that ion.[6]

The purpose of this investigation is to study the nature of the interaction between the solvate molecules and the metal chelates. A previous study[7] has shown that the heat of solvation between 8-quinolinol and the thorium(IV) and uranium(VI) chelates was from −4.9 to −6.5 kcal. mole^{-1}. It was of interest to determine the effect of the methyl group in the 2-position on the heat of solvation of the 2-methyl-8-quinolinol metal chelates. The methyl group in this position is responsible for the non-formation of an aluminum chelate with 2-methyl-8-quinolinol, the effect being attributed to steric hindrance.[8]

Experimental

Reagents.—2-Methyl-8-quinolinol was obtained from the Aldrich Chemical Co., Milwaukee, Wisc. It was purified before use by recrystallization from an ethanol-water mixture; the resulting product had a m.p. of 72–73°. Scandium oxide, 99.8% purity, was obtained from A. D. Mackay Inc., New York, N.Y.; thorium nitrate 4-hydrate from the Lindsay Chemical Co., West Chicago, Ill.; uranium nitrate 6-hydrate from Merck and Co., Rahway, N.J.

A solution of 3.00 ± 0.03 N hydrochloric acid was prepared and standardized against a carbonate-free sodium hydroxide solution.

All other chemicals were of C.P. quality.

Calorimeter.—The heat of solution calorimeter has previously been described.[7] It was modified slightly in that the unbalance potential from the thermister bridge was amplified by a Honeywell, Model 2HLA-7, low-level d.c. amplifier and then recorded on a Varian, Model G-10, strip-chart potentiometric recorder. A chart speed of $^5/_8$ in. per min. was used to record the bridge output. The procedure for the measurements was the same as previously described.[7]

Thermobalance.—The thermobalance has previously been described.[9] Sample sizes ranged in weight from 80–100 mg. and were run in duplicate or triplicate. A linear heating rate of 6.6° per min. was employed on all runs.

Infrared Studies.—The infrared absorption spectra were obtained with a Perkin-Elmer Model 112 single beam double pass instrument. The fused KBr pellet technique

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[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.

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was employed, using a metal complex to KBr weight ratio of 1:400.

Preparation of Metal Chelates.—The yellow 3:1 scandium chelate, $Sc(C_{10}H_8NO)_3$, was prepared by heating the 4:1 chelate $Sc(C_{10}H_5NO)_3.C_{10}H_8NOH$, at 80° under a vacuum of 0.05 mm. for 5 hr. The 2-methyl-8-quinolinol in the resulting compound was determined by a bromometric titration[10]; found, 90.65%; theor., 91.37%.

The 5:1 thorium chelate, $Th(C_{10}H_8NO)_4{\cdot}C_{10}H_8NOH$, was prepared by a modification of the method previously described.[4] To 100 ml. of solution containing 0.316 g. of thorium nitrate 4-hydrate were added 15 g. of ammonium acetate and 0.44 g. of 2-methyl-8-quinolinol dissolved in 20 ml. of 2 N acetic acid. The resulting yellow colored solution had a pH of 5.3. Precipitation was initiated by the drop-wise addition of 2 N ammonium hydroxide until the pH was 7.6. The yellow colored precipitate was allowed to digest for five min., filtered off and washed repeatedly with water. After air drying overnight, the precipitate was dried in a 75° oven for 30 min.

The thorium content was determined by ignition of the dried compound at 800° in a platinum crucible: thorium, found, 22.95%; theor., 22.67%; 2-methyl-8-quinolinol, found, 77.76%; theor., 77.32%.

The 3:1 uranium chelate, $UO_2(C_{10}H_8NO)_2{\cdot}C_{10}H_8HOH$, was prepared as previously described.[4] Conversion to the brown 2:1 chelate, $UO_2(C_{10}H_8NO)_2$, was effected by heating the 3:1 chelate at 170° at a pressure of 20 mm. for 8 hr.; uranium found, 40.60%; theor., 40.65%; 2-methyl-8-quinolinol, found, 53.51%; theor., 53.90%.

Experimental Results

Heat of Solution Studies.—The heats of solvation, ΔH_4, for the reactions (where MeOxH is $C_{10}H_8NOH$)

$$\mathrm{Th(MeOx)_4(s) + MeOxH(s) = Th(MeOx)_4{\cdot}MeOxH(s)}\ \Delta H_4 \quad (1)$$

$$\mathrm{UO_2(MeOx)_2(s) + MeOxH(s) = UO_2(MeOx)_2{\cdot}MeOxH(s)}\Delta H \quad (2)$$

were determined by measuring the heats of solution of the solvated chelates, the unsolvated chelates and the chelating agent in 3.00 N hydrochloric acid. It is assumed that these dissociation reactions take place

$$\mathrm{Th(MeOx)_4{\cdot}MeOxH(s) + 9H^+(aq) + 9Cl^-(aq) = Th^{+4}(aq) + 5MeOxH_2{}^+(aq) + 9Cl^-(aq)}\ \Delta H_1 \quad (3)$$

$$\mathrm{Th(MeOx)_4(s) + 8H^+(aq) + 8Cl^-(aq) = Th^{+4}(aq) + 4MeOxH_2{}^+(aq) + 8Cl^-(aq)}\ \Delta H_2 \quad (4)$$

$$\mathrm{UO_2(MeOx)_2{\cdot}MeOxH(s) + 5H^+(aq) + 5Cl^-(aq) = UO_2{}^{+2}(aq) + 3MeOxH_2{}^+(aq) + 5Cl^-(aq)}\ \Delta H_1 \quad (5)$$

$$\mathrm{UO_2(MeOx)_2(s) + 4H^+(aq) + 4Cl^-(aq) = UO_2{}^{+2}(aq) + 2MeOxH_2{}^+(aq) + 4Cl^-(aq)}\ \Delta H_2 \quad (6)$$

$$\mathrm{MeOxH(s) + H^+(aq) + Cl^-(aq) = MeOxH_2{}^+(aq) + Cl(aq)}\ \Delta H_3 \ (7)$$

The heat of solvation ΔH_4 was calculated by using the law of Hess and is $\Delta H_4 = \Delta H_2 + \Delta H_3 - \Delta H_1$.

The heats of solution of the thorium and uranium solvated and unsolvated chelates and 2-methyl-8-quinolinol are given in Table II. From these data, ΔH_4 was calculated to be 2.5 ± 0.5 and −2.9 ± 0.5 kcal. mole^{-1} for the thorium and uranium chelates, respectively. Because of the limited amount of the scandium chelate available, the heat of solvation was not determined.

Thermostability Studies.—The thermal decomposition curve of $Th(C_{10}H_8NO)_4{\cdot}C_{10}H_8NOH$ revealed that the solvate molecule began to sublime at 70°, the process being completed at 155°. A horizontal weight level corresponding to $Th(C_{10}H_8NO)_4$ was then observed to 265°. Beyond this temperature the complex decomposed rapidly, giving the ThO_2 weight level beginning at 460°. This behavior is in contrast to that found for the 8-quinolinol chelate in which an intermediate compound was found.[7] The thermal stability of the 5:1 compound was similar to that found for the 5:1 8-quinolinol chelate.[11]

TABLE I

HEATS OF SOLUTION OF THE THORIUM AND URANIUM(VI) 2-METHYL-8-QUINOLINOL CHELATES IN 3.00 N HYDROCHLORIC ACID AT 25.00 ± 0.01°

Compound	Sample wt., mg.	Heat of soln.,[a] kcal. mole^{-1}	Av., ΔH, kcal. mole^{-1}
		$-\Delta H_1$	
$\mathrm{Th(MeOx)_4{\cdot}MeOxH(s)}$	377.0	53.4	53.4 ± 0.1
	456.5	53.5	
		$-\Delta H_2$	
$\mathrm{Th(MeOx)_4(s)}$	379.0	46.6	46.9 ± .3
	419.3	47.2	
		$-\Delta H_1$	
$\mathrm{UO_2(MeOx)_2{\cdot}MeOxH(s)}$	416.4	21.5	21.4 ± .1
	637.2	21.4	
		$-\Delta H_2$	
$\mathrm{UO_2(MeOx)_2(s)}$	418.0	20.5	20.3 ± .2
	384.6	20.2	
		$-\Delta H_3$	
MeOxH(s)	2384.4	4.0	4.0 ± .1
	1705.6	4.0	
	2080.3	4.1	

[a] Mole ratio of metal complex to solution of about 1:30,000.

Infrared Studies.—The infrared absorption spectra of both the solvated and the unsolvated chelates of 2-methyl-8-quinolinol with scandium, thorium and uranium(VI) all gave a strong absorption at 9 μ. This band has been attributed to the formation of the $\mathrm{M{-}O{-}C}\!\begin{smallmatrix}/\!\!/\\ \backslash\end{smallmatrix}$ bond,[12] or particularly, the diatomic vibration associated with the C–O group involved in the formation of the metal chelate. Little difference was observed between the spectra of the solvated and unsolvated scandium and thorium chelates. With uranium, a shift was observed from 11.1 to 11.3 μ on going from the unsolvated to the solvated complex. Otherwise, the two curves were identical. The presence of similar spectra indicated that the solvate molecule has little affect on the vibrations of the unsolvated metal complex. It was not possible to determine if the O–U–O linearity was affected by the presence or absence of the solvate molecule because the chelating agent itself has an absorption at 11.6 μ.[13]

Discussion

The solvated 2-methyl-8-quinolinol chelates appear to be less stable than the corresponding 8-quinolinol chelates of these metal ions. It is not possible to prepare the 3:1 scandium 8-quinolinol chelate by vacuum thermal decomposition of the

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4:1 chelate; however, the 3:1 2-methyl-8-quinolinol chelate can be prepared. Likewise, the 4:1, and under certain conditions, the 5:1 2-methyl-8-quinolinol thorium chelate can be precipitated from solution while only the 5:1 8-quinolinol chelate can be obtained.

The heats of solvation of the 2-methyl-8-quinolinol thorium and uranium chelates are decidedly more positive than those found for the 8-quinolinol chelates. In fact, the thorium chelate has a positive value. Little can be said about the nature of the interaction between the solvate molecule and the metal chelate because the heat of rearrangement of the complex, after removal of the solvate molecule, is not known.

The structures of the solvated metal chelates remain unknown. It is thought, however, that the structures of the thorium and scandium chelates differ from that for uranium. The exact structural assignment will have to await further studies by X-ray methods.

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[CONTRIBUTION FROM THE JOHN CURTIN SCHOOL OF MEDICAL RESEARCH, AUSTRALIAN NATIONAL UNIVERSITY, CANBERRA AUSTRALIA]

Rhodium(III) Complexes with Ethylenediaminetetraacetic Acid

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Aquo-(ethylenediaminetriacetatoacetic acid)-rhodium(III) has been obtained from rhodium(III) hydroxide and aqueous ethylenediaminetetraacetic acid at 145–150° and the potassium and ammonium salts of this acidic complex by neutralization. Resolution was effected through the active *cis*-dinitro-bis-(ethylenediamine)-cobalt(III) cation. Racemization occurred at 96° (half-life, 163 min.), and at 20° in Pyrex vessels in sunlight. The dichloro and dibromo complexes, in which the ethylenediaminetetraacetic acid behaved as a quadridentate ligand, were obtained in optically active forms, which did not exhibit photoracemization, but decomposed in aqueous solution very slowly to yield the active aquo complex.

On the basis of photometric studies,[1] complexometric titrations,[2] ion-exchange[3] and chromatographic[4] separations, it was concluded originally that rhodium complexes with ethylenediaminetetraacetic acid were not formed. Recently, however, it has been found that when freshly prepared solutions of rhodium(III) chloride were heated with ethylenediaminetetraacetic acid, the *p*H of the solution slowly decreased, a new absorption band appeared at 353 mμ, and after a time rhodium hydroxide was no longer precipitated by alkali.[5] The previous failures to detect complex formation were ascribed, reasonably enough, to the inertness of the anionic rhodium complexes present in the aged solutions. The composition of the complex was not ascertained.

In the present work, the preparation, properties and resolution of some of the complexes are described. Ethylenediaminetetraacetic acid was found to react in boiling aqueous solution with rhodium(III) chloride and nitrate, and pale yellow solids could be isolated as the ammonium salts. None of the products could be characterized by analysis and they apparently consisted of mixtures. Fractionation of the material obtained from the rhodium(III) chloride reaction gave a series of yellow substances of different solubilities none of which could be identified. With silver nitrate, some silver chloride precipitated slowly, and the infrared curves showed the presence of free carboxylic acid group(s) in all fractions.

Freshly precipitated rhodium(III) hydroxide, free from chloride ion, failed to dissolve in boiling aqueous ethylenediaminetetraacetic acid even after 6 hr., but in an autoclave at 145–150° dissolution was complete in 4 hr. The bright yellow solution was freed from excess acid by concentration and cooling at 4°, and the solid rhodium complex then separated on the addition of ethanol. The infrared spectrum showed a free carboxylic group, and analysis, the presence of a molecule of water, from which the formula [RhH_2O(HEDTA)] has been deduced. From *p*H titrations, for the reactions

$$[\mathrm{RhH_2O(HEDTA)}] \rightleftarrows \mathrm{H^+} + [\mathrm{RhH_2O(EDTA)}]^- \rightleftarrows \mathrm{H^+}[\mathrm{Rh(EDTA)OH}]^{-2}$$

we deduce $pK_1 = 2.32 \pm 0.08$ and $pK_2 = 9.12 \pm 0.02$. The aquo group is thus much less acidic than in [Cr H_2O(HEDTA)], ($pK_2 = 7.52$).[6] The color of the hydroxo complex anion $[\mathrm{Rh(EDTA)OH}]^{-2}$ is not visibly different from that of the aquo complex (absorption maxima at 293 and 359 mμ).

The potassium and ammonium salts were obtained by neutralization of the complex acid. Resolution was effected readily with the active *cis*-dinitro-bis-(ethylenediamine)-cobalt(III) cation. Solutions of the active potassium salts retained their rotations unchanged for three months in the dark, but $[\alpha]_{5461}$ had decreased from −180 to −100° in a year. The half life at 96° in the dark was 163 min. which is comparable with the cobalt complex[7] ($t/2 = 168$ min. at 100°). The absorption spectra of various samples collected during racemization showed that apparently little decomposition en-

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