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# Proton Nuclear Magnetic Resonance Studies of the 8-Quinolinol Complexes of Thorium(IV) and Uranium(VI)

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The proton nmr spectra of the 8-quinolinol (oxine, HOx) complexes of thorium(IV) and uranium(VI) in DMSO solutions have been recorded and analyzed. The data establish that the "solvated" complexes of thorium and uranium, $ThOx_4 \cdot HOx$ and $UO_2Ox_2 \cdot HOx$, only exist in the solid phase and dissociate to $ThOx_4$ and $UO_2Ox_2$ in solution. The oxines in the latter complexes are equivalent on the basis of the nmr data. Studies of the $UO_2Ox_3^-$ complex also confirm that the three oxines are equivalent. Drying studies and differential thermograms of the various solvated oxine complexes of thorium and uranium have been used to characterize the solid species. The red form of $UO_2Ox_2 \cdot HOx$ has a much greater thermal stability than the orange form and can be dried to constant weight at 150°. The maroon hydrate, $UO_2Ox_2 \cdot 3H_2O$, also is stable up to 150°.

Metal chelates of 8-quinolinol (8-hydroxyquinoline, oxine, $C_9H_7NO$) generally correspond to the formula $MOx_n$, where $Ox^-$ represents the oxine anion and $n$ is the valence state of the metal ion M. However, early work[1,2] established that uranium(VI) and thorium(IV) can add an extra molecule of oxine to form the "solvated" chelates $UO_2Ox_2 \cdot HOx$ and $ThOx_4 \cdot HOx$ and that these compounds can be transformed to their normal oxinates by heating. Since that time much controversy has developed over the nature of the bonding for the extra oxine molecule.

Moeller and Ramaniah[3,4] have concluded that the additional ligand is held only by weak lattice forces in the solid phase and is completely removed in solution. In the case of the thorium chelate this contention is generally accepted, but for the uranium compound some workers feel that the third ligand actually is coordinated to the metal ion through either the oxygen or the nitrogen atom.[5,6] Still others feel that all three ligands are equivalently bound, yielding the complex anion $UO_2Ox_3^-$.[7-9]

A previous study has shown that the proton nmr spectra of metal–oxine chelates can be determined in dimethyl sulfoxide solutions.[10] Consideration of the chemical shifts for the protons of the phenolic ring and hetero ring in the ligand provides a means of monitoring the electronic environments of the coordination sites. Thus, changes in the chemical shifts relative to their positions for the free ligand yield information about the nature of the metal–ligand bonds. The present paper summarizes the results of such a study for the uranium(VI)- and thorium(IV)-oxine complexes.

## Experimental Section

All nmr spectra were recorded using a Varian Model HA-100 nmr spectrometer equipped with a 100-Mc Oscillator and a variable-temperature probe. Reagent grade dimethyl sulfoxide (DMSO, J. T. Baker Chemical Co.) was used as the solvent for the nmr spectra and in addition served as an internal lock signal for the spectrometer. Chemical shifts were measured downfield ($\delta$) from the DMSO lock signal; the latter is $2.840 \pm 0.002$ ppm downfield from an external tetramethylsilane (TMS) reference.

Infrared spectra were recorded on a Perkin-Elmer Model 621 double-beam grating instrument with the samples contained in either potassium bromide disks or solutions of DMSO retained between sodium chloride plates.

A Perkin-Elmer Model DSC-1 differential scanning calorimeter with a heating rate of 10°/min and an atmosphere of dry nitrogen was used to determine differential thermograms of the complexes.

8-Quinolinol (mp 74–76°) was obtained from Matheson Coleman and Bell. Thorium(IV) nitrate tetrahydrate and uranium(VI) nitrate hexahydrate were Analyzed Reagent grade and were supplied by J. T. Baker Chemical Co.; all other materials were reagent grade.

**Thorium Oxinates.**—The "solvated" chelate $ThOx_4 \cdot HOx$ was prepared by the method of Moeller and Ramaniah[3] except that the drying was accomplished by placing the compound in a vacuum desiccator at room temperature for a 1-week period. The 1:4 chelate ($ThOx_4$) was prepared by heating $ThOx_4 \cdot HOx$ at 170° for 5 hr. *Anal.* Calcd for $ThOx \cdot HOx$: Th, 24.33; oxine, 76.67. Found: Th, 24.34; oxine, 75.94. Calcd for $ThOx_4$: Th, 28.69; oxine, 71.31. Found: Th, 28.83; oxine, 71.51.

**Uranium Oxinates.**—A number of synthetic procedures were attempted which yielded physical mixtures of several compounds. The final procedures were selected to give the desired product consistently in pure form.

(a) **$UO_2Ox_2 \cdot HOx$.**—The red form and the orange form of the "solvated" complex were both prepared by homogeneous precipitation according to the method of Bordner, Salesin, and Gordon;[11] the red form precipitated at pH 5.0 and the orange form at pH 6.8. In the original paper[11] the composition of the orange compound was reported to be $(UO_2Ox_2)_2 \cdot HOx$, but analysis of the isolated complexes confirmed that the metal-to-ligand ratio was 1:3 for both the red and orange forms. *Anal.* Calcd for $UO_2Ox_2 \cdot HOx$: $UO_2$, 38.38; oxine, 61.62. Found for the red compound: oxine, 61.50. Found for the orange compound: $UO_2$, 37.96; oxine, 61.35.

(b) **$UO_2Ox_2 \cdot 4H_2O$ and $UO_2Ox_2 \cdot 3H_2O$.**—The tetrahydrate was prepared by adding a solution of 4.5 g of oxine in 10 ml of glacial acetic acid to 300 ml of water containing 5.0 g of

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[1] F. Hecht and W. Reich-Rohrwig, *Monatsh.*, **53–54**, 596 (1929).

[2] F. J. Frere, *J. Am. Chem. Soc.*, **55**, 4362 (1933).

[3] T. Moeller and M. V. Ramaniah, *ibid.*, **75**, 3946 (1953).

[4] T. Moeller and M. V. Ramaniah, *J. Am. Chem. Soc.*, **76**, 5251 (1954).

[5] R. J. Magee and I. Woodward, *Talanta*, **13**, 709 (1966).

[6] D. Hall, A. D. Rae, and T. N. Waters, *Acta Cryst.*, **22**, 258 (1967).

[7] E. P. Bullwinkle and P. Noble, Jr., *J. Am. Chem. Soc.*, **80**, 2955 (1958).

[8] J. H. Van Tassel, W. W. Wendlandt, and E. Sturm, *ibid.*, **83**, 810 (1961).

[9] J. E. Tackett and D. T. Sawyer, *Inorg. Chem.*, **3**, 692 (1964).

[10] B. C. Baker and D. T. Sawyer, *Anal. Chem.*, **40**, 1945 (1968).

[11] J. Bordner, E. D. Salesin, and L. Gordon, *Talanta*, **8**, 579 (1961).

TABLE I

CHEMICAL SHIFTS FOR THORIUM OXINATE, URANIUM OXINATES, AND OXINE IN DIMETHYL SULFOXIDE AT 35°

| Compound | | δ, ppm vs. DMSO (±0.01 ppm) | | | | | |
|---|---|---|---|---|---|---|---|
| | | 2 | 3 | 4 | 5 | 6 | 7 |
| | | | A. | | | | |
| $ThOx_4$ | | 6.32 | 4.76 | 5.57 | 4.36 | 4.79 | 4.13 |
| | | | B. | | | | |
| $UO_2Ox_2 \cdot HOx$ (red) | M | 7.65 | 5.45 | 6.04 | 4.71 | 5.18 | 4.62 |
| | m | 6.28 | 4.96 | 5.73 | 4.82 | 4.87 | 4.58 |
| $UO_2Ox_2 \cdot HOx$ (orange) | M | 7.64 | 5.46 | 6.05 | 4.71 | 5.17 | 4.61 |
| | m | 6.27 | 4.96 | 5.72 | 4.81 | 4.86 | 4.58 |
| $UO_2Ox_2 \cdot 4H_2O$ | | 7.69 | 5.45 | 6.05 | 4.70 | 5.18 | 4.64 |
| $UO_2Ox_2 \cdot 3H_2O$ | | 7.69 | 5.45 | 6.05 | 4.70 | 5.18 | 4.63 |
| $UO_2Ox_2$ | | 7.65 | 5.46 | 6.05 | 4.70 | 5.18 | 4.62 |
| $KUO_2Ox_3$ | | 7.55 | 5.18 | 5.88 | 4.81 | 5.07 | 4.62 |
| | | | C | | | | |
| HOx | | 6.27 | 4.94 | 5.71 | 4.82 | 4.87 | 4.58 |

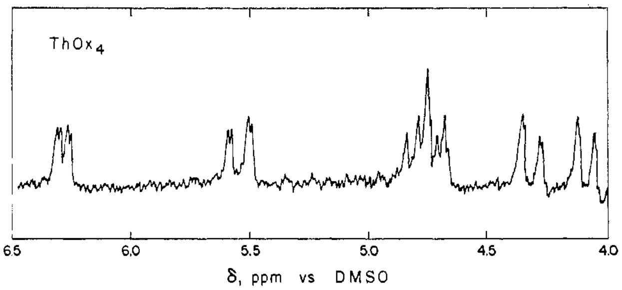

Figure 1.—The 100-Mc proton nmr spectrum for the "normal" thorium oxinate.

uranyl nitrate and 5 ml of 6 *F* nitric acid; 35 g of urea was added and the solution was stirred until it dissolved. Dilute ammonium hydroxide was added dropwise with continued stirring, allowing any precipitate which formed to dissolve completely before the next drop was added. At the point where a slight turbidity persisted in the solution for several minutes, the addition of base was halted (*ca.* pH 3.1). The solution was then heated on a steam bath for 5 hr. The precipitate consisted of microcrystalline particles that appeared black when moist but became dark purple after drying. The crystals were washed with several volumes of boiling water and then dried in a vacuum desiccator at room temperature for 1 week. The trihydrate was obtained by drying the tetrahydrate at 140° for 3–4 hr. *Anal.* Calcd for $UO_2Ox_2 \cdot 4H_2O$: $UO_2$, 42.84; oxine, 45.73. Found: $UO_2$, 42.79; oxine, 45.47. Calcd loss in weight on drying at 140° to form $UO_2Ox_2 \cdot 3H_2O$: 2.86%. Found: 2.86%.

(c) **$UO_2Ox_2$.**—The "normal," olive green, unsolvated 1:2 chelate was prepared by heating the orange form of $UO_2Ox_2 \cdot HOx$ or either of the hydrates to 175° for about 6 hr. Conversion of the red form of $UO_2Ox_2 \cdot HOx$ was found to be incomplete under these conditions.

(d) **$KUO_2Ox_3$.**—The potassium salt of the complex anion $UO_2Ox_3^-$ was prepared by adding a solution of 4.5 g of oxine in 10 ml of glacial acetic acid to a solution of 5.0 g of uranyl nitrate and 5 ml of 6 *F* nitric acid in 300 ml of water. The pH of the resulting solution was increased rapidly to pH 12.0 with potassium hydroxide. After digesting on a steam bath for several hours, the bright red-orange precipitate was filtered and washed with boiling water and then dried in a vacuum desiccator at room temperature for 1 week. *Anal.* Calcd for $KUO_2Ox_3$: oxine, 58.31. Found: oxine, 57.70.

## Results

**Thorium Oxinates.**—The proton nmr spectrum for the "normal" 1:4 thorium oxinate is shown in Figure 1. The chemical shifts (*vs.* DMSO) for the six protons of the oxinate ligand are given in Table IA. These assignments have been made on the basis of previous nmr studies of oxine complexes[10] and a first-order analysis. The fact that only one set of ligand resonances is observed indicates that all four oxinate ligands are magnetically equivalent. In the nmr spectrum of the "solvated" 1:5 chelate ($ThOx_4 \cdot HOx$) the observed peaks are severely broadened which indicates ligand exchange about the thorium atom.

The thermal stability of the 1:5 oxinate has been determined by heating samples to a fixed temperature for a given period of time and then cooling in a desiccator prior to weighing. At 80° the chelate attains a constant weight after 3–4 hr and has a weight loss of 0.28%. This can be accounted for as additional adsorbed water not removed in the vacuum desiccator. Samples dried at 110° for 4 hr lose 8.50% of their initial weight (equivalent to more than half of the extra oxine ligand). Heating the 1:5 chelate at 170° until constant weight is attained (4–5 hr) causes a weight loss of 15.73%; this is equivalent to the weight percentage of the "solvate" oxine in $ThOx_4 \cdot HOx$ (15.22%).

Differential thermograms for the temperature range from 30 to 300° indicate only two exothermic peaks for the 1:5 oxinate: a sharp peak with a maximum at 135° corresponding to the removal of the "extra" oxine ligand and a broad peak at 258° due to the decomposition of the 1:4 chelate. This corresponds closely to previous work with an argon atmosphere.[12,13]

The instability of $ThOx_4 \cdot HOx$ in solution is indicated by the precipitation of $ThOx_4$ (yellow) after the dissolution of $ThOx_4 \cdot HOx$ (orange) in DMSO or alcohol. Further, freshly precipitated $ThOx_4 \cdot HOx$ gradually changes in color when washed with methanol or 95% ethanol to give a yellow precipitate, $ThOx_4$. If $ThOx_4 \cdot HOx$ is allowed to dry before washing with alcohol, the extra oxine ligand is much more difficult to remove.

**Uranium Oxinates.**—The proton nmr spectra for several of the uranium–oxine chelates and for free

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[12] W. W. Wendlandt and G. R. Horton, *Anal. Chem.*, **34**, 1098 (1962).

[13] G. R. Horton and W. W. Wendlandt, *J. Inorg. Nucl. Chem.*, **25**, 247 (1963).

oxine are illustrated in Figure 2; the chemical shifts (*vs.* DMSO) are summarized in Table IB.

The spectra of the red and orange forms of $UO_2Ox_2 \cdot HOx$ are essentially equivalent. They consist of two distinct sets of resonances (M and m, Table IB) with 2:1 intensity ratios, which indicate that two of the ligands are in equivalent magnetic environments while that of the third ligand is quite different.

The spectra for $UO_2Ox_2 \cdot 4H_2O$, $UO_2Ox_2 \cdot 3H_2O$, and $UO_2Ox_2$ are identical (Table IB) with the proton chemical shifts equal to the major set (M) of ligand peaks in the spectra of the red and orange forms of $UO_2Ox_2 \cdot HOx$. In addition, the shifts for the minor set (m) of peaks in the latter spectra are equal to those in the spectrum for free oxine (Table IC and Figure 2).

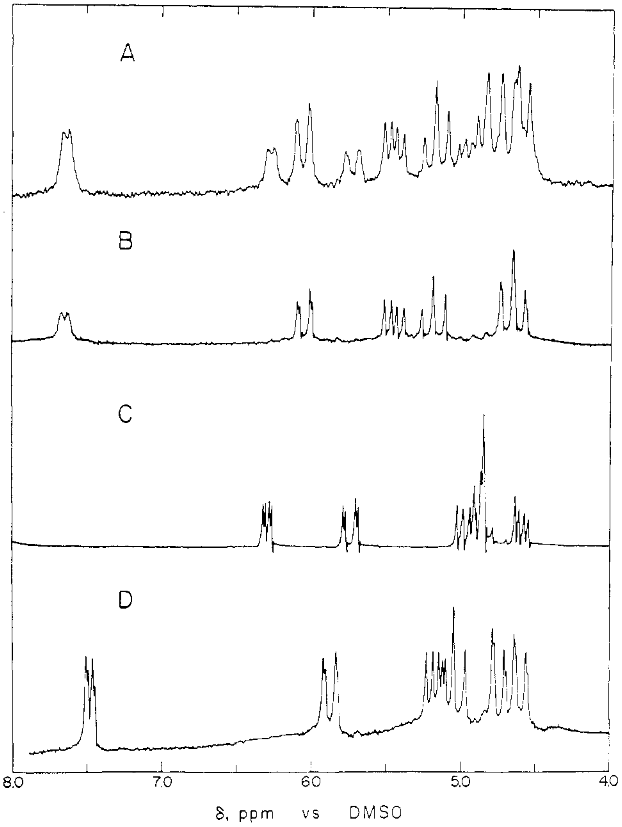

Figure 2.—The 100-Mc proton nmr spectra for $UO_2Ox_2 \cdot HOx$ (curve A), $UO_2Ox_2$ (curve B), oxine (curve C), and $KUO_2Ox_3$ (curve D).

Nmr spectra also have been recorded for DMSO solutions of the red and orange forms of $UO_2Ox_2 \cdot HOx$ to which an equimolar amount of oxine has been added. The spectra do not exhibit any new peaks but only an increase in intensity for the minor set (m) of ligand resonances. Similar additions of oxine to solutions of $UO_2Ox_2$ and $K_2UO_2Ox_3$ give spectra with peaks for the free oxine superimposed on the normal spectrum for the pure chelate. In no case is there evidence of line broadening due to ligand exchange with the chelate.

Infrared spectra of the various uranyl oxinates in KBr disks do not exhibit significant differences from those described by other workers.[9,14] The broad absorption band at 2650 $cm^{-1}$, which has been assigned to the N–H–O hydrogen-bond deformation,[15] is present in the spectra of both the red and the orange forms of $UO_2Ox \cdot HOx_3$ but absent in all of the other compounds. However, when the "solvate" compounds are studied as solutions in DMSO, the absorption band at 2650 $cm^{-1}$ is not observed.

Because of the similarities in the nmr and infrared spectra for several of the uranyl oxinates, differential thermograms have been recorded as a further means of characterization. The red and orange forms of $UO_2Ox_2 \cdot HOx$ give identical dta curves; from 30 to 300° only a single endothermic peak is observed with a maximum at 264°. Over the same temperature range the purple tetrahydrate exhibits three endotherms with maxima at 153, 260, and 283°; the peak at 153° is somewhat broadened. The thermogram for the maroon trihydrate is identical but for the absence of the peak at 153°. The green oxinate $UO_2Ox_2$ and the potassium salt $K_2UO_2Ox_3$ do not give peaks in their dta curves over the temperature range investigated.

Because the conditions for obtaining dta data are different from those of normal drying procedures, the thermal stabilities of the chelates have been determined at a constant temperature over an extended period of time; the results are summarized in Table II. The red and orange forms of $UO_2Ox_2 . HOx$, which appear identical in other experiments, do not behave the same when heated. While the orange chelate is converted readily to $UO_2Ox_2$ at 175°, the red compound has just begun to lose weight slowly at this temperature and does not yield $UO_2Ox_2$ until about 210°.

Table II

Weight Loss at Various Temperatures for the Uranyl Oxinates[a]

| Compound | Drying temp, °C | Time | % wt lost |
|---|---|---|---|
| Red $UO_2Ox_2 \cdot HOx$ | 150 | 4 hr | 0.0[b] |
| | 175 | Slow continual loss | . . . |
| Orange $UO_2Ox_2 \cdot HOx$ | 80 | 1.5 hr | 0.28 |
| | 110 | 4 hr | 4.62 |
| | 175 | 5 hr | 20.81 |
| $UO_2Ox_2 \cdot 4H_2O$ | 110 | Slow continual loss | . . . |
| | 150 | 3 hr | 2.86 |
| | 150 | 2 days | 2.86[b] |
| $UO_2Ox_2 \cdot 3H_2O$ | 180 | 4 hr | 9.27 |
| $UO_2Ox_2$ | 180 | Slow continual loss | . . . |
| $KUO_2Ox_3$ | 110 | 2–24 hr | ~1[b] |

[a] Each sample was previously dried in a vacuum desiccator at room temperature for several days. [b] Can be dried to constant weight at this temperature.

The purple tetrahydrate loses weight only slowly at 110° but can easily be dried to constant weight at 140–150° to the trihydrate. Continued heating for several days at 150° causes no further weight loss. Heating of either the trihydrate or the tetrahydrate at 180° for 3–4 hr quantitatively yields the green $UO_2Ox_2$ chelate.

The potassium salt of the complex anion $UO_2Ox_3^-$ can be dried to constant weight at 110°. Weight losses

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(14) R. J. Magee and L. Gordon, *Talanta*, **12**, 445 (1965).

(15) A. Corsini, J. Abraham, and M. Thompson, *Chem. Commun.*, 1101 (1967).

varied with the samples but averaged about 1%, indicating that some adsorbed water is retained after vacuum drying. This probably accounts for the low results in the analyses for oxine content.

As the synthesis procedures indicate, one of the major factors determining the nature of the chelate is the pH of the solution at the time of precipitation. To study this dependence, a series of nmr spectra have been recorded at intervals of pH for a solution $UO_2Ox_2 \cdot HOx$ in DMSO containing about 10% water and adjusted to pH 2.5 with HCl. An aqueous 50% sodium hydroxide solution diluted to a 1:3 ratio with methanol has been used to increase the pH. At pH 2.5 the nmr spectrum is characteristic of free oxine in a weakly acidic solution. However, the spectrum begins to broaden slightly at pH 2.8, especially for protons 2 and 7 (those closest to the coordinating atoms), and by pH 3.0 proton 7 has split into two separate resonances while proton 2 continues to give a single broadened peak. Between pH 3.0 and 4.5 the spectrum broadens further with the proton 2 resonance splitting at pH 4.5. Above pH 4.5 the spectrum continues to sharpen until at pH 6.5 it becomes equivalent to that for the red or orange forms of $UO_2Ox_2 \cdot HOx$, with the normal 2:1 intensity ratio of ligand resonances. The spectrum does not change between pH 6.5 and 7.5, but at pH 7.8 a third set of ligand resonances begins to appear and continues to increase in intensity as the pH is increased. At pH 10 this is the only set of resonances remaining; the spectrum is identical with that for the complex anion $UO_2Ox_3^-$.

## Discussion and Conclusions

**Thorium Oxinates.**—The present data for the 1:5 and 1:4 thorium–oxine chelates confirm the conclusions from previous investigations.[3,9,12,13] Thus, $ThOx_4 \cdot HOx$ appears to exist only in the solid phase. Most of the controversy concerning this species results from the various conditions that have been used. For example, Frere[2] recommended drying the 1:5 compound at 130–140°, which gave an average oxine content of 73.5% rather than the theoretical 75.7%. Other recent work has suggested drying temperatures sufficient to cause decomposition.[9,16] Drying studies establish that the 1:5 thorium oxinate is stable up to 80° but slowly decomposes above that temperature; this is in agreement with Moeller and Ramaniah.[3] The "solvate" species is converted to $ThOx_4$ in 4–6 hr at a temperature of 150°.

The additional oxine ligand is removed when the 1:5 compound is dissolved in DMSO. This is established by the gradual reprecipitation of the yellow $ThOx_4$ chelate from solutions of $ThOx_4 \cdot HOx$ and by the broad nmr spectrum for the latter chelate. The 1:5 complex also appears to be nonexistent in alcoholic solutions.

There still is a question as to whether the fifth ligand is coordinated to the thorium atom in the solid phase and is subsequently displaced by coordinated solvent (thus making thorium(IV) nine- or ten-coordinate, depending on how the ligand is bonded). The alternative is that it is held by weak intermolecular forces which are overcome by the action of solvent.

**Uranium Oxinates.**—Most previous studies of the "solvated" uranyl oxinate have used the synthesis procedure of Moeller and Wilkins.[17] However, the resulting product is inhomogeneous and contains orange, red-orange, and purple particles along with the desired red product $UO_2Ox_2 \cdot HOx$. This inhomogeneity of color has been mentioned previously.[18] The low ligand-to-metal ratio of the synthesized material has been attributed to solvent competing with oxine for the additional coordination sites of $UO_2Ox_2$.[19] The presence of some of the purple tetrahydrate in the precipitate tends to support this conclusion; a slight modification of the synthesis method[17] yields the tetrahydrate exclusively.

The synthesis procedures of Bordner, Salesin, and Gordon[11] are superior and yield homogeneous compounds; the red form of $UO_2Ox_2 \cdot HOx$ that is obtained at pH 5.0 is the same as the major product from the Moeller and Wilkins method.[17] However, the orange form of this "solvated" compound that is obtained at pH 6.8 has not been reported previously. This is surprising because the same orange compound forms when oxine in acetone or alcohol is added to an aqueous solution of the uranyl ion or when ammonia is added to an acidic solution of uranyl ion and oxine until precipitation occurs. Both of these procedures commonly are used for preparation of other metal oxinates.

The composition of the orange form of $UO_2Ox_2 \cdot HOx$ has been reported to be $(UO_2Ox_2)_2 \cdot HOx$.[11] However, the nmr spectrum of such a compound probably would consist of two separate ligand resonances with an intensity ratio of 4:1 while the observed ratio is 2:1. Furthermore, the spectrum is identical with that of the red form of $UO_2Ox_2 \cdot HOx$. Thus, the reported low ligand-to-metal ratio[11] for the orange form probably was due to partial decomposition from drying at elevated temperatures.

The X-ray structure[6] of the red form of $UO_2Ox_2 \cdot HOx$ indicates that the ligand molecules lie in a plane normal to the linear uranyl group and that two of the ligands are coordinated through both oxygen and nitrogen while the "extra" oxine molecule is bound only through the oxygen atom. The phenolic proton is assumed to form a hydrogen bond between the oxine nitrogen and the oxygen atom of the adjacent oxinate ligand. The nmr spectrum for this chelate in DMSO solution indicates that the "extra" oxine is displaced by solvent to give the free oxine (Figure 2A).

Because the "extra" oxine also is displaced in solutions of the orange chelate, its solid-phase structure cannot be ascertained from nmr data. The close similarity of the infrared spectra for the red and orange compounds implies that the bonding is quite similar. However, the lower thermal stability of the orange chelate indicates that the extra oxine bonding is more labile

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

[17] T. Moeller and D. H. Wilkins, *Inorg. Syn.*, **4**, 101 (1953).

[18] J. E. Tackett, Ph.D. Thesis, University of California at Riverside, 1964.

[19] A. Corsini and J. Abraham, *Talanta*, **15**, 562 (1968).

than it is in the red form. Models of the possible structures confirm that the only other configuration in which the "extra" oxine bonding is similar is that with the nitrogen hydrogen bonded to one of the uranyl oxygens instead of an adjacent ligand oxygen. This configuration has a less dense packing in the ligand coordination plane, which may account for the lower thermal stability of the orange form.

In solution both the red and orange forms of $UO_2Ox_2 \cdot HOx$ are converted at high pH to the complex anion $UO_2Ox_3^-$, in which all three oxinates act as bidentate ligands. Although previous studies[7,8,13] have concluded that the $UO_2Ox_3^-$ structure is retained under acidic conditions, the present work establishes that both the red and orange forms of $UO_2Ox_2 \cdot HOx$ yield solvated $UO_2Ox_2$ and free oxine in DMSO solutions. However, titrations of $UO_2Ox_3^-$ with acid indicate the presence of a species that is a stronger acid than free oxine.[7,8,13] A possible explanation is that at the equivalence point the keto form of the "solvate" oxine is stabilized by coordination through the oxygen atom to uranium to give a protonated ring nitrogen (and stronger acid than free oxine). Neutralization of this proton frees the ring nitrogen to occupy a coordination site on the uranium atom. The nmr spectrum of the complex anion (Figure 2D) indicates that all three ligands are bound equivalently which implies that the uranyl group has a coordination number of 6 in this compound. Because of steric considerations, the three ligands probably are twisted, "propeller fashion," out of the plane normal to the linear uranyl group.

Earlier workers[7] have suggested that the red color which results from the dissolution of the olive green $UO_2Ox_2$ complex is due to the decomposition of the "normal" chelate

$$3UO_2Ox_2 \xrightarrow{\text{solvent}} UO_2^{2+} + 2UO_2Ox_3^-$$

However, the nmr data establish that there is no decomposition of $UO_2Ox_2$ and that it is $UO_2Ox_2 \cdot HOx$ which decomposes to give solvated $UO_2Ox_2$ and free oxine. The color change associated with dissolution of the green chelate probably is due to coordination by the solvent because the complexes of higher coordination number are red in both solid and solution phases. The maroon trihydrate may contain the three water molecules in the coordination sphere also because high temperatures are required for their removal. This is consistent with other observations that the uranyl group tends to coordinate "extra" donor molecules.[20-22]

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(20) H. A. C. McKay, *J. Inorg. Nucl. Chem.*, **4**, 375 (1947).
(21) L. Sacconi, G. Caroti, and P. Paoletti, *J. Chem. Soc.*, 4257 (1958).
(22) M. Bartušek and L. Sommer, *J. Inorg. Nucl. Chem.*, **27**, 2397 (1965).

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# Fluxional Behavior of Group IV Trimethylindenyl Compounds

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The indenyltrimethyl compounds of silicon, germanium, and tin have been investigated by variable-temperature proton magnetic resonance spectroscopy and shown to be fluxional molecules. For $(CH_3)_3SnC_9H_7$ the complete range from limiting high- to limiting low-temperature behavior was observed. The presence of tin to ring hydrogen coupling confirms the *intra*molecular nature of the rearrangement. Relative signs of the proton–proton and tin–proton coupling constants in $(CH_3)_3SnC_9H_7$ have been determined.

Our studies[1] of main group cyclopentadienyl compounds showed, for all of the tin compounds studied, only limiting, high-temperature, "dynamic" spectra even as low as −100°. Furthermore, as expected, only average values of $^{117}Sn$ and $^{119}Sn$-H coupling constants were observed for ring methyl protons and the ring hydrogens. In view of the observation of Cotton and coworkers[2] that $(\pi\text{-}C_5H_5)Fe(CO)_2(\sigma\text{-}C_9H_7)$ apparently exhibits nonfluxional behavior, we felt the scope of our investigation should be extended to include the σ-indenyl compounds of the group IV elements.

## Experimental Section

**General Data.**—All manipulations were carried out under a dry $N_2$ atmosphere or *in vacuo*. Infrared spectra were recorded as liquid films between KBr plates on a Perkin-Elmer 337 spectrometer. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU6-D spectrometer. Nmr spectra were obtained at 60 MHz utilizing a Varian Associates A-60 spectrometer equipped with a variable-temperature probe. Temperature calibrations were made with methanol or ethylene glycol. The spectra of indenyltrimethylsilane and -germane were recorded on neat liquids, while those for indenyltrimethylstannane were recorded in 50% v/v $CS_2$ in the range 0 to −60° and as the neat liquid from 0 to +140°. Cyclohexane was used as an internal reference.

**Preparation of Indenyltrimethylsilane.**—A modification to the published procedure[3] was used to obtain indenyltrimethylsilane

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(1) A. Davison and P. E. Rakita, *J. Am. Chem. Soc.*, **90**, 4479 (1968).
(2) F. A. Cotton, A. Musco, and G. Yagupsky, *ibid.*, **89**, 6136 (1967).
(3) L. H. Sommer and N. S. Marans, *ibid.*, **73**, 5138 (1951).