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Complexes of Thorium and Uranium With Sulphoxides

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Uranium (IV) chloride and uranyl chloride form complexes with diphenyl sulphoxide and thianthrene-5-oxide, but not with the corresponding sulphides or diphenyl sulphone. The infrared spectra indicate that co-ordination occurs through oxygen. Some complexes of thorium (IV) with dimethyl sulphoxide have been prepared.

INTRODUCTION

Thorium tetrachloride, uranium tetrachloride, and uranyl chloride form complexes with phosphine oxides more readily than phosphines[1,2] Sulphides, like phosphines, have comparatively weak donor properties with respect to Class A electron acceptors.[3] Sulphoxides, with alternative donor sites provided by electrons on sulphur (IV) and oxygen, form complexes with most metals. Sulphones, with potential donor sites on the two oxygens bonded to sulphur (VI), are much weaker electron donors.

Uranium tetrachloride reacts with diphenyl sulphoxide in acetonitrile to give green crystalline $UCl_4 \cdot 4Ph_2SO$, having the same stoichiometry as the colourless complex formed by thorium tetrachloride,¹ which oxidises on attempted recrystallisation from ethanol in air to give yellow crystalline $UO_2Cl_2 \cdot 3Ph_2SO$. This complex, obtained also from the reaction of uranyl chloride with an excess of diphenyl sulphoxide in ethyl acetate, recrystallises from warm ethyl acetate but decomposes on boiling to give yellow crystalline $UO_2Cl_2 \cdot 2 Ph_2SO$. Diphenyl sulphoxide is recovered from the filtrate. The S = O stretching band occurs at

1040 cm^{-1} in diphenyl sulphoxide[4], and shifts to lower frequencies on complex formation. The complex $\text{UO}_2\text{Cl}_2 \cdot 3\text{Ph}_2\text{SO}$ exhibits a doublet with well-defined maxima at 990 and 965 cm^{-1} and the other complexes exhibit a broad band in the region 980–960 cm^{-1} , indicating that bonding takes place through oxygen.

Thorium tetrachloride, uranium tetrachloride, and uranyl chloride do not form complexes with diphenyl sulphide or diphenyl sulphone under the conditions investigated, or with thianthrene, $(\text{C}_6\text{H}_4\text{S})_2$, which contains two bivalent sulphur atoms. Complexes are formed with thianthrene-5-oxide (thianox), of composition $\text{ThCl}_4 \cdot 4\text{thianox}$, $\text{UCl}_4 \cdot 4\text{thianox}$, and $\text{UO}_2\text{Cl}_2 \cdot 2\text{thianox}$. Complexes of uranyl chloride containing a higher proportion of thianox were not obtained, even in the presence of a large excess of ligand. The $\text{S}=\text{O}$ stretching band occurs at 1075 cm^{-1} in thianox, and appears as a doublet with maxima near 990 and 960 cm^{-1} in the thorium and uranyl complexes. The spectrum of the complex $\text{UCl}_4 \cdot 4\text{thianox}$ exhibits a maximum at 970 cm^{-1} and a very broad band in the region 930–890 cm^{-1} , of quite different appearance from the $\text{U}=\text{O}$ stretching band at 920 cm^{-1} in uranyl compounds.

The complexes formed by the uranium chlorides with both sulphoxides are nonelectrolytes in acetonitrile. Their solubilities are too low for molecular weight determinations but it is likely that thorium (IV) and uranium (IV) exhibit the co-ordination number 8, and uranium (VI) exhibits the co-ordination numbers 6 and 7.

Dimethyl sulphoxide forms complexes with many metals[5], and its versatile behaviour is illustrated by the reactions of thorium salts. Complexes of composition $\text{ThCl}_4 \cdot 3\text{Me}_2\text{SO}$, $\text{ThCl}_4 \cdot 5\text{Me}_2\text{SO}$, and $\text{ThBr}_4 \cdot 6\text{Me}_2\text{SO}$, have been reported[6.] Thorium nitrate forms a complex with three moles of diphenyl sulphoxide,¹ and a similar complex with dimethyl sulphoxide, $\text{Th}(\text{NO}_3)_4 \cdot 3\text{Me}_2\text{SO}$, has now been prepared. The repeated recrystallisation of hydrated thorium (IV) bromide and nitrate from dimethyl sulphoxide gives products containing twelve moles of ligand, $\text{ThX}_4 \cdot 12\text{Me}_2\text{SO}$ ($\text{X} = \text{Br}, \text{NO}_3$). The infrared spectra of these complexes contain bands at *ca.* 1050 cm^{-1} and *ca.* 960

cm^{-1} which can be attributed to $\text{S}=\text{O}$ stretching in the free and co-ordinated ligands respectively.

EXPERIMENTAL

Diphenyl sulphoxide, m. p. 71° , and thianox, m. p. 143° , were prepared by oxidation of the sulphides. Reactions between the metal salts and the appropriate quantity of sulphoxide were carried out in anhydrous acetonitrile or ethyl acetate. Yields, m. ps., and analytical data for the products are recorded in the Table.

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TABLE

Compound	Yield (%)	M. p. (°C)	C	Found (%)		S	Formula	Required (%)			
				H	Hal/N			C	H	Hal/N	S
UCl ₄ ·4Ph ₂ SO	92	130°	48.4	3.3	11.75	10.75	C ₄₈ H ₄₀ Cl ₄ O ₄ S ₄ U	48.5	3.4	11.9	10.8
UCl ₄ ·4thianox	20	93*	41.3	2.6	11.1	19.6	C ₄₈ H ₃₂ Cl ₄ O ₄ S ₄ U	44.0	2.5	10.8	19.6
UO ₂ Cl ₂ ·3Ph ₂ SO	85	218	45.6	3.2	7.3	10.1	C ₃₆ H ₃₀ Cl ₂ O ₅ S ₃ U	45.6	3.2	7.3	10.1
UC ₂ Cl ₂ ·2Ph ₂ SO	65	216-222	38.7	2.8	9.4	8.4	C ₂₄ H ₂₀ Cl ₂ O ₄ S ₂ U	38.7	2.7	9.5	8.6
UO ₂ Cl ₂ ·2thianox	91	264*	36.35	2.2	8.9	16.0	C ₂₄ H ₁₆ Cl ₂ O ₄ S ₂ U	35.8	2.0	8.8	15.9
ThCl ₄ ·4thianox	63	204*	44.4	2.8	10.3	16.2	C ₄₈ H ₃₂ Cl ₄ O ₄ S ₄ Th	44.3	2.5	10.9	19.6
ThCl ₄ ·5Me ₂ SO	75	143*	15.6	4.1	—	21.0	C ₁₀ H ₃₀ Cl ₄ O ₅ S ₃ Th	15.7	3.9	18.6	20.9
ThBr ₄ ·12Me ₂ SO	71	194	19.4	5.2	—	25.7	C ₂₄ H ₇₂ Br ₄ O ₁₂ S ₁₂ Th	19.3	4.9	21.5	25.8
Th(NO ₃) ₄ ·3Me ₂ SO	85	188	10.5	2.5	7.8	—	C ₆ H ₁₈ N ₄ O ₁₃ S ₃ Th	10.1	2.5	7.8	13.4
Th(NO ₃) ₄ ·12Me ₂ SO	80	60*	19.7	5.6	3.8	—	C ₂₄ H ₇₂ N ₄ O ₂₄ S ₁₂ Th	20.3	5.0	3.8	27.1

*Decomposition.

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ÖZET

Unanyum (IV) klorür ve uranil klorür, difenil sülfoksit ve tiantren-5-oksit ile çeşitli kompleksler meydana getirmelerine rağmen bunlara tekabül eden difenil sülfür ve difenil sülfon ile kompleks meydana getirmezler.

Bu komplekslerin infrared spektrumları koordinasyonun oksijen üzerinden olduğunu göstermektedir. Bunlardan başka toryum (IV) ün de dimetil sülfoksit ile bazı kompleksleri hazırlandı.

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