

485. Some Acetamide Complexes of the Actinide Tetrachlorides. Part II.* Thorium.

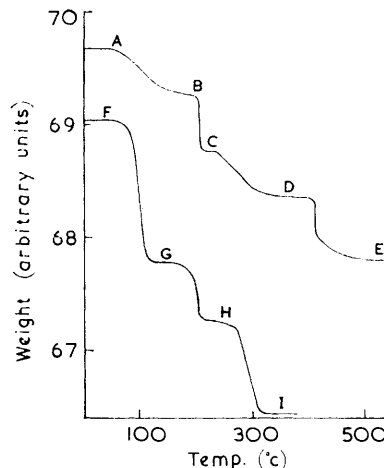
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Thorium tetrachloride forms a complex with *NN*-dimethylacetamide (DMA), of composition $\text{ThCl}_4 \cdot 4\text{DMA}$, from which the corresponding nitrate $[\text{Th}(\text{NO}_3)_4 \cdot 2 \cdot 5\text{DMA}]$, thiocyanate $[\text{Th}(\text{SCN})_4 \cdot 4\text{DMA}]$, and perchlorate $[\text{Th}(\text{ClO}_4)_4 \cdot 6\text{DMA}]$ complexes have been prepared. The perchlorate complex, like the uranium(IV) analogue, forms a trihydrate. The tetrachloride complex loses dimethylacetamide when heated under a vacuum, giving products with three ($160\text{--}204^\circ$), two ($212\text{--}236^\circ$), and one ($340\text{--}400^\circ$) molecule of dimethylacetamide, the last molecule being lost above 412° . A uranium tetrachloride-*N*-methylacetamide (NMA) complex, $\text{UCl}_4 \cdot 4\text{NMA}$, has also been prepared.

THORIUM TETRACHLORIDE has been reported¹ to form a dimethylformamide (DMF) complex of composition $\text{ThCl}_4 \cdot 4\text{DMF}$, and, since the analogous uranium, neptunium, and plutonium *NN*-dimethylacetamide complexes² appear to be dimers of composition $\text{MCl}_4 \cdot 2 \cdot 5\text{DMA}$, it was of interest to prepare the corresponding thorium complex and, from

Thermal degradation of (A—E) $\text{ThCl}_4 \cdot 4\text{DMA}$ and (F—I) $\text{UCl}_4 \cdot 4\text{NMA}$.

A, $\text{ThCl}_4 \cdot 4\text{DMA}$. B, $\text{ThCl}_4 \cdot 3 \cdot 03\text{DMA}$.
C, $\text{ThCl}_4 \cdot 1 \cdot 96\text{DMA}$. D, $\text{ThCl}_4 \cdot 0 \cdot 98\text{DMA}$.
E, ThCl_4 . F, $\text{UCl}_4 \cdot 4\text{NMA}$. G, $\text{UCl}_4 \cdot 2 \cdot 36\text{NMA}(\?)$.
H, $\text{UCl}_4 \cdot 1 \cdot 42\text{NMA}(\?)$. I, UCl_4 .



it, the nitrate, perchlorate, and thiocyanate complexes for a comparison with their uranium(IV) counterparts.³⁻⁵

The chloride complex was obtained by dissolving anhydrous thorium tetrachloride in a mixture of acetone and excess of *NN*-dimethylacetamide, followed by precipitation of the crude complex with isopentane and re-dissolution in hot acetone; the complex $\text{ThCl}_4 \cdot 4\text{DMA}$ crystallised on standing, analogously to the dimethylformamide complex. The compound is somewhat hygroscopic, unlike the uranium(IV) complex, and melts at $125\text{--}127^\circ$. On thermal decomposition under a vacuum (see Figure) it begins to decompose at 60° , with breaks in the decomposition-temperature curve, corresponding to adducts with three, two, and one molecule of dimethylacetamide, at $160\text{--}204$, $212\text{--}236$, and $340\text{--}400^\circ$, respectively, the last molecule of dimethylacetamide being lost between 412

* Part I, *J.*, 1961, 1611.

¹ Moeller and Smith, U.S. report Air Force Office of Scientific Research-TN-58-559 (1958).

² Bagnall, Deane, Markin, Robinson, and Stewart, *J.*, 1961, 1611.

³ Bagnall, Robinson, and Stewart, *J.*, 1961, 4060.

⁴ Bagnall, Brown, and Deane, *J.*, 1962, 1655.

⁵ Bagnall, Brown, and Colton, preceding Paper.

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and 490°. Molecular-weight determinations in acetone gave values between 300 (41.6—43.4 g./kg. of solvent) and 216 (14.3 g./kg. of solvent), whilst in methylene chloride the values ranged from 448 (38.7 g./kg. of solvent) to 373 (8.33 g./kg. of solvent), indicative of extensive ionisation or dissociation in these solvents. Conductivity measurements show that the compound is virtually a non-electrolyte, the values of Λ_{500} and Λ_{1000} being 16.3 and 17.7 mhos and 10.8 and 12.8 mhos, respectively, in nitromethane and in acetone.

The corresponding nitrate, perchlorate, and thiocyanate amide complexes were prepared in the same way as their uranium(IV) analogues.³⁻⁵ The nitrate had the composition $\text{Th}(\text{NO}_3)_4 \cdot 2.5\text{DMA}$, and melted with decomposition at 126—128°, whereas a hydrated complex of composition $\text{Th}(\text{NO}_3)_4 \cdot 3\text{DMA} \cdot 3\text{H}_2\text{O}$ is reported to be formed from hydrated thorium tetranitrate by treatment with excess of dimethylacetamide.⁶ The perchlorate, $\text{Th}(\text{ClO}_4)_4 \cdot 6\text{DMA}$, formed a trihydrate on exposure to moist air, the water being lost under a vacuum at room temperature, just as for the uranium(IV) complex; the anhydrous compound melts with some decomposition at 133—134°, and deflagrates violently at higher temperatures. The thiocyanate, $\text{Th}(\text{SCN})_4 \cdot 4\text{DMA}$ melts without decomposition at 162—163°, but a study of its thermal decomposition under a vacuum was inconclusive. Apart from the ligand hydration observed for the perchlorate, all three complexes are non-hygroscopic white solids exactly analogous to the corresponding uranium(IV) complexes, and X-ray powder photography indicates that they are isostructural with the uranium compounds.

The infrared spectra of the four complexes were almost identical with those of the uranium(IV) complexes (Table). The slight splitting in the spectrum of the hydrated

Infrared spectra of thorium(IV) and uranium(IV) complexes.

Complex	Anion vibrations (cm. ⁻¹)	C=O stretch (cm. ⁻¹)	$\Delta\nu$ (cm. ⁻¹)	Ref.
$\text{ThCl}_4 \cdot 4\text{DMA}$	—	1603	44	—
$\text{UCl}_4 \cdot 2.5\text{DMA}$	—	1618	29	2
$\text{Th}(\text{SCN})_4 \cdot 4\text{DMA}$	C≡N stretch; 2033vs	1605	42	—
$\text{U}(\text{SCN})_4 \cdot 4\text{DMA}$	C≡N stretch; 2047vs	1606	41	5
$\text{Th}(\text{NO}_3)_4 \cdot 3\text{DMA} \cdot 3\text{H}_2\text{O}$	—	1610	37	6
$\text{Th}(\text{NO}_3)_4 \cdot 2.5\text{DMA}$	Covalent nitrate; 1500vb, 1306, 1286, 1027, 809, 744, 739, 702w	1610	37	—
$\text{U}(\text{NO}_3)_4 \cdot 2.5\text{DMA}$	Covalent nitrate; 1517, 1277, 1020, 807, 743, 739, 702w	1613	34	3
$\text{Th}(\text{ClO}_4)_4 \cdot 6\text{DMA}$	ClO_4^- ; 1098, 623	1614	33	—
$\text{U}(\text{ClO}_4)_4 \cdot 6\text{DMA}$	ClO_4^- ; 1091, 640sh, 623	1618	29	4
$\text{Th}(\text{ClO}_4)_4 \cdot 6\text{DMA} \cdot 3\text{H}_2\text{O}$	ClO_4^- ; 1116, 1051, 624	1613	34	—
$\text{U}(\text{ClO}_4)_4 \cdot 6\text{DMA} \cdot 3\text{H}_2\text{O}$	ClO_4^- ; 1112, 1065, 623	1616	31	4

uranium tetraperchlorate complex was again present. However, the presence of a single peak in the anhydrous complexes [a peak at 1032 for $\text{U}(\text{ClO}_4)_4 \cdot 6\text{DMA}$, and 1022 cm.⁻¹ for $\text{Th}(\text{ClO}_4)_4 \cdot 6\text{DMA}$, is probably due to dimethylacetamide and not perchlorate] indicates that the perchlorate is ionic and not covalently bound as at first reported.⁴

All four thorium complexes are very soluble in acetone, nitromethane, methyl cyanide, hot methyl alcohol, and hot methylene chloride (perchlorate only very slightly soluble), but insoluble in benzene, diethyl ether, methyl acetate, ethyl acetate, and methyl isobutyl ketone, hot or cold. The chloride and perchlorate complexes, but not the nitrate or thiocyanate complexes, are also soluble in hot ethyl alcohol.

The use of *N*-methylacetamide (NMA) as a ligand was also investigated; with caesium hexachlorouranate(IV) as starting material, a green crystalline complex, $\text{UCl}_4 \cdot 4\text{NMA}$, was obtained in the same way as the dimethylacetamide complex.² This compound is slightly hygroscopic and appears to be much less stable to heat than the uranium(IV) dimethylacetamide complex, decomposing above 60°. Breaks in the decomposition-temperature curve (Figure) occurred at 120—170 and 220—250°, corresponding very approximately with the compositions $\text{UCl}_4 \cdot 2.5\text{NMA}$ and $\text{UCl}_4 \cdot 1.5\text{NMA}$ (cf. $\text{UCl}_4 \cdot 2.5\text{DMA}$), but attempts

* Bull, Madan, and Willis, *Inorg. Chem.*, 1963, 2, 303.

to isolate these intermediates were unsuccessful, the very hygroscopic products ranging in composition from $\text{UCl}_{3.2}\cdot 2\cdot 8\text{NMA}$ to $\text{UCl}_{3.43}\cdot 2\cdot 9\text{NMA}$, so that the apparent compositions observed in the decomposition-temperature curve may be fortuitous. The complex is soluble in acetic acid, acetone, ethanol, methanol, methyl cyanide, and nitromethane, but insoluble in benzene, diethyl ether, methyl acetate, and ethyl acetate.

EXPERIMENTAL

Infrared spectra were taken for mulls in Fluorube and Nujol, using a Hilger H800 spectrometer with sodium chloride and caesium bromide prisms. *X*-Ray powder photographs were taken with a 19-cm. Unicam Debye-Scherrer camera and a Guinier focusing camera, using filtered Cu-K_α radiation. The complexes, which all gave quite good *X*-ray diffraction patterns, are evidently of low symmetry, probably monoclinic or triclinic.

Preparations.—Thorium tetrachloride-amide complex. Hydrated thorium tetrachloride was refluxed with thionyl chloride and vacuum-dried. The product (4 g.) was dissolved in a mixture of *NN*-dimethylacetamide (12 ml.) and acetone (25 ml.), with warming, centrifuged to remove sediment, and cooled. A few crystals separated, and the bulk of the product was precipitated with isopentane, redissolved in acetone, and the precipitation-redissolution cycle repeated. On standing, the resulting acetone solution deposited crystals of the complex (~50%). These were recrystallised from acetone or methylene chloride, finely ground, and vacuum-dried at room temperature (Found: Th, 32.3; Cl, 19.5; N, 7.6. $\text{ThCl}_4\cdot 4\text{DMA}$ requires Th, 32.1; Cl, 19.63; N, 7.75%). Molecular weights were determined ebullioscopically as described previously.²

Thorium tetranitrate-amide complex. The calculated quantity of silver nitrate in methyl cyanide was added to a solution of the thorium tetrachloride-DMA complex in a mixture of hot acetone and excess of amide; after removal of silver chloride by centrifugation, the crude complex was precipitated with isopentane, redissolved in acetone, and reprecipitated. The oily product was washed with isopentane, ground with ethyl acetate (2 washes), and vacuum-dried. The product contained 3–5% of excess dimethylacetamide which was removed by recrystallisation from nitromethane-methyl isobutyl ketone as described for the uranium tetraperchlorate complex⁴ (Found: Th, 33.1; NO_3^- , 35.1; total N, 12.8. $\text{Th}(\text{NO}_3)_4\cdot 2\cdot 5\text{DMA}$ requires Th, 33.3; NO_3^- , 35.5; total N, 13.0%).

Thorium tetra-perchlorate-amide complex. This compound was prepared from the tetrachloride complex in exactly the same way as the tetranitrate, using silver perchlorate in acetone (Found: Th, 20.1; ClO_4^- , 34.3; N, 7.25. $\text{Th}(\text{ClO}_4)_4\cdot 6\text{DMA}$ requires Th, 20.1; ClO_4^- , 34.5; N, 7.3%). On standing in a moist atmosphere the weight increase due to hydration was 4.40% (+3 H_2O requires 4.47%); the water content of the hydrate, determined by the Karl Fischer method,^{7a} was 4.1%.

Thorium tetrathiocyanate-amide complex. The compound was prepared in the same way as the tetranitrate-amide complex, using potassium thiocyanate in acetone. The initial isopentane precipitate was solid, rather than an oil; after two cycles of dissolution in hot acetone and precipitation with isopentane, the crude product was dissolved in the minimum volume of hot acetone and allowed to crystallise overnight. The crystals were then ground and vacuum-dried (Found: Th, 28.65; SCN^- , 28.5; organic N, 7.0; total N, 13.7. $\text{Th}(\text{SCN})_4\cdot 4\text{DMA}$ requires Th, 28.55; SCN^- , 28.55; organic N, 6.9; total N, 13.8%).

Uranium tetrachloride-N-methylacetamide complex. This compound was prepared in the same way as the *NN*-dimethylacetamide complex² (Found: U^{4+} , 35.2; Cl^- , 20.4; N, 8.2. $\text{UCl}_4\cdot 4\text{NMA}$ requires U^{4+} , 35.4; Cl^- , 21.1; N, 8.3%).

Analysis.—Thorium was weighed as ThO_2 following upon air-ignition either of the compound moistened with water to hydrolyse it, or of thorium hydroxide precipitated from an aqueous solution of the complex. Chloride was determined by potentiometric titration against silver nitrate. Nitrate was weighed as nitron nitrate,^{7b} after removal of thorium as hydroxide with ammonia. Perchlorate was weighed as the tetraphenylarsonium salt,⁸ again after removal of thorium. Thiocyanate was determined volumetrically against mercuric nitrate,^{7c} after removal of thorium. Total nitrogen (nitrate and thiocyanate complexes) and amide nitrogen

⁷ Vogel, "A Text-book of Quantitative Inorganic Analysis," Longmans, London, 1953, (a) p. 698; (b) p. 505; (c) p. 266; (d) p. 248.

⁸ Willard and Smith, *Ind. Eng. Chem. (Analyt.)*, 1939, **11**, 186, 305.

(chloride, perchlorate, and thiocyanate complexes) were determined by the Kjeldahl method.^{7d} In the case of the thiocyanate the anion was first removed by treatment with silver sulphate in dilute sulphuric acid solution in order to determine amide nitrogen alone. Uranium(IV) was determined volumetrically by titration to uranium(VI) with dichromate.⁸

Thermogravimetric data were obtained with a conventional quartz-fibre thermobalance (sensitivity 4.5 mg./cm. extension); the heating rate was 2°/min. and the operating pressure 0.02— 2×10^{-3} mm.

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⁸ Cf., e.g., Rodden and Warf, "The Analytical Chemistry of the Manhattan Project," Nat. Nuclear Energy Series, ed. Rodden, McGraw-Hill, New York, 1950, Vol. VIII—I, p. 68.
