

659. *Amide Complexes of Thorium(IV) and Uranium(IV) Iodides*

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The *NN*-dimethylacetamide (DMA) complexes of thorium and uranium tetraiodide, $\text{ThI}_4 \cdot 6\text{DMA}$ and $\text{UI}_4 \cdot 4\text{DMA}$, have been prepared from the corresponding iodides. Uranium(IV) mixed halide complexes, $\text{UI}_2\text{Cl}_2 \cdot 5\text{DMA}$ and $\text{UI}_3\text{Cl} \cdot 5\text{DMA}$, have been prepared from the chloride complex, $\text{UCl}_4 \cdot 2 \cdot 5\text{DMA}$. The last three compounds appear to be chlorine-bridged dimers in which the uranium is eight-covalent.

COMPLEXES of thorium or uranium tetraiodide with donor molecules, apart¹ from $\text{ThI}_4 \cdot \text{MeCN}$, appear to be unknown, probably because of the ease of oxidation of the iodide ion and because of the instability of the uranium compound, which decomposes appreciably into uranium tri-iodide at relatively low temperatures. Since the *NN*-dimethylacetamide (DMA) complexes of the unstable uranium tetranitrate² and tetraperchlorate³ and their thorium analogues⁴ are readily obtained from the corresponding chloride complexes by double decomposition with the appropriate silver salt in non-aqueous media, it was of interest to attempt the preparation of the iodide complexes in a similar manner.

The uranium tetrachloride complex, $\text{UCl}_4 \cdot 2 \cdot 5\text{DMA}$, reacts readily with an excess of sodium iodide in *NN*-dimethylacetamide solution, but only 50% of the chloride precipitates as the sodium salt. Addition of ethyl acetate to the filtrate precipitates the pale apple-green complex $\text{UI}_2\text{Cl}_2 \cdot 5\text{DMA}$; uranyl compounds formed by oxidation of the uranium(IV) during the preparation remain in the ethyl acetate–DMA solution together with the excess sodium iodide. The dichlorodi-iodide complex is also obtained when the metathesis is carried out in methyl cyanide with some DMA present, the filtrate evaporated to dryness, and the resulting solid dissolved in DMA. However, if the solid is dissolved in nitromethane instead of DMA, a further precipitation of sodium chloride occurs and the addition of ethyl acetate to the filtrate precipitates the pale apple-green complex, $\text{UI}_3\text{Cl} \cdot 5\text{DMA}$. The remaining chloride ion in either complex is not replaced by iodide even on prolonged heating at 100° in an inert atmosphere with an excess of sodium iodide in DMA solution, from which the chloroiodide complexes are recovered unchanged on addition of ethyl acetate. In boiling methyl cyanide solution, however, a small yield of the tetraiodide–DMA complex is obtained, but extensive oxidation of uranium(IV) to uranium(VI) occurs under these conditions. The most satisfactory method of preparing the uranium and thorium tetraiodide–DMA complexes is to treat the tetraiodides with an excess of DMA either alone or in methyl cyanide solution. Whereas the uranium(IV) complex, $\text{UI}_4 \cdot 4\text{DMA}$, is readily obtained pure by cycles involving dissolution in methyl cyanide and precipitation with ethyl acetate, it is more difficult to remove excess DMA from the thorium(IV) complex, $\text{ThI}_4 \cdot 6\text{DMA}$, which crystallises from methyl cyanide–DMA or acetone–DMA mixtures with excess ligand co-ordinated to it ($\text{ThI}_4 \cdot 8\text{DMA}$ to $\text{ThI}_4 \cdot 11\text{DMA}$). This

¹ K. W. Bagnall, D. Brown, P. J. Jones, and J. G. H. du Preez, *J.*, 1965, 350.

² K. W. Bagnall, P. S. Robinson, and M. A. A. Stewart, *J.*, 1961, 4060.

³ K. W. Bagnall, D. Brown, and A. M. Deane, *J.*, 1962, 1655.

⁴ K. W. Bagnall, D. Brown, P. J. Jones, and P. S. Robinson, *J.*, 1964, 2531.

excess ligand is strongly held, and treatment with hot ethyl acetate is necessary to obtain the pure complex. The ligand content is reduced to less than 6DMA on prolonged treatment, when loss of iodine is also observed; similarly, attempts to purify the complex by dissolution in nitromethane and precipitation with di-isobutyl ketone or acetone and isopentane yield partially hydrolysed products, presumably because of the presence of traces of water in these solvents.

All the complexes are soluble in methyl cyanide, nitromethane, and DMA and are insoluble in methyl acetate, ethyl acetate, benzene, carbon tetrachloride, and methylene dichloride. They are hygroscopic and oxidise slowly in dry air with the liberation of iodine, but are more stable in an inert atmosphere. Thermogravimetric analysis shows that DMA is rapidly lost at temperatures below 100° [ThI₄,6DMA (70°), UI₂Cl₂,5DMA (65°), and UI₃Cl,5DMA (82°)]; the tri-iodochloride complex appears to decompose to an intermediate compound, UI₃Cl,3DMA, which is moderately stable between 130 and 170°. Absorption spectra of 0.012–0.025M-solutions of the uranium(IV) complexes in nitromethane have been examined between 400 and 1000 m μ (Table 1). The 465 m μ peak observed for the tetrachloride DMA complex is masked by electron-transfer bands in those complexes containing iodide. Almost identical spectra were obtained from DMA solutions of the complexes.

TABLE 1
Absorption spectra of the uranium(IV) complexes

Complex	Principal peaks (m μ); ϵ_M in parentheses
UCl ₄ ,2.5DMA	465(29), 675(34), 650(22), 930(25)
UI ₂ Cl ₂ ,5DMA	675(32), 920(25)
UI ₃ Cl,5DMA	670(26), 920(10), 900(10)
UI ₄ ,4DMA	660(16), 865(19)

TABLE 2
Molar conductivities of uranium(IV) and thorium(IV) DMA complexes

Complex	Λ_{500} (mhos/cm. ²)	Λ_{1000} (mhos/cm. ²)	Prep. ref.	Complex	Λ_{500} (mhos/cm. ²)	Λ_{1000} (mhos/cm. ²)	Prep. ref.
2UCl ₄ ,5DMA	36.2	36.6	5	U(ClO ₄) ₄ ,6DMA	273	305	3
ThCl ₄ ,4DMA	14.2	15.4	4	Th(ClO ₄) ₄ ,6DMA	197	230	4
2U(NO ₃) ₄ ,5DMA	38.4	40.4	2	[UI ₃ Cl,5DMA] ₂	269	274	This work
2Th(NO ₃) ₄ ,5DMA	54.0	56.0	4	[UI ₂ Cl ₂ ,5DMA] ₂	284	290	"
U(SCN) ₄ ,4DMA	16.9	22.6	6	UI ₄ ,4DMA	240	275	"
Th(SCN) ₄ ,4DMA	9.8	13.0	4	ThI ₄ ,6DMA	138	162	"

The molar conductivities of all the uranium(IV) and thorium(IV) DMA complexes, measured in nitromethane solution, are shown in Table 2. The change of conductivity with concentration in every case indicates an appreciable degree of ion association at concentrations above 0.002M and is still observable at 0.0001M. The observed conductances increase slowly with time, a phenomenon which is frequently observed with investigations in non-aqueous solvents and is ascribed to a "slow ionisation" of the compounds in such media,⁷ so that the observed values could be in error. However, the values of Λ_{1000} for both UI₂Cl₂,5DMA and UI₃Cl,5DMA are close to those expected for 2:1 electrolytes if the complexes are assumed to be monomeric (137 and 145 mhos, respectively). In addition, potentiometric titration of either complex against silver perchlorate in methyl cyanide solution gives an extremely sharp first end-point at 2 gram-ions of halide, and the precipitate in each case consists of silver iodide only, so that some reliance may obviously be placed on the conductivity data. It seems unlikely that the compounds contain uranium(IV) with a co-ordination number seven, that is, that they can be represented as the monomeric

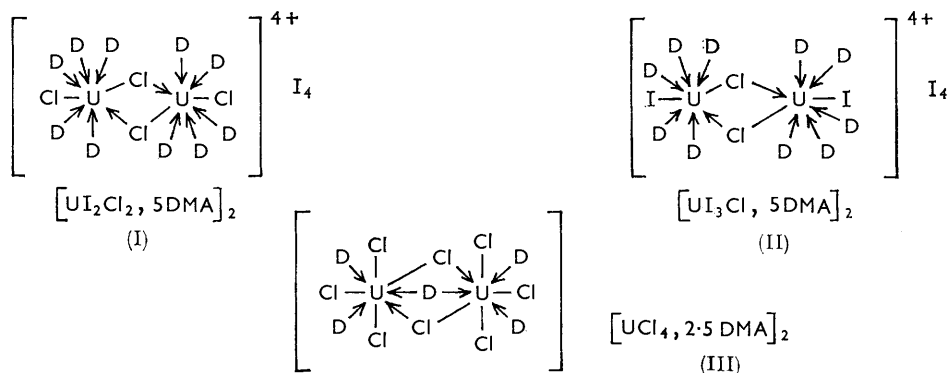
⁵ K. W. Bagnall, A. M. Deane, T. L. Markin, P. S. Robinson, and M. A. A. Stewart, *J.*, 1961, 1611.

⁶ K. W. Bagnall, D. Brown, and R. Colton, *J.*, 1964, 2527.

⁷ *E.g.*, C. M. French and I. G. Roe, *Trans. Faraday Soc.*, 1953, **49**, 314, 791.

complexes $[\text{UCl}_2, 5\text{DMA}]^{2+}\text{I}_2$ and $[\text{UICl}, 5\text{DMA}]^{2+}\text{I}_2$, in contrast to the more usual co-ordination number of six, as in the hexachlorouranates(IV), M_2UCl_6 , or eight, as in the thiocyanate complexes $\text{M}_4\text{U}(\text{NCS})_8$ and in $\text{U}(\text{SCN})_4, 4\text{DMA}$.⁶ The difficulty of replacing the last chlorine atom by iodine suggests that this chlorine might be present as a bridging atom so that the constitution of the complexes might be represented as (I) and (II), in which the species are dimeric. This in turn indicates that the chloride complex, $\text{UCl}_4, 2 \cdot 5\text{DMA}$, which is virtually a non-electrolyte, can be represented as (III); all three complexes would thus contain eight-co-ordinated uranium(IV), in agreement with preliminary observations of their back-reflectance spectra.⁹

We are indebted to a referee for bringing to our attention a recent Paper,* in which it is shown that the complexity of an ionic species of this kind can be ascertained from conductivity measurements. These authors have shown that the value of the constant B in the equation $\Lambda_e = \Lambda_0 - B\sqrt{c_e}$, where Λ_e is the equivalent conductivity of a solution of equivalent concentration c_e , depends on the charge Z of a $Z:1$ electrolyte. Thus, for solutions in nitromethane, B is 151–216 for a 1:1, 392–465 for a 2:1, and 1020 for a 3:1 electrolyte. Measurements of the conductivity of a nitromethane solution of $\text{U}(\text{ClO}_4)_4, 6\text{DMA}$ gave a value of about 1700 for the constant B , whereas those for the UI_2Cl_2 and UI_3Cl complexes in nitromethane solution were usually twice as large, but the results were neither meaningful nor reproducible because oxidation to uranium(VI) occurred rapidly, even when the conductivities were measured in an argon-filled dry-box. The values of B for solutions in dry methyl cyanide were 4000 for $\text{U}(\text{ClO}_4)_4, 6\text{DMA}$ and 3600 ± 300 for $\text{UI}_2\text{Cl}_2, 5\text{DMA}$, supporting the view that the latter is dimeric and a 4:1 electrolyte. However, with $\text{UI}_3\text{Cl}, 5\text{DMA}$ the value of B increased continually with dilution to well over 7000 (below $3 \cdot 9 \times 10^{-5}\text{M}$ -solution), suggesting that the iodide within the co-ordination sphere was being displaced by the solvent at these dilutions.



Alternative formulation of $\text{UCl}_4, 2 \cdot 5\text{DMA}$, again as a dimer, has been suggested¹⁰ with three bridging DMA molecules, but this would not explain the difficulty of replacing the last chlorine atom by iodine. The uranium(IV) and thorium(IV) nitrate complexes, $\text{M}(\text{NO}_3)_4, 2 \cdot 5\text{DMA}$, are probably also dimeric containing the eight-co-ordinated element, whilst the corresponding thiocyanates and the thorium tetrachloride–DMA complex, all non-electrolytes and of the form $\text{MX}_4, 4\text{DMA}$, are simple eight-co-ordinated species. The thorium tetraiodide–DMA complex appears to be a 2:1 electrolyte at concentrations above $\text{m}/500$ but the conductivity increases very rapidly with dilution, Λ_m being 262 for $0 \cdot 00019\text{M}$ -solution, suggesting that iodide is displaced from the co-ordination sphere by the solvent. A similar effect occurs with the uranium tetraiodide complex which appears to be a 4:1 electrolyte, like the perchlorate complexes, even in $\text{M}/1000$ solution.

* R. D. Feltham and R. G. Hayter, *J.*, 1964, 4587.

⁸ V. P. Markov and E. N. Trageim, *Zhur. neorg. Khim.*, 1961, 6, 2316.

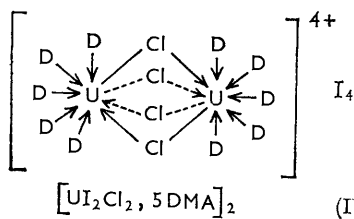
⁹ B. J. Hathaway, personal communication, 1964.

¹⁰ P. Gans, Thesis, London University, 1964.

It was hoped that the presence of the bridging chlorine atoms in species (I)—(III) could be confirmed by studying the isotopic exchange between the chlorine in each of them and a ^{36}Cl labelled organic chloride. Unfortunately, quinolinium hydrochloride, the only chloride to have suitable solubility properties in the most satisfactory solvent system, DMA-ethyl acetate, caused rapid oxidation of the uranium(IV). Evidence for chlorine bridging was also sought from an examination of the far-infrared spectra ($300\text{--}200\text{ cm.}^{-1}$) of the tetrachloride, tetraiodide, and mixed halide complexes.

If the complexes are as shown (I)—(III), then (I) and (III) should exhibit bands arising from U-Cl and U-Cl \rightarrow U vibrations, whereas (II) should exhibit only bands arising from the latter. In fact, the infrared spectrum of (III) between 200 and 300 cm.^{-1} shows a weak band at 292 cm.^{-1} and a broad band centred at 252 cm.^{-1} which can be resolved into a sharp band at 259 cm.^{-1} and a shoulder at 245 cm.^{-1} , whereas the spectra of (I) and (II) show only a relatively sharp band at 254 cm.^{-1} , the absorption in the case of (II) being roughly half that of (I), as might be expected. The band at 292 cm.^{-1} in the spectrum of (III) is too weak to be due to a U-Cl stretching mode and is probably an overtone of a deformation (presumably at about 146 cm.^{-1}) which is absent from the spectra of (I) and (II). The spectrum of the uranium tetraiodide complex shows only a single very weak band at 242 cm.^{-1} which is probably due to a ligand skeletal vibration.

These results suggest that U-Cl stretching and deformation modes may be present in (III) which are absent in the others, and one cannot exclude the possibility that the uranium atoms in the three complexes are linked by four chlorine bridges, making the uranium 9-coordinate [as in (IV)], the dotted lines indicating bonds normal to the plane of the paper;



the probable structure is then two bipyramids with a shared tetragonal face. There are, however, very few assignments available for U-Cl modes, and an investigation of the far-infrared spectra of complexes derived from uranium tetrachloride is therefore being undertaken in order to obtain such information. The infrared spectra of the iodide and chloriodide complexes in the region $2\text{--}15\ \mu$ were very similar to those previously observed²⁻⁵ for other DMA complexes. A slightly greater shift in carbonyl stretching frequency was observed; the C=O stretching vibration occurred at 1600 , 1587 , 1593 , and 1593 cm.^{-1} in the thorium tetraiodide, uranium tetraiodide, uranium dichloro-iodide, and uranium chlorotri-iodide complexes, respectively.

The magnetic properties of the uranium tetraiodide and the mixed halide complexes were examined (Table 3) between 89 and 312°K . The temperature dependence of the magnetic susceptibility of each of the complexes resembled that of the uranium tetrachloride complex,⁵ which suggests that the environment of the uranium atom is similar in the three cases as indicated above.

TABLE 3

Magnetic susceptibilities (χ_m , 10^6 c.g.s. units)					
$\text{UI}_2\text{Cl}_2, 5\text{DMA}$		$\text{UI}_3\text{Cl}, 5\text{DMA}$		$\text{UI}_4, 4\text{DMA}$	
T ($^\circ\text{K}$)	χ_m	T ($^\circ\text{K}$)	χ_m	T ($^\circ\text{K}$)	χ_m
312	3480	305	3171	304	2820
273	3650	273	3330	266	3030
235	3840	229	3540	229	3218
198	4100	191	3790	191	3464
162	4330	152	3840	156	3660
125	4330	125	3720	119	3790
112	4420	108	3741	105	3790
94	4400	95	3764	89	3790

EXPERIMENTAL

Owing to the hygroscopic nature of the compounds all work was carried out in a dry-box, and, in the case of the uranium chlorotri-iodide and tetraiodide complexes, in an atmosphere of argon because of their ready oxidation in air. Conductivity⁵ and magnetic¹ measurements

were made as described previously. X-Ray powder diffraction photographs were taken with a 19-cm. Debye-Scherrer camera using filtered Cu K_{α} radiation; the complexes were all of low symmetry and the films were not indexed. Thermogravimetric analyses were carried out using a conventional quartz-fibre balance described elsewhere;⁵ the apparatus was slightly modified to permit samples to be mounted in a dry atmosphere. Infrared spectra were measured between 2 and 15 μ using a Hilger H 800 spectrometer and between 33 and 50 μ using a Grubb-Parsons DM4 spectrometer. Samples were mounted as mulls in Nujol, between silver chloride plates in the former instance and between Polythene plates in the latter. All solvents were purified and dried as described previously.¹¹

Uranium Dichlorodi-iodide Complex.—The chloride complex, $UCl_4 \cdot 2.5DMA$ (2.09 g.) was dissolved in cold DMA (8 ml.) and the solution added to anhydrous sodium iodide (4.9 g.) in DMA (10 ml.). The dissolution of sodium iodide in DMA is highly exothermic, which suggests that some complex formation may occur; any undissolved solid becomes pale yellow. The filtrate from the precipitated sodium chloride and undissolved sodium iodide was added to dry ethyl acetate (60 ml.), and the resulting bright green solid *complex* washed with dry ethyl acetate (3×35 ml.) and vacuum-dried at room temperature (yield 46%) (Found: U, 23.7; Cl, 7.2; I, 25.35; N, 7.0. $UI_2Cl_2 \cdot 5DMA$ requires U, 23.85; Cl, 7.1; I, 25.45; N, 7.0%).

Uranium Chlorotri-iodide Complex.—The chloride complex $UCl_4 \cdot 2.5DMA$ (3.0 g.) was dissolved in methyl cyanide (15 ml.) containing DMA (1.4 ml.), and a saturated solution of anhydrous sodium iodide in methyl cyanide (68 ml.) added to the mixture. The solution was stirred for 20 min., after which the precipitated sodium chloride was filtered off and the supernatant evaporated to dryness in a vacuum. The resulting solid was dissolved in nitromethane (20 ml.), the precipitated sodium chloride filtered off, and the filtrate added to ethyl acetate (20 ml.). The precipitated green complex was dissolved in methyl cyanide and reprecipitated with ethyl acetate (2 complete cycles). The *product* was washed with ethyl acetate (2×25 ml.) and vacuum-dried at room temperature (yield 31%) (Found: U, 21.7; Cl, 3.2; I, 35.0; N, 6.4. $UI_3Cl \cdot 5DMA$ requires U, 21.85%; Cl, 3.25; I, 34.95; N, 6.45%).

Uranium Tetraiodide Complex.—Uranium tetraiodide (1.4 g.), prepared as described elsewhere,¹ was stirred with methyl cyanide (40 ml.) containing DMA (1.5 ml.) for 20 min. and filtered. The filtrate was vacuum-evaporated to 10 ml. and the yellow-green solid *complex* precipitated by the addition of ethyl acetate (30 ml.). The complex was further purified in the same manner as the chlorotri-iodide complex and vacuum-dried at room temperature (yield 40%) (Found: U, 21.55; I, 45.9; N, 5.25. $UI_4 \cdot DMA$ requires U, 21.75; I, 46.4; N, 5.1).

Thorium Tetraiodide Complex.—Thorium tetraiodide (4 g.) was dissolved in hot DMA (20 ml.), and the crystalline *product* obtained on addition of acetone (20 ml.) was washed with hot ethyl acetate (2×10 ml.) and cold ethyl acetate (10 ml.), and vacuum-dried at room temperature. Attempted preparations using the method for the uranium tetraiodide complex yielded products contaminated with excess of DMA (Found: Th, 18.35; I, 40.1; N, 6.31. $ThI_4 \cdot 6DMA$ requires Th, 18.4; I, 40.25; N, 6.65%).

Analysis.—The compounds were dissolved in water and the thorium or uranium precipitated with aqueous ammonia. Thorium was determined by ignition of the precipitated hydroxide to ThO_2 at 800°, and for uranium, after redissolution of the hydroxide precipitate in dilute hydrochloric acid, the solution was passed down a lead column and titrated to uranium(VI) with dichromate.¹² Iodide in the ammoniacal filtrates was determined by titration against iodate,¹³ and total halogen was weighed as the silver salts; chloride was calculated from the difference between these last two determinations. Nitrogen was determined by the Kjeldahl method as already described.⁵

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¹¹ K. W. Bagnall, D. Brown, and P. J. Jones, *J.*, 1964, 2396.

¹² Cf., e.g., C. J. Rodden and J. C. Warf, "The Analytical Chemistry of the Manhattan Project," Nat. Nuclear Energy Series, ed. C. J. Rodden, McGraw-Hill, New York, 1950, vol. VIII—1, p. 68.

¹³ A. I. Vogel, "Textbook of Quantitative Inorganic Analysis," 2nd edn., Longmans, London, 1951, p. 361.