

484. *The Magnetic and Spectral Properties of Some Uranium(IV) Complexes.*

By K. W. BAGNALL, D. BROWN, and R. COLTON.

A uranium tetrathiocyanate-*NN*-dimethylacetamide (DMA) complex, $U(SCN)_4 \cdot 4DMA$, and tetrapotassium octaisothiocyanate, $K_4U(NCS)_8$, have been prepared. Their magnetic properties and absorption spectra, and those of the analogous chloride, nitrate, and perchlorate amide complexes, have been investigated. The attempted preparation of a uranium tetracyanide-DMA complex gave inconclusive results.

THE recent preparation of stable, probably dimeric, dimethylacetamide complexes of uranium tetrachloride¹ and tetranitrate² ($UX_4 \cdot 2 \cdot 5DMA$; $X = Cl$ or NO_3), in which some of the chloride and nitrate ions are evidently within the co-ordination sphere, and of the tetraperchlorate complex,³ $U(ClO_4)_4 \cdot 6DMA$, where the amide is the only ligand co-ordinated to the U^{4+} ion, suggested that it might be of interest to attempt the preparation of the corresponding thiocyanate and cyanide complexes, so obtain a series in which the anions were of increasing ligand-field ($Cl^- \sim NO_3^- < SCN^- < CN^-$), and then investigate their magnetic properties and absorption spectra. The grey-green, non-hygroscopic thiocyanate complex, $U(SCN)_4 \cdot 4DMA$, was obtained by boiling the chloride analogue ($UCl_4 \cdot 2 \cdot 5DMA$) with an excess of potassium thiocyanate in a mixture of acetone, nitromethane, and dimethylacetamide. At room temperature, and with less than 50% excess of potassium thiocyanate, the final product always contained chloride ion which could not be removed by repeated recrystallisation, the composition being close to $U(SCN)_{3.5}Cl_{0.5} \cdot 4DMA$, suggesting that there might be a chlorine bridge in the tetrachloride-DMA complex. The tetrathiocyanate complex melts, without decomposition, at 158°; it is very soluble in chloroform, ethanol, methanol, methyl cyanide, and nitromethane, less soluble in acetone (~32 g./l.), and only slightly soluble in benzene, hot diethyl carbonate, hot methyl acetate, methyl isobutyl ketone, and toluene. It is insoluble in carbon tetrachloride or diethyl ether, and can be recovered from its solutions in organic solvents by precipitation with isopentane, acetone being added where necessary to achieve miscibility with the hydrocarbon. The infrared spectrum shows organic ligand frequencies almost identical with those for the uranium tetrachloride complex,¹ with the C=O stretching frequency at 1606 cm^{-1} ($\Delta\nu_{CO}$ 41 cm^{-1}) and the $C \equiv N$ stretching frequency occurring as a very sharp single peak at 2047 cm^{-1} . The low conductivity of the compound in nitromethane (Λ_{500} and Λ_{1000} being 16.9 and 22.6 mhos cm^2 , respectively, at 16°) indicates that it is almost a non-electrolyte; the attempted ebullioscopic determination of the molecular weight in acetone gave very low results (~270) but much oxidation to uranium(VI) occurred in these experiments.

The attempted preparation of uranium tetrathiocyanate by reaction of uranium tetrachloride with potassium thiocyanate yielded only the grey-green tetrapotassium octaisothiocyanate, $K_4U(NCS)_8$, the isothiocyanate bonding being shown by the appearance⁴ of the very weak C-S stretching frequency at 815 cm^{-1} and the bending mode at 474 cm^{-1} . This compound is an analogue of the recently reported⁵ rubidium, caesium, and dipyrilidium salts, obtained from aqueous solution, which are probably also isothiocyanates, but, unlike them, it is readily oxidised to uranium(VI) in dry air at room temperature (~50% oxidation in one day). The potassium salt is soluble in acetone, chloroform, ethyl acetate,

¹ Bagnall, Deane, Markin, Robinson, and Stewart, *J.*, 1961, 1611.

² Bagnall, Robinson, and Stewart, *J.*, 1961, 4060.

³ Bagnall, Brown, and Deane, *J.*, 1962, 1655.

⁴ Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

⁵ Markov and Trageim, *Zhur. neorg. Khim.*, 1961, **6**, 2316.

and nitromethane, slightly soluble in methyl cyanide, and insoluble in benzene, carbon tetrachloride, and diethyl ether.

The preparation of a uranium(IV) cyanide-DMA complex was attempted by reaction of the chloride or thiocyanate compounds with mercuric cyanide or iodine monocyanoide in methyl cyanide solution but the products were unstable, blackening in a few hours in dry air.

The magnetic behaviour of the amide and some other uranium(IV) complexes was observed in the range 86–300°K (Table I). Cæsium and tetramethylammonium hexa-

TABLE I.

Magnetic susceptibility (c.g.s. units) of uranium(IV) complexes (temperature in °K).

UCl ₄ ·2·5DMA		UCl ₄ ·4NMA		U(NO ₃) ₄ ·2·5DMA		Cs ₂ U(NO ₃) ₆	
Temp.	10 ⁶ χ _m	Temp.	10 ⁶ χ _m	Temp.	10 ⁶ χ _m	Temp.	10 ⁶ χ _m
304	2649	—	—	—	—	303	2392
—	—	—	—	292	3312	292	2440
267	2733	264	3575	271	3511	274	2526
—	—	—	—	253	3602	261	2595
235	2825	236	3642	233	3804	244	2693
—	—	—	—	—	—	229	2806
199	2937	204	3658	219	3940	212	2894
—	—	—	—	198	4240	191	3048
—	—	177	3665	184	4414	175	3232
161	3001	—	—	164	4820	156	3488
—	—	154	3658	151	5182	141	3704
122	3081	124	3625	131	5686	123	3920
112	3097	—	—	120	6138	107	4283
98	3105	101	3575	104	6719	—	—
88	3113	—	—	—	—	—	—
87	3080	87	3291	—	—	—	—
(Et ₄ N) ₂ U(NO ₃) ₆		U(ClO ₄) ₄ ·6DMA·3H ₂ O		U(SCN) ₄ ·4DMA		K ₄ U(NCS) ₈	
Temp.	10 ⁶ χ _m	Temp.	10 ⁶ χ _m	Temp.	10 ⁶ χ _m	Temp.	10 ⁶ χ _m
302	2421	—	—	302	3596	—	—
286	2505	295	3853	282	3703	296	3102
269	2630	—	—	266	3909	260	3513
260	2655	256	4457	249	4024	—	—
242	2733	233	4658	—	—	240	3972
226	2849	—	—	229	4229	—	—
211	2955	206	4960	207	4399	214	4019
192	3149	—	—	192	4702	186	4290
178	3279	—	—	177	4950	—	—
163	3461	—	—	157	5381	157	4774
150	3650	152	5934	145	5613	—	—
133	3891	125	6337	123	6112	131	5383
115	4268	108	7008	110	6460	—	—
—	—	—	—	—	—	104	5987
95	4594	92	7478	93	6935	94	6324
—	—	—	—	—	—	—	—

chlorouranate(IV) are temperature-independent paramagnetic, with molar susceptibilities of 1944 and 1994 × 10⁻⁶ c.g.s. units, respectively, in reasonable agreement with the recorded temperature-independent values of 2063⁶ and 2243 (or 7 1931) × 10⁻⁶ c.g.s. units, respectively. The uranium tetrachloride-DMA complex shows Curie-Weiss dependence at 304–125°K, but with a very large value of the Weiss constant (θ = -800°); the molar susceptibility is then virtually temperature-independent (χ_m ~ 3100 × 10⁻⁶ c.g.s. units) down to 90°K, where it appears to begin to decrease, indicating antiferromagnetism. Since this behaviour might be due in part to metal-metal interaction in the dimer, particularly in view of the suspected chlorine bridging mentioned earlier, the probably monomeric N-methylacetamide (NMA) complex, UCl₄·NMA, was also examined, but this shows much

⁶ Candela, Hutchison, and Lewis, *J. Chem. Phys.*, 1959, **30**, 246.

⁷ Hutchison and Candela, *J. Chem. Phys.*, 1957, **27**, 707.

the same behaviour, being temperature-independent at 265–105°K (the latter being the Néel point), with a much larger molar susceptibility (3660×10^{-6} c.g.s. units). The magnetic properties of the uranium(IV) nitrate analogues are markedly different; all three compounds show Curie–Weiss dependence above 185°K, but with rather large Weiss constants [$\theta = -226, -192, \text{ and } -165^\circ$, for the caesium and tetramethylammonium hexanitratouranates(IV) and the uranium tetranitrate–DMA complex, respectively] so that the magnetic moments of 3.16, 3.07, and 3.47 B.M. probably have little significance. Below 185°K the susceptibilities increase much more rapidly with decreasing temperature, still showing Curie–Weiss dependence and still field-independent, the magnetic transition being at 185°K in each case. The tetrathiocyanate–DMA complex, potassium octaithiocyanatouranate(IV), and the tetraperchlorate–DMA complex all show Curie–Weiss dependence in the range 90–300°K but again with rather large Weiss constants ($\theta = -126, -119, \text{ and } -126^\circ$, respectively), so that the effective magnetic moments (3.48, 3.26, and 3.63 B.M.) again have little significance. These results are of little assistance in making an orbital assignment of the two unpaired electrons in the U^{4+} ion, for they lie between the $6d^2$ spin-only value of 1.63–2.83 B.M. (ground state 3F_2) and the $5f^2$ values of 3.81 B.M. (jj -coupling) or 3.58 B.M. (Russell–Saunders coupling), being nearest to this last.

The absorption spectra of the complexes in nitromethane solution (Table 2) also do

TABLE 2.
Absorption spectra of uranium (IV)–amide complexes.

$UCl_4 \cdot 2.5DMA$		$U(NO_3)_4 \cdot 2.5DMA$		$U(ClO_4)_4 \cdot 6DMA$		$U(SCN)_4 \cdot 4DMA$	
λ (m μ)	ϵ	λ (m μ)	ϵ	λ (m μ)	ϵ	λ (m μ)	ϵ
994	8.1	Broad band of low intensity at					
930	24.8	800–940 m μ					
775	6.2	—	—	—	—	—	—
675	34.0	680	47.9	—	—	685	125
650	22.2	—	—	656	50.1	655	57
630	15.5	—	—	630	42.8	—	—
590	13.9	—	—	—	—	—	—
555	8.3	545	13.6	543	13.0	565	23.3
500	17.1	—	—	497	16.8	500	46.3
465	29.2	480	35.1	478	22.9	—	—
450	19.6	425	23.4	430	22.7	450	28.2
400	9.9	—	—	—	—	—	—

not show any marked changes other than those which might be expected from ligand-field effects, and are much the same as those observed in aqueous solutions. However, a series of analogous thorium(IV)–DMA complexes has been prepared,⁸ the hygroscopic chloride having the composition $ThCl_4 \cdot 4DMA$, whereas the nitrate, perchlorate, and thiocyanate complexes are identical in composition and behaviour with their uranium counterparts. Since the $6d$ - and $5f$ -orbitals are even closer in energy at thorium than is the case with uranium,⁹ but with the $5f$ -orbitals slightly higher in energy than the $6d$, it seems probable that the thorium tetrachloride complex may involve dsp -hybridisation whereas, in the thorium complexes of anions of higher ligand-field, the hybridisation may involve d -, s -, and f -orbitals, analogous to the probable situation with all the uranium(IV) complexes. Thus, although the results do not permit an unambiguous assignment, it seems very probable that the U^{4+} ion has the $5f^2$ -configuration in all cases.

EXPERIMENTAL

Infrared spectra were taken as mulls in Fluorube and Nujol using a Hilger H800 spectrometer with sodium chloride and caesium bromide prisms. Absorption spectra were taken with an Optika CF 4 DR double-beam recording spectrophotometer and a Unicam S.P. 500 spectrophotometer using 1-cm. cells. X-Ray powder photographs were taken with a 19-cm. Unicam

⁸ Bagnall, Brown, Jones, and Robinson, following Paper.

⁹ *E.g.*, Seaborg and Katz, "Chemistry of the Actinide Elements," Methuen, London, 1957, p. 465.

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Debye-Scherrer camera and a Guinier focusing camera, using filtered Cu- K_{α} radiation. Magnetic susceptibilities were measured by the Gouy method, using a balance constructed by one of us,¹⁰ observations being made at 5900, 4400, and 2550 gauss. Because of the sensitivity of the potassium octaisothiocyanatouranate(IV) towards moist air, the Gouy tube was filled in a dry-box and stoppered.

Preparations.—(a) *Uranium tetrathiocyanate-amide complex.* The tetrachloride-DMA complex (1.74 g.) was dissolved in nitromethane (5 ml.); dimethylacetamide (3 ml.), acetone (5 ml.), and ~20% excess of potassium thiocyanate (1.34 g. in 20 ml. of acetone) were added, and the mixture was heated on a water-bath for 5 min., centrifuged to remove the precipitated potassium chloride, and the supernatant liquid, after cooling, added to an equal volume of chloroform in which the uranium(IV) thiocyanate complex, but not the potassium thiocyanate, is soluble. Since AnalaR chloroform appeared to oxidise the uranium to the hexavalent state, the solvent was left over ferrous ammonium sulphate for 48 hr. before use and no further trouble was encountered. The supernatant liquid, after removal of the precipitated potassium salt, was added to an equal volume of isopentane, and the oily *product* separated by centrifugation, washed with isopentane (2×10 ml.), and recrystallised from a small volume (~5 ml.) of hot acetone, the solvent being recycled to minimise losses due to the relatively high solubility of the complex in acetone at room temperature (~32 g./l.). The yield is low (0.81 g., 34%) but a further crop of crystals can be obtained from the recrystallisation liquor on standing and added to subsequent preparations at the recrystallisation stage, so increasing subsequent yields [Found: U, 28.8; SCN, 28.7; organic N, 6.9. $U(SCN)_4 \cdot 4DMA$ requires U, 29.1; SCN, 28.4; organic N, 6.8%].

(b) *Tetrapotassium octaisothiocyanate.* Uranium tetrachloride (0.4 g.) was dissolved in acetone (15 ml.); ~15% excess of potassium thiocyanate (1.32 g. in 20 ml. of acetone) was added, and the precipitated potassium chloride removed by centrifugation. The supernatant liquid was added to an equal volume of chloroform to remove excess potassium thiocyanate, and the resulting supernatant liquid added to an equal volume of isopentane. The oily precipitate so obtained was dissolved in ethyl acetate (10 ml.); a small quantity of potassium thiocyanate again separated and was removed by centrifugation, after which the crude product was reprecipitated by addition to isopentane (20 ml.) and the ethyl acetate-isopentane precipitation repeated until no further white solid separated (usually three cycles). The final oily *product* was ground with isopentane (3×10 ml.), vacuum dried, again ground with isopentane (2×10 ml.), and vacuum dried (340 mg., 30%) [Found: K, 17.95; U, 28.3; SCN, 50.4. $K_4U(NCS)_8$ requires K, 18.2; U, 27.7; SCN, 54.1%]. The low thiocyanate and rather high uranium analyses are probably due to the rapid oxidation to uranium(VI).

Analysis.—Thiocyanate was determined volumetrically^{11a} against mercuric nitrate, after removal of uranium(IV) as hydroxide, since it interfered seriously with the determination. Chloride ion was detected by precipitation of bismuth oxychloride,^{11a} and subsequently weighed as silver chloride. Amide nitrogen was determined by Kjeldahl digestion^{11b} after precipitation of thiocyanate with silver sulphate. Potassium was weighed as the tetraphenylboron derivative,¹² and uranium, after re-dissolution of the hydroxide precipitate from the thiocyanate determination, was passed down a lead column and determined volumetrically by titration to uranium(VI) with dichromate.¹³

CHEMISTRY DIVISION, U.K.A.E.A. RESEARCH GROUP,
HARWELL, DIDCOT, BERKS.

[Present address (R. C.): DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MELBOURNE,
PARKVILLE N.2, VICTORIA, AUSTRALIA.] [Received, October 15th, 1963.]

¹⁰ Colton, A.E.R.E. Report R-4186, 1963.

¹¹ Vogel, "A Text-book of Quantitative Inorganic Analysis," Longmans, London, 1953, (a) p. 266; (b) p. 248.

¹² Raff and Brotz, *Z. analyt. Chem.*, 1951, **133**, 241.

¹³ 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.