The Chemistry of the Trivalent Actinides. Part II.[1] Uranium(III) Double Chlorides and Some Complexes with Oxygen-Donor Ligands

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Two series of hydrated double chlorides have been isolated and characterised. Compounds of the red series, $M^IUCl_4,5H_2O$ (M^I = K, Rb, or NH_4), have an intense absorption at 18,000 cm^{-1} in their reflectance spectra and in the spectra of their solutions in methanol and 11M hydrochloric acid. There are also bands at 230 and 196 cm^{-1} in the spectrum of $RbUCl_4,5H_2O$ which can be assigned to U–Cl stretching vibrations. These electronic and far i.r. bands are absent from the spectra of the green series, M^IUCl_4,xH_2O (M^I = Rb or NH_4), as these closely resemble the reflectance spectra of the uranium(III) sulphates and double sulphates and the spectrum of the hydrated uranium (III) ion. In water the red series gave the spectrum of the hydrated uranium(III) ion. Thus the red series is believed to contain co-ordinated chloride while the green compounds contain uranium(III) in a more ionic environment. Owing to the presence of a small amount of M^ICl, the degree of hydration of the green series is uncertain. Corresponding bromides could not be isolated. Like the lanthanide(III) metal ions, uranium(III) forms complexes; $[U(phaz)_6]Cl_3$ or $(Ph_4B)_3$, and $[U(dmaz)_4](Ph_4B)_3$, with the oxygen-donor ligands phenazone (phaz, 1-phenyl-2,3-dimethyl-5-pyrazolone) and 4-dimethylaminophenazone (dmaz), which were isolated from alcoholic solutions of the red double chlorides and the ligands. These complexes are readily oxidised by air and water, and this reactivity prevents an extensive study of the complexing ability of trivalent uranium; many other oxygen-donor ligands were investigated but oxidation of the uranium(III) occurred even under nitrogen.

THE first hydrated compounds of uranium(III) to be reported[1] were the simple sulphate and various double sulphates. They were prepared by electrolytic reduction of acidified uranyl(VI) sulphate solutions at a mercury cathode, and were moderately stable in dry air. From solutions of these compounds and by electrolytic reduction in hydrochloric acid, two series of double chlorides, the red compounds, $M^IUCl_4,5H_2O$ ($M^I = K$, Rb, or NH_4), and the green ones, M^IUCl_4,xH_2O ($M^L =$ Rb or NH_3), have now been isolated. The isolation

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[1] Part I, R. Barnard, J. I. Bullock, and L. F. Larkworthy, *J.C.S. Dalton*, 1972, 964.

depends upon the rigorous exclusion of oxygen, rapid manipulation of cooled solutions, and the use of pure reagents. The dry compounds are more susceptible to oxidation by air than the sulphates. A simple chloride, UCl_3,xH_2O, or bromides could not be prepared using similar methods. There is a preliminary account of part of this work.[2]

The red compounds resemble $CsAmCl_4,2H_2O$ which[3] was prepared from concentrated hydrochloric acid. No hydrated chlorides with this stoicheiometry are known for neptunium(III), plutonium(III), and the trivalent lanthanides. Changing the relative quantities of the starting materials did not affect the stoicheiometry of the product, *e.g.*, to give M_3UCl_6,xH_2O.

The red compounds, unlike the uranium(III) sulphates,[1] are soluble in methanol, ethanol, or dimethylformamide, and have proved suitable starting materials for the investigation of complex formation by uranium(III). The recently reported[4] uranium(III) formate is insoluble in organic solvents and is decomposed by water, and consequently is unsuitable. Although trivalent lanthanides form many complexes with oxygen-donor ligands such as β-diketones, carboxylic acids,[5] and phenazone[5,6] [antipyrine or 1-phenyl-2,3-dimethyl-5-pyrazolone (I), phaz], little is known of the corresponding actinide (III) complexes. In this paper the preparation of some uranium(III) complexes with phenazone and related ligands is reported, but with most ligands investigated oxidation occurred even under nitrogen. These appear to be the first complexes of uranium(III) with organic ligands to be obtained.

TABLE 1

Analytical and magnetic results

Compound [a]	Uranium Found	Uranium Calc.[b]	Chloride Found	Chloride Calc.[b]	Exp. Cl : U	μ_{eff} [c] 300 K	μ_{eff} [c] 90 K	θ 0°	Diamagnetic correction (c.g.s.u. × 10^6)
Red series:									
$NH_4UCl_4,5H_2O$	48·0	48·8	28·95	29·05	4·06	3·36	2·86	68	218
$KUCl_4,5H_2O$	47·3	46·8	27·85	27·85	3·97	3·35	2·79	70	220
$RbUCl_4,5H_2O$	43·6	42·9	25·6	25·5	3·94	3·32	2·76	80	227
Green series:									
NH_4UCl_4,xH_2O	49·3	48·8	30·1	29·05	4·09	3·32	2·80	80	231
$RbUCl_4,xH_2O$	44·6	42·9	27·2	25·5	4·09	3·37	2·85	65	241

[a] The green chlorides contain some MCl (M = NH or Rb) so that the degree of hydration is uncertain (see Experimental section).
[b] Calculated for penta-hydrates. [c] $\mu_{eff} = 2{\cdot}828\ \sqrt{\chi_A T}$.

RESULTS AND DISCUSSION

Double Chlorides.—The double chlorides (Table 1) were very hygroscopic and rapidly oxidised in air to pale green uranium(IV) compounds. The red chlorides dissolved in water to give red-green solutions which were stable at 0° for 5—6 h under nitrogen. In air the solutions rapidly oxidised to pale green uranium(IV) solutions which soon hydrolysed and became green and cloudy. The red ammonium chloride dissolved readily in reagent grade methanol and 96% ethanol to give red solutions which were stable at 0° for some hours. The red potassium and rubidium chlorides were less soluble. The compounds were poorly soluble in dry methanol and ethanol. The red ammonium compound was soluble in dimethylformamide and dimethylacetamide but dissolution accompanied by oxidation to uranium(IV) was observed for dimethyl sulphoxide, nitromethane, pyridine, ethylenediamine, and tetrahydrofuran containing 5% water. It was insoluble in tetrahydrofuran, methyl cyanide, diethyl ether, dioxan, carbon tetrachloride, acetone, benzene, 2-methylbutane, dichloromethane, chloroform, and ethyl acetate. The solubility tests were carried out with deoxygenated solvents and under nitrogen. The green double chlorides are more reactive towards oxygen and water than the red ones.

Attempts to obtain the anhydrous double chlorides by thermal decomposition of the red chlorides were unsuccessful. A sample of $RbUCl_4,5H_2O$ showed negligible weight loss on heating to 160° for five hours at low pressure. At higher temperature oxidation took place.

The bromide and iodide solutions of uranium(III) prepared by electrolytic reduction decomposed more readily than those of the chloride and it was not possible to isolate solids.

Electronic Spectra.—None of the spectra (Table 2) contains a band near 6500 cm^{-1} which is typical[1] of uranium(IV) impurity.

The diffuse reflectance spectra of $U_2(SO_4)_3,8H_2O$,[1] the uranium(III) double sulphates,[1] anhydrous uranium(III) chloride,[7] and the green double chlorides (Table 2) and the solution spectra of uranium(III) in M perchloric,[8] M deuteriated perchloric,[9] and M sulphuric acids,[1] and of uranium(III) in M hydrochloric, hydrobromic, and hydriodic acids and water (Table 2) are almost identical.

The addition of concentrated hydrochloric acid to a

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[2] R. Barnard, J. I. Bullock, and L. F. Larkworthy, *Chem. Comm.*, 1968, 960.

[3] K. W. Bagnall, J. B. Laidler, and M. A. A. Stewart, *J. Chem. Soc.* (*A*), 1968, 133.

[4] B. Jezowska-Trzebiatowska and J. Drozdzynski, *J. Inorg. Nuclear Chem.*, 1969, **31**, 727.

[5] T. Moeller, D. F. Martin, L. C. Thompson, R. Ferrus, G. R. Feistel, and W. J. Randall, *Chem. Rev.*, 1965, **65**, 1.

[6] L. J. Sauro and T. Moeller, *J. Inorg. Nuclear Chem.*, 1968, **30**, 953.

[7] B. J. Gellatly, unpublished results.

[8] D. C. Stewart, U.S. Report ANL-4815, 1952.

[9] D. Cohen and W. T. Carnall, *J. Phys. Chem.*, 1960, **64**, 1933.

solution of uranium(III) produces[10] a new, strong, absorption at 18,000 cm^{-1}. This result was confirmed in the present work and the absorption was also present in the diffuse reflectance spectra of the red double chlorides and their solutions in methanol but not in water (Table 2). Apart from this single absorption all the spectra here quoted are very similar. The 18,000 cm^{-1} band was absent for dilute hydrobromic acid solutions but appeared at 18,300 cm^{-1} if the acid concentration was raised above 11M (see Experimental section). Aqueous solutions of the red chlorides exhibited the spectrum of the hydrated ion.

Jorgensen[10] attributes the change in the absorption spectrum to complex chloride formation but this does not imply, as is erroneously stated by Silcox and Haendler,[11] that anionic complexes such as UCl_4^- are formed. The intense band at 18,380 cm^{-1} in concentrated lithium chloride is attributed[12] to $5f^3$–$5f^26d^1$ transitions which arise from the UCl^{2+} ion. It is not possible to identify the complex ion for the red double chlorides but it would appear that the interaction of uranium(III) with the anion is more specific than in the ionic uranium(III) chloride and the green double chlorides. The oxygen environment for uranium(III) in the sulphates and the aqueous solutions gives rise to spectra similar to that of uranium(III) chloride so that it might be supposed that ligand fields have little effect on the absorption spectra in these cases. On the other hand, there is no reason to assume that the co-ordination number of uranium in the red chlorides is less than in the anhydrous chloride and the hydrated uranium(III) ion.

Infrared Spectra.—The uranium(III) sulphates and double sulphates[1] had very similar far-i.r. spectra with broad envelopes centred at 190—200 cm^{-1} which extended from 120 to 230 cm^{-1}. None of the bands was well resolved.

Red $RbUCl_4,5H_2O$ however, had well resolved bands at 230s, 204sh, 196s, 166m, 130s, 122s, and 102m cm^{-1} with a single strong Raman line at 232 cm^{-1}. In comparison green $RbUCl_4,xH_2O$ had a broad i.r. band centred at 190 cm^{-1} with no well resolved bands and the strong Raman line was absent.

The americium(III) chloro-complexes, $CsAmCl_4,4H_2O$, $CsAmCl_4$, $Cs_2NaAmCl_6$, and Cs_3AmCl_6 absorb[3] in the i.r. at 235 and 197, 218, 242, and 214 cm^{-1}, respectively. These frequencies were assigned to americium(III)–chloride stretching vibrations and by analogy the absorptions at 230 and 196 cm^{-1} in the spectrum of $RbUCl_4,5H_2O$ are uranium(III)–chloride vibrations. The green double chloride is clearly similar to the uranium(III) compounds which do not contain the 18,000 cm^{-1} absorption in the visible spectrum.

Magnetic Susceptibility Measurements.—The variation of the atomic susceptibilities in the temperature range 300—87 K, the effective magnetic moments, and the θ

TABLE 2

Diffuse reflectance and solution spectra (cm^{-1})

(*a*)	(*b*)	(*c*)	(*d*)	(*e*)	(*f*)	ε	(*g*)	ε	(*h*)	(*i*)	(*j*)
27,700vsb	28,000vsb	27,900vsb	28,500vsb	28,600vsb			42,680	1155			
(24,450)vs	24,350vsb	24,350vsb	25,700vsb	25,500vsb			36,600	1160			
21,700vsb	21,650vsb	(21,800)	24,500vsb	24,500vsb			31,600	1015			
(19,550)s	(19,220)	21,630vsb	23,650vsb	23,600vsb			27,950	1096			
17,850vsb	18,000vsb	(19,200)	(22,900)	(22,180)			(24,900)	521			24,200
16,350vs	(17,150)	18,000vsb	(21,550)	(21,500)	22,150	76·4	22,000	385	22,100	22,050	22,050
(15,600)s	(16,230)	(16,280)	(19,930)	(19,950)	(20,150)	39·1			(20,100)	(20,100)	(20,050)
14,800m	(15,530)	14,790w	(19,200)	(19,400)	(19,720)	99·5			(19,600)	(19,600)	(19,600)
(14,750)m	14,750w	(14,700)	18,950s	18,980s	19,150	153	19,200	602	19,050	19,050	19,050
(13,500)m	(14,650)	(13,450)	(18,520)	(18,580)	(18,400)	49·7	18,300	900	(18,450)	(18,400)	(18,500)
13,400m	13,410m	13,350m	(18,030)	(18,050)			18,000	911	(18,250)	(18,200)	(18,250)
(13,200)m	13,320m	(13,150)	(16,920)	(17,800)w	(17,100)	57·6	(17,300)	580	17,000	17,050	17,050
11,400s	(13,180)	11,350s	16,430s	(17,100)w	(16,480)	83·1	(16,500)	323	(16,450)	(16,400)	(16,400)
(11,250)s	11,350s	10,020m	(15,880)	(16,900)	16,200	94·5			16,100	16,050	16,150
(11,150)s	10,000m	(9520)	(15,480)	16,400s	15,700	51·5			15,600	15,600	15,600
(11,000)s	(9450)	9300m	14,670w	(15,900)	14,900	9·8	15,000	40·1	(14,800)	(14,800)	(14,800)
10,050s	9280m	(8200)	13,300m	(15,200)w	13,720	40·0	13,500	40·3	13,600	13,600	13,600
(9500)s	9170m	8050s	11,250s	14,700w			(11,800)	125			
9350s	(8400)	7020w	9950m	13,280m	11,400	186	(11,400)	192	11,300	11,400	11,350
(9000)m	(8200)	(4750)	9350m	11,300s	11,140	164	11,110	242		10,800	
(8450)s	8050	4480s	8200s	9950m	10,220	51·3	10,180	118	10,150	10,200	10,150
(8250)s	(7880)		8000s	9320m	(9950)	33·8			(9800)	(9800)	(9800)
8100s	7020w		7000w	8200s	(9580)	38·8	(9550)	53·7	(9450)	(9500)	(9400)
(7900)s	(4730)		(4900)	8000s	9320	44·1	9320	55·6	9250	9200	9200
7100w	4600s		4530s	7000w			(9110)	48·3			
4750s				(4900)			(8290)	104			
4450s				4530s	8180	172	(8110)	152	8050	8050	8050
4250s					7200	7·1	7080	11·5	7200	7200	7200
					4750	42·3	(4650)	53·7		(4750)	(4750)
					4470	65·7	4400	82·1	4500	4500	4500

(*a*) Red $NH_4UCl_4,5H_2O$. (*b*) Red $KUCl_4,5H_2O$. (*c*) Red $RbUCl_4,5H_2O$. (*d*) Green NH_4UCl_4,xH_2O. (*e*) Green $RbUCl_4,xH_2O$. (*f*) (*a*) In water. (*g*) (*a*) In methanol. (*h*) U^{III} In 1M-HCl solution. (*i*) U^{III} In 1M-HBr solution. (*j*) U^{III} In 1M-HI solution. Parentheses indicate a shoulder.

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[10] C. K. Jorgensen, *Acta Chem. Scand.*, 1956, **10**, 1503.

[11] N. W. Silcox and H. M. Haendler, *J. Phys. Chem.*, 1960, **64**, 303.

[12] M. Shiloh and Y. Marcus, *Israel J. Chem.*, 1965, **3**, 123.

values for the uranium(III) chlorides are given in Tables 1 and 3. The values obtained are close to those previously reported [1,4,13,14] for uranium(III) compounds. The magnetic moments are higher [1] than those usually observed for uranium(IV). In all cases the plots of the reciprocal susceptibilities against temperature curve below the Curie–Weiss line at temperatures lower than *ca.* 120 K. This is usually observed [1,13] for uranium(III) and often [15,16] for uranium(IV) and it may be the case for all magnetically dilute uranium-(III) and -(IV) compounds.

TABLE 3

Variation with absolute temperature of atomic susceptibilities (c.g.s.) and magnetic moments (B.M.) of the compounds

$NH_4UCl_4,5H_2O$ (red)									
Temp. (K)	292·3	262·5	226·0	190·2	153·6	118·4	86·0		
$10^6\chi_A$	4801	5250	5902	6739	7821	9351	11,830		
μ_{eff}	3·36	3·33	3·28	3·22	3·11	2·99	2·86		
$KUCl_4,5H_2O$ (red)									
Temp. (K)	292·0	264·7	228·7	192·7	156·0	118·2	107·3	97·5	87·4
$10^6\chi_A$	4743	5110	5742	6540	7592	9126	9681	10,310	11,020
μ_{eff}	3·35	3·30	3·26	3·19	3·09	2·95	2·89	2·85	2·79
$RbUCl_4,5H_2O$ (red)									
Temp. (K)	290·0	264·0	228·0	192·5	156·2	118·4	108·0	97·5	87·5
$10^6\chi_A$	4772	5105	5707	6450	7434	8873	9453	10,040	10,780
μ_{eff}	3·32	3·30	3·24	3·16	3·06	2·91	2·87	2·81	2·76
NH_4UCl_4,xH_2O (green)									
Temp. (K)	290·5	265·0	228·7	193·2	157·1	118·5	87·5		
$10^6\chi_A$	2692	5098	5671	6401	7461	9015	11,090		
μ_{eff}	3·32	3·30	3·23	3·16	3·08	2·94	2·80		
$RbUCl_4,xH_2O$ (green)									
Temp. (K)	292·0	265·5	229·0	193·6	158·3	118·6	108·5	98·0	87·5
$10^6\chi_A$	4812	5205	5799	6603	7581	9296	9906	10,610	11,510
μ_{eff}	3·37	3·34	3·27	3·22	3·11	2·98	2·94	2·90	2·85

Complexes of Oxygen-donor Ligands.—The earlier preparation [17] of $[U(phaz)_6]Cl_3$ from $RbUCl_4,5H_2O$ has been repeated and the corresponding tetraphenylborate isolated. Attempts to crystallise the iodide or tetrafluoroborate were unsuccessful. The compound $[U(dmaz)_4][Ph_4B]_3$, where dmaz is 4-dimethylaminophenazone, has also been isolated, and if this compound is analogous to known complexes [6] it is likely to contain bidentate ligand.

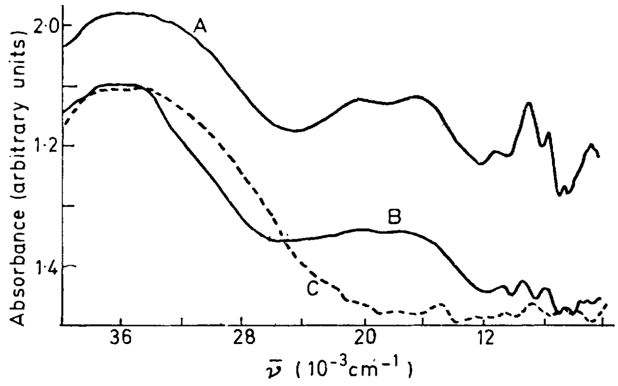

FIGURE 1 Reflectance spectra of A, $U(phaz)_6Cl_3$; B, $[U(phaz)_6][Ph_4B]_3$; C, oxidised B

Extensive physical investigations of these compounds are precluded by their slow decomposition even under nitrogen or in Pyrex tubes sealed *in vacuo*. The diffuse reflectance spectra of the compounds are shown in Figures 1 and 2. The spectra all show broad, intense absorption bands extending from *ca.* 12,000 cm^{-1} into the u.v. which are assigned to Laporte-allowed *f–d* transitions as are similar bands in other uranium(III) compounds.[1,10] On oxidation the red-brown, purple, or orange compounds became pale green and the broad absorptions at lower frequency were replaced by weaker *f–f* transitions of the uranium(IV) oxidation products.

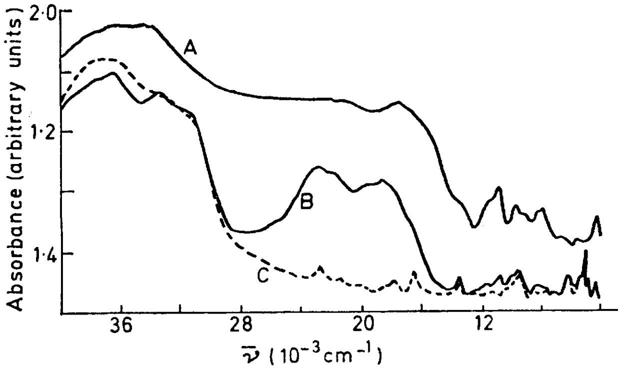

FIGURE 2 Reflectance spectra of A, $[U(dmaz)_4](Ph_4B)_3$; B, orange uranium(III)–hexamethylphosphoramide complex; C, oxidised B

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[13] C. A. Hutchison, jun., and P. Handler, *J. Chem. Phys.*, 1956, **25**, 1210.

[14] M. Berger and M. J. Sienko, *Inorg. Chem.*, 1967, **6**, 324.

[15] C. A. Hutchison and N. Elliott, *J. Chem. Phys.*, 1948, **16**, 920.

[16] K. W. Bagnall, D. Brown, and P. J. Jones, *J. Chem. Soc.* (*A*), 1966, 741.

[17] R. Barnard, Ph.D. Thesis, University of Surrey, 1969.

Each complex shows a similar pattern of weak *f–f* bands in the visible and i.r. regions which resembles the spectra of the chloro-complexes and the sulphates. However, there are differences in frequency and relative intensity which might be due to ligand field effects, but it must be borne in mind that these compounds are extremely difficult to handle, some of the bands are broad and poorly resolved, and small amounts of oxidation product could affect the spectra. Solutions of hexakis(phaz)-uranium(III) chloride decomposed before their spectra could be measured.

Several attempts were made to prepare the recently reported[18] phenazone complex $[U(phaz)_6][Cr(CNS)_6]$ from methanol or water under nitrogen but, as described in the Experimental section, without success, owing to reduction of the hexathiocyanatochromate(III) anions to chromium(II) species. The preparations of complexes $[UL_6][Cr(CNS)_6]$, L = pyridine, dimethylformamide, or 4-dimethylaminophenazone (UL_3), have also been reported,[18] but the addition under nitrogen of pyridine to solutions of ammonium uranium(III) chloride in methanol or dimethylformamide gave uranium(IV) products almost immediately. No solids could be precipitated by the addition of sodium tetraphenylborate to the solutions of the double chlorides in methanol or dimethylformamide. These results are inconsistent with those earlier reported. Previous workers[18] obtained their hexathiocyanatochromate(III) salts by a slightly different procedure, *i.e.* from uranium(III) chloride prepared by electrolytic reduction, but it seems likely that reduction of the anion would have occurred in their experiments too.

EXPERIMENTAL

Because of the rapid oxidation of uranium(III) by air and water all operations and physical measurements were performed under nitrogen or *in vacuo* using de-oxygenated solvents in all-glass apparatus or in a nitrogen- or argon-filled box.

Electrolytic Reduction Procedures.—Aqueous solutions of uranium(III) may be conveniently prepared from uranium(VI) in hydrochloric, hydrobromic, and hydriodic acids. The electro-reductions using a platinum anode and a mercury cathode are complete in 3—4 h in 1M acid solutions with a uranium concentration of 0·15M.

The reductions were carried out in a Quickfit 700 ml reaction vessel fitted with a five socket flat flange and the necessary ancillary equipment for stirring, electrolysis, and atmosphere control. Using this equipment it is possible to prepare solutions containing only uranium(III) by electrolytic reduction at a mercury cathode contrary to a report[4] by Jezowska-Trzebiatowska and Drozdzynski. A small peak was observed at 6500 cm^{-1} in the halogenic acid solutions of uranium(III) but this slight oxidation to uranium(IV) probably occurred during the manipulations involving the recording of the spectrum.

Uranyl chloride was used as supplied; uranyl bromide and iodide were prepared by mixing stoicheiometric quantities of uranyl sulphate and the appropriate barium halide in water, filtering off the precipitated barium sulphate, and adjusting the acidity with the halogenic acid. The halogens liberated at the anode were removed in a stream of nitrogen and collected in traps cooled with solid carbon dioxide.

The Red Double Chlorides.—There are three methods available. (*a*) The appropriate double sulphate[1] [*ca.* 10 g; $(NH_4)_2SO_4,U_2(SO_4)_3,9H_2O$; $K_2SO_4,U_2(SO_4)_3,10H_2O$; $3K_2SO_4,U_2(SO_4)_3,xH_2O$; $Rb_2SO_4,U_2(SO_4)_3,8H_2O$ was dissolved in hydrochloric acid (11M, 100 ml)]. The appropriate halide, MCl (M = NH_4, K, or Rb), was added in stoicheiometric quantity to the red-purple solution. On shaking at 0° a red-purple solid was obtained (M = K), but for the ammonium and rubidium salts an olive-green solid separated which was transformed into a red-purple solid after 1 h at 0°. The red-purple solids were filtered off, washed with cold, dry acetone (110 ml), dried, and stored in sealed evacuated tubes. Analytical figures are given in Table 1. Typical yields were: $NH_4UCl_4,5H_2O$, 5 g, 71%; $KUCl_4,5H_2O$ from $K_2SO_4,U_2(SO_4)_3,10H_2O$, 3·9 g, 43%; $KUCl_4,5H_2O$ from $3K_2SO_4,U_2(SO_4)_3,xH_2O$, 1·5 g, 24%; $RbUCl_4,5H_2O$, 3·5 g, 39%.

(*b*) Potassium chloride (4 g) was dissolved in a solution (100 ml) of uranium(III) in M hydrochloric acid prepared by electrolytic reduction. The solution was cooled in a solid CO_2–ethanol bath and saturated with pure, dry hydrogen chloride and nitrogen for 45 min. The red-purple precipitate was collected, washed, dried, and stored as before.

(*c*) $U_2(SO_4)_3,8H_2O$ (6·4 g) and potassium chloride (3·2 g) were dissolved with shaking at 0° in hydrochloric acid (11M, 120 ml). The red-purple precipitate (5 g, 73%) was treated as before.

The Green Double Chlorides.—The saturation of the red-purple solution of uranium(III), prepared by adding ammonium (6 g) or rubidium (5 g) chloride to the solution (100 ml) obtained by electrolytic reduction in M hydrochloric acid, at 0° for 45 min with hydrogen chloride and nitrogen produced an olive-green solid. The solids were treated as before. Analytical figures are given in Table 1. The analyses and reflectance spectra show that the compounds contain uranium(III) but heating the ammonium salt produced a purple double chloride with some loss of NH_4Cl and water. The presence of the ammonium or rubidium chloride makes the degree of hydration uncertain.

Caesium Uranium(III) *Double Chlorides.*—Method (*c*) gave a green solid which was rapidly oxidised at 0° under nitrogen. The other preparative methods gave no solid compounds.

Investigations with Other Chlorides.—Lithium, beryllium, magnesium, calcium, strontium, barium, zinc, hydrazinium, and triphenylphosphonium chlorides did not yield uranium(III) compounds using the methods described above.

A Simple, Hydrated Uranium(III) *Chloride.*—The isolation[1] of the sulphates, $U_2(SO_4)_3,xH_2O$ (x = 8, 5, or 2), prompted these investigations. (*a*) The evaporation of a solution of uranium(III) obtained by electro-reduction in M hydrochloric acid caused oxidation to a pale green solution. The use of concentrated hydrochloric acid (11M) gave the same result although the oxidation was more rapid. The electro-reduction of uranyl chloride in hydrochloric acid (0·3M) produced some hydrolysis but eventually a red-green solution was formed which, on evaporation, gave an air-stable, green-brown crystalline solid. This did not give a red colouration in concentrated hydrochloric acid and the reflectance spectrum was that of uranium(IV).

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[18] A. S. Vyatkina and V. V. Serebrennikov, *Radiokhimiya*, 1971, **13**, 1157.

(*b*) The addition of ethanol and acetone to uranium(III) solutions, prepared by electro-reduction, in hydrochloric acid (1 and 11M) gave no precipitate. Heat was evolved with the concentrated acid and the uranium was oxidised.

(*c*) A solution of uranium(III), prepared by electro-reduction, was saturated with hydrogen chloride. Freezing the solution produced only ice.

Reactions of Uranium(III) *in Hydrobromic Acid Solutions.*—These solutions are less stable to oxidation than those in hydrochloric acid. (*a*) Red ammonium uranium(III) chloride (1 g) was dissolved in hydrobromic acid (9M, 25 ml). This red solution was stable at 0° for 24 h. Addition of excess of sodium, caesium, or ammonium bromides gave no precipitation even on prolonged cooling. There was no intense absorption at 18,000 cm^{-1} in the electronic spectrum.

(*b*) Ammonium bromide (6 g) was added to an aqueous uranium(III) bromide solution obtained electrolytically. The solution was cooled in a solid CO_2–ethanol bath and a mixture of hydrogen bromide and nitrogen passed through the solution. At saturation the red-brown solution rapidly evolved hydrogen and a white solid, presumably ammonium bromide, precipitated. Within 15 min the uranium(III) was completely oxidised. No coloured precipitates were observed.

(*c*) $(NH_4)_2SO_4,U_2(SO_4)_3,9H_2O$ (4 g) Was dissolved in hydrobromic acid (11M, 60 ml) and the resulting red solution was cooled at 0° for 1 h. The green precipitate obtained was a sulphate. The spectrum of the freshly prepared solution had an intense absorption at 18,300 cm^{-1} indicating the presence of a bromide complex but rapid oxidation occurred. The iodide solutions were even more unstable.

Hexakis(*phenazone*)*uranium*(III) *Chloride.*—The purple compound, $RbUCl_4,5H_2O$ (1·03 g), was dissolved with vigorous shaking in a solution of six molecular proportions (2·10 g) of (I) in dried ethanol (40 ml). The reactants were carefully weighed out since any excess would be present after evaporation to dryness. The dark red solution was cooled in a solid carbon dioxide–ethanol bath for half an hour and filtered under nitrogen to remove the rubidium chloride which precipitated quantitatively. During the filtration solid carbon dioxide was packed around the filter to reduce decomposition. The solution was evaporated to dryness and the solid obtained dried further in a non-static vacuum. This took about 12 h altogether. The dark purple *solid* was then powdered under argon. It was necessary to take the solution to dryness because no crystals separated, and the addition of organic solvents caused oxidation. The complex was very hygroscopic and frequently formed gums on evaporation of the solvent. On exposure to air it rapidly became grey, and after some hours, pale green. Analyses were performed immediately after preparation because even when sealed in evacuated Pyrex tubes the complex decomposed in a few days (Found: C, 52·9; H, 5·2; N, 11·4. $C_{66}Cl_3N_{72}N_{12}O_6U$ requires C, 53·8; H, 4·9; N, 11·4%). These analyses are not as significant as usual because the solvent was taken to dryness, but the colour change on oxidation, the reflectance spectrum, and the isolation of the following compound indicate complex formation.

Hexakis(*phenazone*)*uranium*(III) *Tetraphenylborate.*—The chloro-complex, $NH_4UCl_4,5H_2O$ (0·6 g) was dissolved in a solution of (I) (1·4 g) in methanol (100 ml). To the dark red solution was added slowly with shaking a solution of sodium tetraphenylborate (1·3 g) in methanol (50 ml). The lilac *complex*, which separated from a red solution, was filtered off, washed with methanol, and dried for 3 h in a non-static vacuum. No solids separated on the addition of concentrated methanolic solutions of ammonium iodide or potassium tetrafluoroborate. On exposure to air, the lilac solid, and its red solution in methanol, immediately became pale green (Found: C, 70·6; H, 5·8; N, 7·2; U, 10·0. $C_{138}H_{132}B_3N_{12}O_6U$ requires C, 71·3; H, 5·7; N, 7·2; U, 10·2%).

Tetrakis(4-*dimethylaminophenazone*)*uranium*(III) *Tetraphenylborate.*—This was prepared similarly to the previous compound. In air the dark mauve *complex* immediately became yellow-green. Its red methanolic solution became pale green in air. The analysis, though not of high accuracy, indicated that a tetrakis-compound had formed (Found: C, 73·8; H, 6·1; N, 7·5. $C_{124}H_{128}B_3N_{12}O_4U$ requires C, 71·2; H, 5·9; N, 7·7%).

Further Investigations with Oxygen-donor Ligands.—Attempts to prepare uranium(III) complexes of 4-aminophenazone as the chloride or the tetraphenylborate as above gave brown solids which decomposed even under nitrogen into pale green, uranium(IV) products before they could be isolated. Since no colour change occurred when 4-bromophenazone was added to a methanolic solution of $NH_4UCl_4,5H_2O$, and the addition of sodium tetraphenylborate to the mixture gave no precipitate, it seems that this ligand does not complex with uranium(III) ions.

Addition of acetylacetone or diacetyl to solutions of the ammonium double chloride in water, methanol, or dimethylformamide caused immediate oxidation to pale green solutions.

The addition of acetamide, *N*-methylacetamide, or *NN*-dimethylacetamide, or various orthophosphate esters, to the methanolic ammonium salt did not cause oxidation, but no compounds could be precipitated with sodium tetraphenylborate or with organic solvents. Unstable red gums were obtained when the solutions were evaporated to dryness.

Oxidation to a green compound occurred when triphenylphosphine oxide was added to an ethanolic solution of the ammonium double chloride.

The ammonium double chloride dissolved in dimethyl sulphoxide to give a red solution which rapidly turned pale green.

When a solution of twenty molar proportions of hexamethylphosphoramide (HMPA) in methanol was added to a methanolic solution containing $NH_4UCl_4,5H_2O$ and sodium tetraphenylborate, an orange solution was obtained from which an orange, microcrystalline solid separated on standing. In air it became pale green. The spectral changes are shown in Figure 2. However, the analyses did not fit any formulae of the type $[U(HMPA)_n][Ph_4B]_3$.

Uranium(III) in dilute mineral acid is reported [19] to complex with cupferron (*N*-nitroso-*N*-phenylhydroxylamine), but only a pale green oxidised product was obtained. *N*-Benzoyl-*N*-phenylhydroxylamine behaved similarly.

Investigation of Hexathiocyanatochromate(III) *Salts.*—When potassium hexathiocyanatochromate(III) tetrahydrate [20] was added under nitrogen to solutions of $NH_4UCl_4,5H_2O$ and phenazone in methanol or water a lilac precipitate was obtained. The lilac product analysed poorly for

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[19] L. Rulfs and J. Elving, *J. Amer. Chem. Soc.*, 1955, **77**, 5502; F. S. Grimaldi, *U.S. Geol. Survey Bull.*, 1954, No. 1006, 19.

[20] G. Brauer, ' Handbook of Preparative Inorganic Chemistry,' Academic Press, London, 1965, p. 1374.

[U(phaz)$_6$][Cr(NCS)$_6$], and, unlike the uranium(III)–phenazone derivatives described above, its colour and reflectance spectrum hardly changed on exposure to air. Its reflectance spectrum showed that much uranium(IV) was present. The blue solution A, obtained on filtration of the lilac solid, gave a green solution B on exposure to air. Solution A is believed to contain thiocyanato-chromium(II) species. The only known thiocyanato-chromium(II) complex is the high-spin [21] compound $Na_3[Cr(CNS)_5],11H_2O$. No spectral results are available, but the two-band visible spectrum of A is as might be expected [22] for a distorted octahedral chromium(II) species in which at least four of the donor atoms are nitrogen. The weak band at 24,150 cm^{-1} is ascribed to a small amount of oxidation product since the spectrum of B has a strong band in this region. The spectrum of B (Table 4) is similar to the reflectance and solution [23] spectra of the chromium(III) compound $K_3Cr(CNS)_6,4H_2O$. The lilac product is considered to be a mixture containing little uranium(III).

TABLE 4

	ν (cm^{-1})					
Blue solution A				24,150w	17,550m	15,800sh
Green solution B				23,500vs	17,700s	
$K_3Cr(CNS)_6,4H_2O$		32,850vs [a]		23,650vs	17,800vs	
' U(phaz)$_6$][Cr(CNS)$_6$] ' [a]	37,000sh	32,050vs	29,250sh	23,500sh	17,500w	15,000sh
	37,150vs [a,b]		29,150br,sh	23,400sh 22,600sh	17,500w	15,000sh

[a] Reflectance spectra. [b] ' [U(phaz)$_6$][Cr(CNS)$_6$] ' after exposure to air.

Analyses and Physical Measurements.—Uranium was estimated as described.[1] Halogen was determined gravimetrically. Sulphate was completely absent from the chlorides prepared *via* the sulphates.

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[21] R. W. Asmussen, 'Magnetokemiske Undersogelser over Uorganiske Kompleks forbindelser,' Gjellerups Forlag, Copenhagen, 1944, p. 123.

[22] A. Earnshaw, L. F. Larkworthy, and K. C. Patel, *J. Chem. Soc.* (*A*), 1969, 1339, 2276.

[23] J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, 1956, **10**, 329.