The Chemistry of the Trivalent Actinoids. Part 5.[1] Uranium(III) Complexes with Bidentate Organic Amides

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Uranium(III) forms air-sensitive tetrakis complexes with the amides $Me_2N·CO·[CH_2]_n·CO·NMe_2$ and $Me_2N·CO·CH_2·CMe_2·CH_2·CO·NMe_2$ [series (I; n = 1—4)] and $Et_2N·CO·[CH_2]_n·CO·NEt_2$ and $Et_2N·CO·CH_2·CMe_2·CH_2·CO·NEt_2$ [series (II; n = 1—4)] using $[BPh_4]^-$ or $[PF_6]^-$ as the counter anion. The i.r. spectral results indicate interaction through the ligand oxygen atoms and non-participation of the anions in co-ordination, leading to the UO_8 chromophore which has low symmetry. The complexes are black, mauve, or green. Differences in the energies of *f–d* transitions are explained in terms of nephelauxetic effects. Similar changes have been observed in the energies of bands observed at shorter wavelengths, which are assigned to metal ion-to-ligand electron transfer. The spectra of *NNN′N′*-tetramethyldiamide and corresponding *NNN′N′*-tetraethyldiamide complexes are not noticeably different, indicating that changes in the *N*-alkyl substitution pattern may have little effect on amide base strength. The magnetic properties of the *NNN′N′*-tetramethylmalonamide complex with tetraphenylborate are normal for U^{III} with $\mu_{eff.}$(294 K) = 2.97 B.M. With 4,4′-methylenebis[1,5-dimethyl-2-phenylpyrazol-3(2*H*)-one], air-sensitive, lilac-mauve, tris complexes have been prepared with the same anions. The change in stoicheiometry is attributed to steric effects but, apart from a broadening of the *f–d* transitions, there are no obvious spectral effects which distinguish the UO_6 chromophore.

URANIUM(III) complexes with organic ligands are difficult to prepare for three main reasons. First, oxidation by molecular oxygen is favourable[2] in all cases, secondly organic compounds with active hydrogen atoms (*e.g.* pentane-2,4-dione) are reduced[2] by U^{III}, and thirdly, in the presence of water, ligands with nitrogen-donor atoms tend to produce conditions favourable for the formation of the insoluble uranium(III) hydroxide (as with the trivalent lanthanoids) which is readily oxidised even under anaerobic conditions.[3]

In a preliminary communication[4] we reported the isolation of complexes with *NNN′N′*-tetramethyl-substituted diamides, $Me_2N·CO·[CH_2]_n·CO·NMe_2$ and $Me_2N·CO·CH_2·CMe_2·CH_2·CO·NMe_2$ [series (I; n = 1—4)] with $[BPh_4]^-$ as anion. Previously, complexes with 1,5-dimethyl-2-phenylpyrazol-3(2*H*)-one (mppo) and its 4-dimethylamino-derivative were synthesised in our laboratory.[2] Other workers have isolated the cyclopentadienyl $[U(C_5H_5)_3]$ and its adducts[5] with tetrahydrofuran, (—)-nicotine, and cyclohexyl isocyanide, $[U(C_5H_5)_3L]$, and an adduct[6] with acetonitrile, $UCl_3·MeCN$, from non-aqueous solution.

Our preparative route,[2,4] in which an ethanolic solution of a purple double chloride $M^I[UCl_4]·5H_2O$ is used as starting material under anaerobic conditions, gives solutions which contain water. Hence *NNN′N′*-tetra-alkyldiamides are ideally suited to the method since, in addition, the chelating ligands should lessen the competition for co-ordination positions with water molecules and chloride ion. The use of the precipitating agents tetraphenylborate and hexafluorophosphate allows the rapid isolation of dry solids which are usually[2] more stable towards oxidation than the solutions of the components.

In this paper, the structure of the ligands is systematically varied so that changes in the little studied uranium(III) charge-transfer and *f–d* electronic spectra of a wide range of similar chromophores could be examined for the first time.

RESULTS AND DISCUSSION

The Preparative Method.—Air-sensitive tetrakis complexes were characterised for most of the bidentate amides in series (I) and (II) $\{Et_2N·CO·[CH_2]_n·CO·NEt_2$ (n = 1—4) and $Et_2N·CO·CH_2·CMe_2·CH_2·CO·NEt_2\}$ with $[BPh_4]^-$ or $[PF_6]^-$ as counter anion (analytical results are given in Table 1). However, complexes of teaa with $[PF_6]^-$ and *NN′*-diethylmalonamide (dema) with $[BPh_4]^-$ and $[PF_6]^-$ were not readily isolated, although changes in colour and spectra were observed in solution.

TABLE 1

Analytical data (%) for the complexes $[UL_4][X]_3$ *

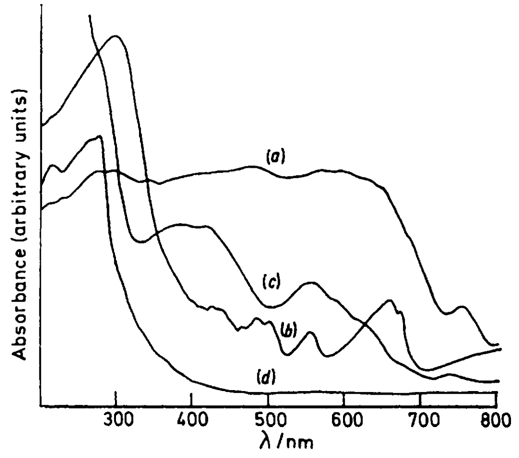
Complex	Found U	Found C	Found H	Found N	Calc. U	Calc. C	Calc. H	Calc. N
X = Tetraphenylborate								
(1) $U(tmma)_4X_3$	12.9	64.9	6.45	6.15	13.0	65.7	6.40	6.15
(2) $U(tmsa)_4X_3$	12.8	65.1	6.40	5.70	12.65	66.3	6.65	5.95
(3) $U(tmga)_4X_3$	12.15	65.85	6.85	5.35	12.25	66.85	6.85	5.75
(4) $U(tmaa)_4X_3$	12.55	65.55	7.00	5.25	11.9	67.35	7.05	5.60
(5) $U(hmga)_4X_3$	11.9	67.45	7.30	5.20	11.6	67.85	7.25	5.45
(6) $U(tema)_4X_3$	12.0	67.4	7.15	5.65	11.6	67.85	7.25	5.45
(7) $U(tesa)_4X_3$	12.45	67.2	7.30	5.35	11.85	68.35	7.45	5.30
(8) $U(tega)_4X_3$	11.9	66.0	7.30	5.25	11.0	68.8	7.60	5.20
(9) $U(teaa)_4X_3$	11.15	67.6	7.35	4.60	10.7	69.2	7.80	5.05
(10) $U(tedmga)_4X_3$	10.5	67.15	8.00	4.45	10.45	69.6	7.95	4.90
X = Hexafluorophosphate								
(11) $U(tmma)_4X_3$		25.5	4.20	8.50		25.75	4.30	8.60
(12) $U(tmsa)_4X_3$		26.9	4.60	8.05		28.2	4.75	8.25
(13) $U(tmga)_4X_3$		28.85	4.90	7.25		30.5	5.10	7.90
(14) $U(tmaa)_4X_3$		31.6	5.55	7.20		32.6	5.45	7.60
(15) $U(hmga)_4X_3$		32.7	5.90	6.90		34.55	5.80	7.30
(16) $U(tema)_4X_3$		34.65	5.90	7.50		34.55	5.80	7.30
(17) $U(tesa)_4X_3$		36.7	6.30	6.75		36.35	6.10	7.05
(18) $U(tega)_4X_3$		38.05	6.40	6.80		38.45	6.00	7.15
(19) $U(tedmga)_4X_3$		40.65	7.00	6.50		41.05	6.90	6.40

* Ligand abbreviations: tmma = *NNN′N′*-tetramethylmalonamide, tmsa = *NNN′N′*-tetramethylsuccinamide, tmga = *NNN′N′*-tetramethylglutaramide, tmaa = *NNN′N′*-tetramethyladipamide, hmga = 3,3-dimethyl-*NNN′N′*-tetramethylglutaramide, tema = *NNN′N′*-tetraethylmalonamide, tesa = *NNN′N′*-tetraethylsuccinamide, tega = *NNN′N′*-tetraethylglutaramide, teaa = *NNN′N′*-tetraethyladipamide, and tedmga = *NNN′N′*-tetraethyl-3,3-dimethylglutaramide. Phosphorus interfered in the uranium analysis for complexes (11)—(19).

With hexamethylmalonamide (hmma) no changes in colour or spectra were observed and no solid complex was precipitated. Steric hindrance with hmma is probably large.

No complex with a unidentate amide has been satisfactorily characterised. The fact that the solids contain chloride indicates that co-ordinated chloride in $[NH_4][UCl_4]\cdot5H_2O$ is not readily replaced although spectral changes were observed with *NN*-dimethylacetamide (dma) in ethanolic solution. So far, our preparative method has produced only one complex $[U(mppo)_6][BPh_4]_3$, having a unidentate ligand.[2] Other potential starting materials,[3] *e.g.* the anhydrous uranium(III) halides, are either insoluble or dissolve with oxidation in most common organic solvents.

A co-ordination number of six was found with the bidentate ligand 4,4'-methylenebis[1,5-dimethyl-2-phenylpyrazol-3(2*H*)-one]. A 4 : 1 stoicheiometry was not found even when an excess of ligand was used in the preparation. This is presumably caused by steric hindrance since each ligand contains two phenyl groups in the 2,2' positions. In the same way, the parent compound mppo gave 6 : 1 complexes, but with the less hindered bidentate 4-dimethylamino-derivative (dmppo) the 4 : 1 stoicheiometry was observed.[2] There seems little doubt in view of the present evidence that the 4-amino-nitrogen atoms are co-ordinated in $[U(dmppo)_4][BPh_4]_3$, in which case this would be only the third well characterised example of a uranium(III) complex with a nitrogen-donor ligand.[5,6]



Electronic spectra of (*a*) $[U(tmma)_4][BPh_4]_3$, (*b*) the uranium(IV) oxidation product of (*a*), (*c*) an ethanolic solution of $[NH_4][UCl_4]\cdot5H_2O$ and tmma, and (*d*) $[La(tmma)_4][BPh_4]_3$

Complex (2) is oxidised only slowly in air (over 48 h), (1) over 2 h, (4) over 1 h, and the rest within minutes of exposure.

Spectroscopic and Other Properties of the Series (I) *and* (II) *Complexes.*—(*a*) *Electronic spectra* (200—2 000 nm). The Figure shows characteristic spectra of $[U(tmma)_4][BPh_4]_3$, the uranium(IV) oxidation product, the corresponding lanthanum(III) complex, and $[NH_4][UCl_4]\cdot5H_2O$ with four molecular proportions of tmma in ethanol. Similar spectra were obtained in the other cases [complexes (1)—(19), Table 1].

For U^{III} the solution spectra at <700 nm had band maxima close in wavelength to those of the uranium(III) double chloride, which contains co-ordinated chloride,[2] but large red shifts were observed on comparing the diffuse-reflectance spectra of the tetraphenylborate or hexafluorophosphate salts with the ethanolic solutions (Figure and Table 2).

Experiments with cerium(III) salts suggest that these results are best explained in terms of incomplete replacement of chloride by amide in ethanolic solution. A 4*f*-5*d* transition was present in both the ethanolic solution (301 nm) and diffuse-reflectance (307 nm) spectra of $CeCl_3\cdot7H_2O$ but not in aqueous solution for which complete dissociation was observed; $NdCl_3\cdot6H_2O$ contains [7] $[Nd(OH_2)_6Cl]^+$. On addition of four molecular proportions of tmma to the ethanolic solution a small shift (2 nm) was observed but the reflectance spectrum of the tetraphenylborate salt is markedly red-shifted (21 nm) with respect to the ethanolic solution spectrum of $CeCl_3\cdot7H_2O$. Ethanolic solutions (10^{-3} mol dm^{-3}) of $CeCl_3\cdot7H_2O$, $CeCl_3\cdot7H_2O$ with four molecular proportions of tmma, $[NEt_4]Br$, and $[NH_4][Cr(NH_3)_2(NCS)_4]\cdot H_2O$ had similar molar conductances (35—40 S cm^2 mol^{-1}) whilst that of $[NEt_4]_2[Co(NCS)_4]$ was 87 S cm^2 mol^{-1} at the same concentration in ethanol. The effects on the spectra in the uranium(III) systems were exactly analogous although the shifts for the solids were larger, as would be expected.

None of the uranium(III) spectra contained an appreciable absorption near 1 540 nm which is typical [4] of U^{IV}. The spectra are conveniently divided into four sections in terms of assignment.

(*i*) *At* <300 *nm.* The complexes $[M(tmma)_4][BPh_4]_3$ (M = La, Ce, or Nd) and tmma absorbed strongly near 210 and 275 nm (Figure). The lower-energy absorption is assigned [8] to an internal, n-π^* ligand transition; typically, $[U(tmma)_4][BPh_4]_3$ absorbed at 277 and 298 nm and the oxidation product at 297 nm.

(*ii*) 350—500 *nm.* Strong absorption was found for all the uranium(III) spectra (Figure and Table 2). On reaction with air these absorptions collapsed and there were no corresponding bands at lower energy in the uranium(IV) spectrum so produced or in the lanthanoid(III) spectra. It is very unlikely that these absorptions are derived from ligand-to-metal ion electron transfer in view of the highly reducing nature of U^{III}. Metal ion-to-ligand (f-π^*) electron transfer is a much more likely explanation. In solution, the hmga complex absorbs at higher energy than that of tmga, which would be expected for a metal ion-to-ligand transfer on the introduction of electron-releasing groups, but no consistent pattern emerges on comparing the solution and solid-state spectra of series (I) (*NNN'N'*-tetramethyldiamides) with series (II) (*NNN'N'*-tetraethyldiamides) complexes. Within series (I), however, the spectral bands shift in the same direction as the *f*-*d* absorptions (see below), *i.e.* with $[BPh_4]^-$, $[PF_6]^-$, and in ethanolic solution the energies vary in the order tmma < hmga < tmsa < tmaa. If the origin of these absorptions is ligand-to-metal ion electron transfer then the energies of the *f–d* transitions should shift in the opposite sense. Similar changes were found for the series (II) amides in ethanolic solution only (tema < tesa ≃ tedmga < tega ≃ teaa).

(*iii*) 500—700 *nm*. Many of the complexes and solutions were mauve with a grey or green colouration caused by the band envelope shifting towards 600 nm and/or the appearance of an additional strong absorption near 625 nm. Absorption coefficients were two to ten times greater and overall bandwidths at half-height were many times greater than for *f–f* transitions found in this region for the hydrated uranium(III) ion in aqueous solution. There is little doubt[9] that the absorption is caused by $5f^3$–$5f^26d$ transitions.

TABLE 2

Principal absorption bands (nm) in the diffuse-reflectance and solution spectra[a]

Ligand	X	Complex	350—500 nm	500—700 nm	Colour
tmma	$[BPh_4]^-$	(1)	450 (sh),[b] 475	575	Black
	$[PF_6]^-$	(11)	445, 475	635	Green
		(in EtOH)	385 (845), 412 (830)	554 (520)	Mauve
tmsa	$[BPh_4]^-$	(2)	382, 416	575, 630	Green
	$[PF_6]^-$	(12)	382, 425	586, 628	Grey-green
		(in EtOH)	364 (1 240), 385 (1 230)	543 (1 130)	Mauve
tmga	$[BPh_4]^-$	(3)	365, 420	547, 626	Mauve
	$[PF_6]^-$	(13)	390, 417	550, 627	Mauve
		(in EtOH)	358 (1 300), 384 (1 270), 407 (1 230)	540 (1 250)	Mauve
tmaa	$[BPh_4]^-$	(4)	420	535	Mauve
	$[PF_6]^-$	(14)	415	509, 529, 623	Brown
		(in EtOH)	352 (1 360), 380 (1 300)	535 (1 200)	Mauve
hmga	$[BPh_4]^-$	(5)	400, 480(sh)	628	Green
	$[PF_6]^-$	(15)	380 (sh), 435	540, 640	Green
		(in EtOH)	367 (1 570), 410 (1 470)	565 (1 300)	Green
tema	$[BPh_4]^-$	(6)	425, 465 (sh)	585, 625 (sh)	Grey
	$[PF_6]^-$	(16)	435	597, 626	Green
		(in EtOH)	385 (1 060), 415 (1 050)	565 (803)	Mauve
tesa	$[BPh_4]^-$	(7)	380, 430	570, 630	Grey
	$[PF_6]^-$	(17)	442	560, 632	Black
		(in EtOH)	365 (1 090), 407 (1 030)	547 (1 080)	Mauve
tega	$[BPh_4]^-$	(8)	378, 402	547, 620	Mauve
	$[PF_6]^-$	(18)	388 (sh), 450	547, 617	Mauve
		(in EtOH)	352 (710), 403 (630), 445 (565)	542 (760)	Mauve
teaa	$[BPh_4]^-$	(9)	334, 485	550, 590	Mauve
		(in EtOH)	352 (1 130), 455 (930)	538 (1 130)	Mauve
tedmga	$[BPh_4]^-$	(10)	373 (sh), 430	565, 630	Grey
	$[PF_6]^-$	(19)	375 (sh), 430	583, 626	Green
		(in EtOH)	360 (895)	562 (840)	Green

[a] Absorption coefficients ($dm^3\ mol^{-1}\ cm^{-1}$) are given in parentheses. For $[NH_4][UCl_4]\cdot 5\ H_2O$ in EtOH: 320 (1 160), 354 (1 105), 447 (555), and 542 nm (1 130 $dm^3\ mol^{-1}\ cm^{-1}$). [b] sh = Shoulder.

A maximum of five transitions is expected if the degeneracy of the 6*d* is completely lost. At least five transitions (including shoulders) are observed in all cases. Some of the weaker ones could be *f–f* transitions. Uranium(III) in dilute sulphuric acid solution absorbs[10] at 523 (ε 147), 543 (ε 52), 588 (ε 55), 610 (ε 78), 617 (ε 89), 639 (ε 49), and 671 nm (ε 11 $dm^3\ mol^{-1}\ cm^{-1}$).

We conclude that the chromophore is UO_8 in the solid complexes because of the i.r. results and the non-co-ordinating nature of the anions, but that the symmetry is low.

In some cases marked red shifts are observed which we assign to nephelauxetic effects. Similar changes were found for the metal ion–ligand electron-transfer spectra. We may expect to observe red shifts as the electron availability at the amide oxygen atom is increased since the metal ion-to-ligand bond might be expected to contain a greater covalent contribution in these cases. Such a change was found on methylation at C^3 of the glutaramides with the hmga spectra red-shifted with respect to those of tmga and similarly with tedmga and tega. However, there was very little difference between the spectra of analogous complexes of *NNN'N'*-tetramethyl- and *NNN'N'*-tetraethylamides, which seems to confirm[11] that variation in the pattern of substitution at the amide nitrogen has little effect on basicity.

As the value of *n* in $R_2N\cdot CO\cdot[CH_2]_n\cdot CO\cdot NR_2$ (R = Me or Et) was increased the spectra of the complexes and the ethanolic solutions were blue-shifted (Table 2). This would imply that the amide base strength decreases with increasing *n*.

(*iv*) 700—2 000 *nm*. The *f–f* spectra observed were very similar for all the complexes so that the co-ordination number remains constant. No consistent shifts assignable to nephelauxetic effects were observed. The most noticeable difference was with respect to a band near 1 220 nm in the solution spectra which appeared as two well-separated bands in the spectra of most of the solids. Generally, the solution spectra were again blue-shifted towards the band positions of the double chloride.

(*b*) *Infrared spectra*. There was a decrease in the frequency of the carbonyl C=O stretching vibration by 30—80 cm^{-1} (see Experimental section) on comparing the spectra of the free ligands with those of the complexes, confirming that co-ordination occurs through the amide oxygen atoms. There are no regular variations which could be related to the ligand structures. Only in the case of complex (1) was there any doubt, since here the absorption splits into two components one of which is only 20 cm^{-1} lower than the frequency found in tmma. The solution spectrum of the tmma complex had smaller absorption coefficients for the *f–d* transition than any other ligand.

In addition, the expected absorptions for tetraphenylborate (735 and 705 cm^{-1} for Na[BPh$_4$]) were observed as were those for hexafluorophosphate in O_h symmetry (828 and 559 cm^{-1} for [NH$_4$][PF$_6$]). Hence no interaction of the complex cation and the anions was present. A broadening and shift to higher wavenumber of the ν_3([PF$_6$]$^-$) band was observed for the complexes of tmaa (14) and hmga (15) and a colour change was noticed on adding [NH$_4$][PF$_6$] to ethanolic solutions of U^{III} and ligand. However, ν_3([PF$_6$]$^-$) was not split and the diffuse-reflectance electronic spectra of these complexes were not noticeably different from the rest, so that there is no reason for supposing that the anion is co-ordinated.

Magnetic Properties.—The magnetic moments of [U(tmma)$_4$][BPh$_4$]$_3$ were typical for uranium(III) complexes: (1), diamagnetic correction {based on measurements for [La(tmma)$_4$][BPh$_4$]$_3$} -882.7×10^{-6} cm^3 mol^{-1}; $\mu_{eff.}$(294 K) 2.97, $\mu_{eff.}$(92 K) 2.58 B.M.,* $\theta = 45$ K.

Complexes of 4,4′-*Methylenebis*[1,5-*dimethyl*-2-*phenylpyrazol*-3(2H)-*one*] (*mbp*) (*Table* 3).—The i.r. results suggested that co-ordination occurs through the carbonyl oxygen atoms and that no metal ion–anion interaction is present leading to the UO$_6$ chromophore. In the diffuse-reflectance spectra the *f–d* absorption bands obscured much of the *f–f* spectrum in the visible region as before, but were broader than those found for the series (I) and (II) complexes whilst the positions of the band maxima and the number of bands and shoulders present were not much different. Thus, the metal ion-to-ligand electron-transfer spectrum was not clearly observable and a shoulder near 435 nm in the diffuse-reflectance spectra is only tentatively assigned. The *f–f* spectrum at >700 nm was similar in overall shape to the solid-state spectra of the double chloride [NH$_4$][UCl$_4$]·5H$_2$O and the diamide adducts, although the relative intensities and positions of bands were different. There was an overall red shift in the *f–f* spectrum for the mbp complexes; some tentative evidence[1] was reported which suggests that large red shifts are indicative of lower co-ordination numbers in the green double chloride [NH$_4$][UCl$_4$]·6H$_2$O and the complex [U(mppo)$_6$][BPh$_4$]$_3$. However, there is no crystallographic evidence for co-ordination numbers lower than eight in uranium(III) complexes, and since we know of only three possible examples of six-co-ordination, namely the mbp and the mppo complexes (additionally, the poorly characterised[12] Cs$_2$Na[UCl$_6$] has magnetic properties consistent with octahedral stereochemistry), there are insufficient data to make firm conclusions. The overall complexity of the electron transfer and *f–d* spectra is such that these transitions are unlikely to be useful in deciding the stereochemistry in complexes with organic ligands, even though they should be subject to larger nephelauxetic and other effects associated with the symmetry of the complex ion than in the *f–f* spectrum.

TABLE 3

Properties of the 4,4′-methylenebis[1,5-dimethyl-2-phenylpyrazol-3(2*H*)-one] (mbp) complexes of uranium(III)

	[U(mbp)$_3$][BPh$_4$]$_3$	[U(mbp)$_3$][PF$_6$]$_3$
	Diffuse-reflectance electronic spectra (nm)	
350—500nm	435 (sh)	435 (sh)
500—700nm	505 (sh), 570, 625 (sh)	500, 560, 585 (sh), 635 (sh)
Colour	lilac	grey-mauve
	Infrared spectra (cm^{-1})	
$\Delta\nu$(C=O) [a]	13	(15) [b]
[BPh$_4$]$^-$	733, 705	
[PF$_6$]$^-$		845, 559
	Analysis (%) [c]	
U	10.1 (10.1)	
C	69.0 (71.7)	45.3 (45.1)
H	5.50 (5.60)	3.90 (3.95)
N	7.10 (7.10)	8.90 (9.10)

[a] Lowering of the frequency on complex formation; mbp 1 645 cm^{-1}. [b] Shoulder on ν(C=C) vibration. [c] Calculated values are given in parentheses.

EXPERIMENTAL

The Diamides.—These were prepared by allowing the acid dichlorides to react with the appropriate dialkylamine in diethyl ether. After purification by standard methods, satisfactory analytical results were obtained in all cases. 4,4′-Methylenebis[1,5-dimethyl-2-phenylpyrazol-3(2*H*)-one] monohydrate (B.D.H.) was used as supplied.

The Diamide Complexes.—All manipulations with U^{III} were performed under purified nitrogen with carefully deoxygenated solvents. The complexes were prepared by adding an ethanolic solution of sodium tetraphenylborate or ammonium hexafluorophosphate (three molecular proportions) to the dark coloured solutions obtained on adding the purple double chloride[2] [NH$_4$][UCl$_4$]·5H$_2$O (one molecular proportion) to a solution of an amide (four molecular proportions) in dry ethanol. The solution of the double chloride and ligand was usually decanted to remove [NH$_4$]Cl which precipitated. The complexes, which precipitated rapidly, were filtered off, washed with dry ethanol, dried, and stored in evacuated sealed tubes. Analytical results and ligand abbreviations are given in Table 1. The tetraphenylborates are less soluble in ethanol than the hexafluorophosphates. The compound teaa gave no precipitate with [PF$_6$]$^-$, no complex was prepared with *NN*′-diethylmalonamide (dema), and hexamethylmalonamide (hmma) gave an intractable red gum with [BPh$_4$]$^-$ Lanthanoid(III) complexes were prepared from hydrated chlorides.

Experiments with Other Amides.—With *NN*-dimethylacetamide (dma) and *NN*-dimethylisobutyramide (dmib), red precipitates, which contained chloride, were obtained using the method described above with various amide to uranium ratios; for dmib, isopentane was added to induce precipitation. However, the analyses did not fit any formula of the type U$_y$(amide)$_n$Cl$_x$X$_{3-x}$ (X = [BPh$_4$]$^-$ or

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* Throughout this paper: 1 B.M. $\approx 9.27 \times 10^{-24}$ A m^2.

$[PF_6]^-$). The same result[2] was found for the unidentate $P(NMe_2)_3O$.

Solution and Other Spectral Measurements.—The spectra of ethanolic solutions containing the double chlorides and four molecular proportions of the amide under a nitrogen atmosphere were recorded using a Beckmann Acta MIV spectrophotometer and 2-mm and 1-cm silica cells. The concentration of uranium was determined by weighing. Diffuse-reflectance spectra were recorded with the solid contained in an evacuated cell. Samples for i.r. spectroscopy were prepared in a nitrogen-filled glove-bag. The position (cm^{-1}) of the carbonyl C=O stretching frequency varied as follows: tmma 1 638, (1) 1 618 and 1 575, (11) 1 615; tmsa 1 620; (2) 1 595, (12) 1 612; tmga 1 646, (3) 1 600, (13) 1 604; tmaa 1 630, (4) 1 585, (14) 1 607; hmga 1 642, (5) 1 588, (15) 1 597; tema 1 635, (6) 1 602, (16) 1 604; tesa 1 640, (7) 1 590, (17) 1 590; tega 1 635, (8) 1 560, (18) 1 582; teaa 1 649, (9) 1 570; tedmga 1 638, (10) 1 565, (19) 1 575. See also Table 3.

Magnetic Measurements.—The magnetic susceptibilities of (1) and $[La(tmma)_4][BPh_4]_3$ were measured by the Gouy method from room to liquid-nitrogen temperatures.

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