The Chemistry of Quadrivalent Lanthanoids. Part 2.† Preparation and Properties of Cerium Tetrachloride Complexes and a Comparison with their Uranium Analogues

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Cerium tetrachloride complexes, *viz.* $[CeCl_4L_2]$ and $[CeCl_4L]$ where L = a uni- or bi-dentate arsine oxide, a phosphine oxide, a sulphoxide, or an amide, have been prepared. The thermal degradation behaviour of the solids could be divided into three patterns, one of which consists of loss of a chlorine atom only. It was indicated that $[CeCl_4(ipae)_2]$ could act as a substitute for the thermally unstable $CeCl_4$ for solution studies [ipae = 1-(di-isopropylamino)ethanal]. Decomposition rate studies of solutions of $[CeCl_4(ipae)_2]$ and $Cs_2[CeCl_6]$ in different solvents indicated that the decomposition reaction is first order with respect to cerium(IV) and its rate is approximately proportional to the donor number of the solvent. Solutions in thionyl chloride are stable for an indefinite period. The compounds studied were compared with their uranium(IV) analogues with respect to co-ordination behaviour, i.r. spectra, non-aqueous conductometric behaviour, and solvoscopic nature. The $CeCl_4$ and UCl_4 complexes proved very similar in almost all respects, except that those of cerium(IV) were more solvoscopic. Some differences between cerium(IV) and uranium(IV) can probably be explained best in terms of differences between 4*f* and 5*f* metal character rather than size differences.

Previous studies on the chloro-complexes of cerium(IV) involved the isolation of solid hexachlorocerate(IV) complexes with a variety of cations, *viz.* caesium,[1] pyridinium,[2] triphenylphosphonium,[3] triethylammonium,[1] tetraethylammonium,[4] tetramethylammonium,[5] and others.[2] The solids were usually precipitated from cold aqueous or non-aqueous solutions at temperatures between 0 and −25 °C. The cerium(IV) solutions were prepared by gradually dissolving dried cerium(IV) hydroxide in either concentrated hydrochloric acid or alcoholic solutions, in both cases while saturating the solution with HCl gas. The cerium(IV) chloro-complexes were unstable to varying degrees, in all the solvent systems used thus far. It was, therefore, difficult to prepare these compounds in high purity, and studies of their behaviour in solution could not be undertaken.

Cerium tetrachloride has not been prepared, owing to its thermal instability. A few of its complexes with neutral donor ligands have been isolated, *viz.* $[CeCl_4(dmso)_3]$,[6] $[CeCl_4(tppo)_2]$,[3] $[CeCl_4(bipyo)_2]$,[3] and $[CeCl_4(tdpo)_2]$[7] [dmso = dimethyl sulphoxide, tppo = triphenylphosphine oxide, bipyo = 2,2′-bipyridyl-*NN*′-dioxide, and tdpo = tris(dimethylamino)phosphine oxide]. All these were prepared from solutions containing hexachlorocerate(IV) and HCl, which made it difficult to isolate the pure compounds even at 0 °C and lower.

The results of the first *X*-ray structural analysis[7] of a $CeCl_4$ complex with an oxygen donor ligand, *viz.* $[CeCl_4(tdpo)_2]$, suggested that Ce^{IV} and U^{IV} are structurally very similar, although other data, *viz.* a significantly bigger P=O shift and greater hygroscopic character, suggested that Ce^{IV} is a stronger Lewis acid than U^{IV}. This study aroused interest in a further, more extensive systematic comparison between the chloro-complex chemistries of the two elements in the solid state and solution.

It was necessary first to obtain improved preparative methods for $CeCl_4$ complexes in order to isolate a $CeCl_4$ complex of a weak donor ligand, since a solution of such a complex would be expected to behave like $CeCl_4$ itself. Secondly, a solvent system was required in which this compound would be stable enough for satisfactory solution studies.

We now report the isolation and characterisation of a variety of $CeCl_4$ complexes of uni- and bi-dentate arsine oxides, phosphine oxides, sulphoxides, and amides. These compounds were obtained by the improved methods of preparation recently published by us.[8] Ligand displacement studies in non-aqueous solution showed that amide complexes of $CeCl_4$ can be used to substitute for $CeCl_4$. The decomposition rates of some of the Ce^{IV} chloro-species in solution have been determined at 0 and 25 °C in various solvent systems, including those used for the preparation of the complexes studied. The thermal behaviour of the solid complexes was also investigated. The properties of the cerium(IV) complexes, as revealed by the application of the various physical methods, have been compared in each case, with those of their uranium(IV) analogues.

Experimental

Ligands.—Commercial triphenylarsine oxide (tpao), tris(dimethylamino)phosphine oxide (tdpo), triphenylphosphine oxide (tppo), di(2-methoxyethyl) ether (dmee), trimorpholinophosphine oxide (tmorpo), dimethyl sulphoxide (dmso), tetramethylurea (tmu), *NN*′-bis(pentamethylene)urea (bpmu), and antipyrine (apn) were used as supplied. 1,2-Bis(diphenylarsoryl)ethane (dpaoe),[9] di-t-butyl sulphoxide (tbso),[10] 1,2-bis(methylsulphonyl)ethane (bmse),[10] 1-di-isopropylaminoethanal (ipae),[11] and 2,2-dimethyl-1-dimethylaminopropanal (dmdap)[11] were prepared as previously described.

Preparation of Complexes.—The complexes were all prepared by the following general method. $H_2[CeCl_6(dmee)_3]$[8] (1 g) was dissolved in ethyl acetate (35 cm^3) and methanol (8 cm^3); the solution was cooled in ice, stirred for 5 min, centrifuged, and decanted. A dichloromethane solution (*ca.* 5 cm^3) of the ligand in 5—10% excess was slowly added to the clear orange-red solution. If necessary, ether was added drop-

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† Part 1 is ref. 8.

Table 1. Analytical data of complexes

Complex	% M		% Cl		% C		% H		% N	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$[CeCl_4(tpao)_2]$	14.8	15.1	15.4	15.3	45.3	46.7	3.3	3.3		
$[CeCl_4(dpaoe)]$	17.3	17.5	17.9	17.7	57.9	60.2	4.4	4.7		
$[CeCl_4(tdpo)_2]$	21.8	21.9	22.0	22.1	22.3	22.5	5.6	5.7	13.2	13.1
$[CeCl_4(tppo)_2]$	16.5	16.7	16.7	16.9	51.4	51.6	3.7	3.6		
$[CeCl_4(tmorpo)_2]$	15.4	15.7	15.7	15.9	31.5	32.3	5.4	5.4		
$[CeCl_4(tbso)_2]$	22.9	23.1	23.4	23.4	31.0	31.7	6.0	6.0		
$[CeCl_4(dmso)_3]$	26.7	27.1	27.1	27.5	13.8	14.0	3.6	3.5		
$[CeCl_4(bmse)_2]$	23.6	23.9	23.9	24.2	15.5	16.4	3.2	3.4		
$[CeCl_4(ipae)_2]$	24.3	24.6	24.6	24.9	33.4	33.8	6.0	6.0	5.0	4.9
$[CeCl_4(dmdap)_2]$	25.9	25.9	26.0	26.2	30.8	31.1	5.7	5.6	5.1	5.2
$[CeCl_4(tmu)_2]$	25.4	27.2	27.4	27.6	23.0	23.4	4.8	4.7	10.9	10.9
$[CeCl_4(bpmu)_2]$	20.2	20.8	20.8	21.0	38.7	39.2	6.0	6.0	8.3	8.3
$[CeCl_4(apn)_2]$	20.8	21.3	21.2	21.5	39.8	40.1	3.8	3.7	8.1	8.5

Complex	% M		% Cl	
	Found	Calc.	Found	Calc.
$[UCl_4(tpao)_2]$	23.1	23.2	13.8	13.8
$[UCl_4(tpdo)_2]$	32.0	32.2	19.3	19.2
$[UCl_4(tppo)_2]$	25.2	25.4	14.9	15.1
$[UCl_4(tmorpo)_2]$	23.8	24.0	14.5	14.3
$[UCl_4(tbso)_2]$	33.6	33.8	20.0	20.1
$[UCl_4(dmso)_3]$	38.4	38.8	22.7	23.1
$[UCl_4(bmse)_2]$	34.1	34.6	20.4	20.6
$[UCl_4(ipae)_2]$	35.4	35.7	21.2	21.3
$[UCl_4(dmdap)_2]$	37.1	37.3	22.1	22.2
$[UCl_4(tmu)_2]$	38.5	38.9	22.9	23.2
$[UCl_4(bpmu)_2]$	30.3	30.8	18.2	18.4

wise (5—15 cm^3) to turbidity. The solution was then left in ice for further crystallisation. The supernatant liquid was decanted, and the crystals washed with ether (twice), vacuum dried at room temperature, and analysed. The crystals were stored in a desiccator in the dark. (Some of the complexes are light sensitive.)

Decomposition Rate Studies.—The thermal decomposition of solutions of each cerium(IV) chloro-complex in various solvents was studied at 0 °C ($\pm$0.1) and 25.0 °C ($\pm$0.1). The disappearance of the charge-transfer band at *ca.* 390 nm was monitored using 1-cm quartz cells and a Beckman Acta MVII u.v. spectrophotometer. All reactions were followed over more than four half-lives.

Conductometric titrations were carried out on 0.0030 mol dm^{-3} $[MCl_4(ipae)_2]$ (M = U or Ce) solutions in acetone at 0 °C using a Metrohm Herisau E518 conductometer and Metrohm EA645-7 conductivity cell as described earlier.[12]

Thermogravimetric Studies.—A Perkin-Elmer TGS-2 thermobalance was used as described earlier.[13] Nitrogen was used as carrier gas. A constant heating rate of 2.5 °C min^{-1} was used unless otherwise stated. The m.p.s were determined using a Mettler FPI apparatus equipped with a microscope.

The charge-transfer spectra were determined using a Beckman Acta MVII instrument and the i.r. spectra using a Beckman IR 4250 instrument.

Analysis.—The cerium(IV),[8] chloride,[8] and uranium[14] analyses were performed as described earlier.

Results and Discussion

The analytical data of the complexes are given in Table 1. They range from orange to red-brown in colour (Table 2) except for the yellow $[CeCl_4(tpao)_2]$ and $[CeCl_4(dpaoe)]$. All can readily be prepared by the general method described here. The complexes of the stronger ligands (arsine oxides) or those which form slightly soluble complexes (bidentate ligands, *e.g.* bmse) could be precipitated from cold methanolic solutions of tetraethylammonium or pyridinium hexachlorocerate(IV). A few complexes can be prepared by using $Cs_2[CeCl_6]$ as starting material,[8] *e.g.* $[CeCl_4(tdpo)_2]$.

In all the complexes where the UCl_4 analogues are known, the stoicheiometries of the $CeCl_4$ and UCl_4 analogues are the same (see Table 2). In the light of the close structural similarities between the $[MCl_4(tdpo)_2]$ species (M = Ce or U) it can be assumed that the structure of the above complexes will also be the same. It has been either proved [15] or strongly indicated [14] that all the above uranium complexes are six-co-ordinate except those of dmso and bmse.

Infrared Spectra.—Although the Ce–Cl stretching frequencies (Table 2) of these assumed six-co-ordinate complexes do not vary greatly (from 243 to 271 cm^{-1}), it is of interest that those of the very strong donor ligands (arsine oxides) are on the lower energy end, which corresponds to slightly longer Ce–Cl bonding and thus weaker metal–halide interaction. This is in agreement with results for the corresponding uranium tetrachloride complexes (Table 2) and also U–Cl bond distances.[15] $[CeCl_4(dmso)_3]$ might be expected to contain cationic $[CeCl_2(dmso)_6]^{2+}$ and anionic $[CeCl_6]^{2-}$ cerium(IV); *cf.* $[UCl_4(dmso)_3]$.[16] The low Ce–Cl stretching frequency of $[CeCl_4(bmse)_2]$ (255 cm^{-1}) can be ascribed almost certainly to eight-co-ordination. {The solid reflectance u.v. spectrum of $[UCl_4(bmse)_2]$ has major peaks at 450, 500, 565, 675, 900br, and 1 150 nm (strongest band) and no band in the region 1 800—2 000 nm.} Comparison of the shifts of E=O (E = P, As, C, or S) stretching frequencies upon complexation for a specific pair of UCl_4 and $CeCl_4$ complexes shows that either

Table 2. Infrared spectral data of complexes [a]

Compound	Colour	ν(E=O)	Δν(E=O)	ν(M–Cl)
$[CeCl_4(tpao)_2]$	Pale yellow	825	56	243, 265(sh)
$[UCl_4(tpao)_2]$	Pale blue-green	835	46	240—255br
tpao		881		
$[CeCl_4(dpaoe)]$		826	57	258
dpaoe		883		
$[CeCl_4(tpdo)_2]$	Brick red	1 035	177	267, 243(sh)
$[UCl_4(tdpo)_2]$	Blue-green	1 036	176	260(sh), 250
tdpo		1 212		
$[CeCl_4(tppo)_2]$	Yellow	1 042	150	265, 242(sh)
$[UCl_4(tppo)_2]$	Pale blue-green	1 068	124	259, 242 (doublet)
tppo		1 192		
$[CeCl_4(tmorpo)_2]$	Orange	1 052	166	*b*
$[UCl_4(tmorpo)_2]$	Blue-green	1 050	168	*b*
tmorpo		1 218		
$[CeCl_4(tbso)_2]$	Orange	922	168	271, 248(sh),
$[UCl_4(tbso)_2]$	Blue-green	922	168	230—252br
tbso		1 090		
$[CeCl_4(dmso)_3]$	Orange	960	85	254—200br
$[UCl_4(dmso)_3]$	Green	956	89	254(sh), 241
dmso		1 045		
$[CeCl_4(bmse)_2]$	Orange	970	50	255
$[UCl_4(bmse)_2]$	Very pale blue-green	971	49	
bmse		1 020		
$[CeCl_4(ipae)_2]$	Yellowish orange	1 570	71	265, 241(sh),
$[UCl_4(ipae)_2]$	Blue-green	1 586	55	244—260br
ipae		1 641		
$[CeCl_4(dmdap)_2]$	Yellowish orange	1 571	59	242—263br
$[UCl_4(dmdap)_2]$	Blue-green	1 580	50	242, 260 (doublet)
dmdap		1 630		
$[CeCl_4(tmu)_2]$	Brick red	1 535	102	243—264br
$[UCl_4(tmu)_2]$	Blue-green	1 540	97	245, 260(sh)
tmu		1 637		
$[CeCl_4(bpmu)_2]$	Brick red	1 542	100	246(sh), 270,
$[UCl_4(bpmu)_2]$	Blue-green	1 563	79	244—260br
bpmu		1 642		
$[CeCl_4(apn)_2]$	Brown	1 553	104	240, 261
apn		1 657		

[a] Values in cm^{-1}; E = P, As, C, or S. [b] Interference of ligand.

the values are similar, or else the value for $CeCl_4$ is significantly larger.

Charge-transfer Spectra.—The charge-transfer spectra of these complexes consist of broad flat absorptions ranging from 16 000 to about 28 000 and peaks between 30 000 and 31 000 cm^{-1} which are very similar for most ligands. The arsine oxide complexes are significantly different insofar as they start to absorb at 20 000 cm^{-1} only, whereas the others, *e.g.* $[NEt_4]_2[CeCl_6]$, start at 18 000 cm^{-1}. Their solution spectra in CH_2Cl_2 are fairly similar. They each have a peak in the region 340—365 nm with ε_M values between 5 200 and 3 200 $dm^3 mol^{-1} cm^{-1}$. For the weaker donor ligand complexes the peaks are broader and the lower energy ' leg ' moves closer to the visible region. Typical curves are given in Figure 1.

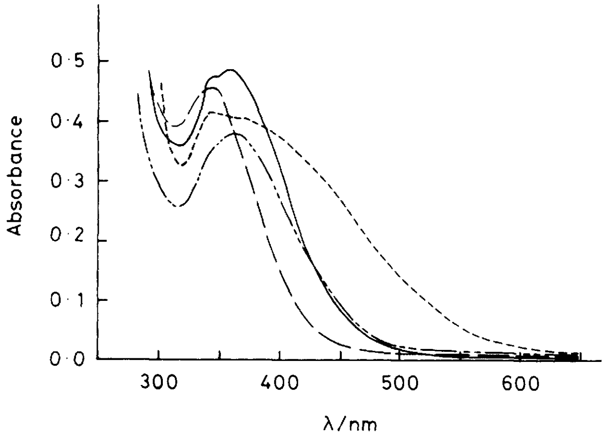

Figure 1. Charge-transfer spectra of 1.0 × 10^{-4} mol dm^{-3} solutions of $[CeCl_4(dmso)_3]$ (——), $[CeCl_4(apn)_2]$ (- - - -), $[CeCl_4(tpao)_2]$ (— —), and $[CeCl_4(dmdap)_2]$ (– - - –) in methylene dichloride

Thermal Studies.—Thermogravimetric analysis shows that the decomposition patterns of the $CeCl_4$ complexes can be divided into three general types. In the first type (tdpo, tmorpo, and bpmu complexes) an initial mass loss step which approximately corresponds to the loss of one chlorine atom is observed. This is followed, in general, at higher temperatures by another degradation step. The decomposition curve of $[CeCl_4(tdpo)_2]$ [curve 1, Figure 2(a)] is an example of this type. This compound gradually changes in colour from orange to red before it melts to a dark red liquid at 185 °C. Between 195 (A) and 205 °C (B) [Table 3(a)] the colour lightens. The mass loss of 5.3% experienced up to 200 °C closely corresponds to the loss of one chlorine atom (5.54%). Gradual darkening due to degradation of the ligand sets in from 200 °C upwards.

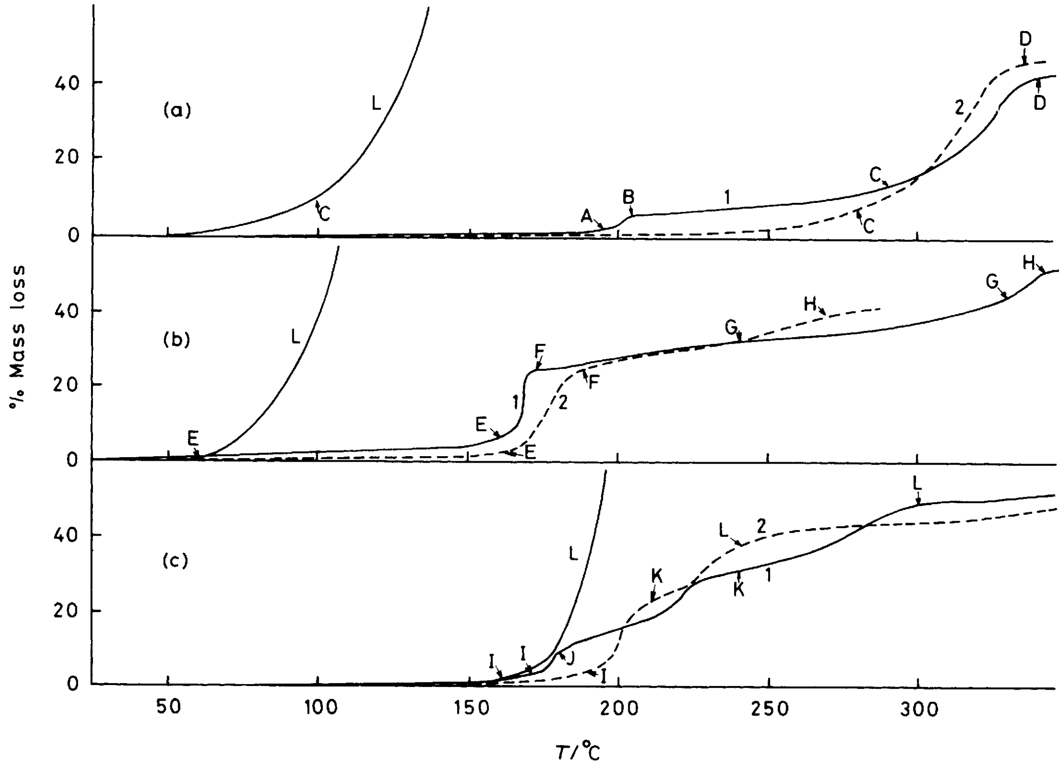

Figure 2. Thermal degradation curves of solid cerium tetrachloride complexes: curves L, 1 (full line), and 2 (dashed line) are in each case those of the free ligand, the $CeCl_4$ complex, and the UCl_4 complex, respectively; (a) $[MCl_4(tdpo)_2]$; (b) $[MCl_4(dmso)_3]$; (c) $[MCl_4(bmse)_2]$; capital letter symbols refer to the temperatures given in the relevant Tables

When the heating rate of $[CeCl_4(tdpo)_2]$ was lowered (1 °C min^{-1}) the initial decomposition step was shifted 10 °C lower, almost exactly to its melting point, and the mass loss up to B was shifted 1% higher, which suggests a greater mass loss due to degradation of the ligand. This process could be expected to be slower than chlorine evolution. Even changing to the fast heating rate of 5° min^{-1} did not separate the two decomposition processes [the molten compound at point B (now 210 °C) was still light brown]. It appears that the chlorine gas produced participates to some extent in ligand degradation.

The uranium(IV) analogue gradually darkens from 240 °C. Partial melting occurs at 252 °C, accompanied by further darkening and degradation. The degradation step corresponds approximately to the second step of $[CeCl_4(tdpo)_2]$. Although these tdpo complexes are not very hygroscopic, that of cerium is more so than its uranium analogue.

In the case of the very similar $[CeCl_4(tmorpo)_2]$ complex the AB step [Table 3(a)] is shifted to higher temperatures. The sublimation temperature of tmorpo is higher than the boiling point of tdpo.

The mass loss, up to point B, for the complex $[CeCl_4(bpmu)_2]$ (11.1%) is considerably higher than that expected for loss of the one chlorine atom (5.3%). Its hygroscopic nature (early mass loss) and simultaneous ligand degradation (the dark red colour hardly becomes lighter during the chlorine loss step) can account for this larger mass loss.

In the second decomposition type (dmso, ipae, dmdap, and tmu complexes) the loss of the chlorine atom occurs simultaneously with the first loss or degradation step of the ligand. In general there are at least two thermal degradation steps, EF and GH [Table 3(b)]. The curve for $[CeCl_4(dmso)_3]$ is given in Figure 2(b). This compound melts sharply at 159 °C, after which the orange colour rapidly becomes lighter to almost white at 170 °C. The overall mass loss up to 170 °C is 25%. A noticeable early mass loss (even from room temperature) is experienced for this compound. Earlier literature [6] interpreted this as decomposition. However, $[CeCl_4(dmso)_3]$ is hygroscopic (much more so than its uranium analogue). Isothermal heating at 110 °C for 280 min resulted in a 3% mass loss with no colour changes. Analysis indicated 26.5% cerium(IV) content {Calc. for $[CeCl_4(dmso)_3]$: 26.3%}. Isothermal heating of the compound at 154 °C for 80 min showed a sharp decomposition step. When the plateau was reached a white product remained and a 25% mass loss was registered. The % chloride coincided almost exactly with $[CeCl_3(dmso)_2]$ (26.8%; calc. 26.15%). The white hygroscopic $[CeCl_3(dmso)_3]$ was also prepared,[17] and the formation of $[CeCl_3(dmso)_2]$ in the vicinity of 160 °C was indicated by a non-isothermal analysis. The 25% mass loss experienced by $[CeCl_4(dmso)_3]$ up to 170 °C can therefore be divided into 3% water, 6.9% for one chlorine atom, and 15.1% for a dmso molecule.

Although the curve for the uranium(IV) analogue appears similar, an unidentified sticky brown mass is obtained at 190 °C. $CeCl_4$ complexes of ipae, dmdap, and tmu closely resemble each other in behaviour [Table 3(b)]. For example, the ipae complex changes in colour from yellow to dark orange before melting at 201 °C to a dark red-brown liquid which darkens with increasing temperature.

In the third type of decomposition (bmse, tppo, and tpao complexes) the initial step (loss of a chlorine atom) appears to overlap with a consecutive ligand loss/degradation step. The curve for $[CeCl_4(bmse)_2]$ is given in Figure 2(c), and the data appear in Table 3(c). The complex melts at 160 °C, with a colour change from orange to yellow. This is rapidly followed by a darkening associated with ligand degradation. The mass loss up to 180 °C (J) is 9% (the equivalent for one chlorine

Table 3. Thermal data of solid complexes

(a)	M.p. (°C)	A (°C)[a]	B (°C)[a]	C (°C)[a]	D (°C)[a]
$[CeCl_4(tdpo)_2]$	185	195	205	290	340
$[UCl_4(tdpo)_2]$	252			280	335
tdpo		100	153[b]		
$[CeCl_4(tmorpo)_2]$	210	203	223	270	350
$[UCl_4(tmorpo)_2]$	295			330	350
tmorpo		220	280[b]		
$[CeCl_4(bpmu)_2]$	decomp.	175	188	250	350
$[UCl_4(bpmu)_2]$	decomp.			230	290
bpmu		140	190[b]		

(b)	M.p. (°C)	E (°C)	F (°C)	G (°C)	H (°C)
$[CeCl_4(dmso)_3]$	159	160	170	330	340
$[UCl_4(dmso)_3]$	decomp.	160	190	240	270
dmso		60	115[b]		
$[CeCl_4(ipae)_2]$	200	190	210		430
$[UCl_4(ipae)_2]$	205	180	225	290	325
ipae		50	125[b]		
$[CeCl_4(tmu)_2]$	decomp.	180	195		430
$[UCl_4(tmu)_2]$	250	190	235	280	315
tmu		50	105[b]		
$[CeCl_4(dmdap)_2]$	decomp.	170	205		400
$[UCl_4(dmdap)_2]$	238	170	225	280	320
dmdap		50	110[b]		

(c)	M.p. (°C)	I (°C)	J (°C)	K (°C)	L (°C)
$[CeCl_4(bmse)_2]$	160	170	180	240	300
$[UCl_4(bmse)_2]$	180	190		210	240
bmse	153	160	210[b]		
$[CeCl_4(tpao)_2]$	295	290	300	340	410
$[UCl_4(tpao)_2]$	302	280	300	370	410
tpao	192	250	350[b]		
$[CeCl_4(tppo)_2]$	280	260	305	450	500
$[UCl_4(tppo)_2]$	304	260	290	330	410
tppo	156	200	300[b]		

[a] Letters (A, B, *etc.*) correspond with those in Figure 2. [b] Corresponds with 100% mass loss due to distillation or sublimation.

Table 4. First-order decomposition rate constants of some Ce^{IV} chloro-complexes in various solvents

Solvent	Donor no.	$10^{-2}\ k$/min^{-1} $[CeCl_4(ipae)_2]$	$10^{-2}\ k$/min^{-1} $[CeCl_4(tpao)_2]$
Pyridine	33.1	Very fast	137
NN-Dimethylformamide	26.6	50	137
Tetrahydrofurane	20.0	4.4	
Water	18.0	1.9	12
Methanol		0.39	
Methylene dichloride		0.25	
Acetone	17.0	0.22	0.70
Acetonitrile	14.1	0.05	0.16
Thionyl chloride	0.4	<0.003	<0.003

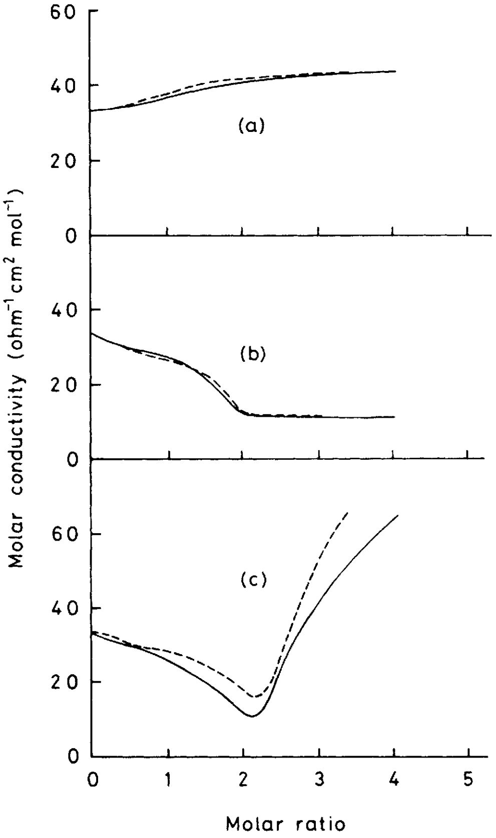

Figure 3. Conductometric titration curves of $[CeCl_4(ipae)_2]$ and $[UCl_4(ipae)_2]$ (dashed line) for (a) dmso; (b) tdpo; and (c) tpao

atom is 6%), and up to 240 °C is 32% (one chlorine + one bmse = 32%). For $[UCl_4(bmse)_2]$ the mass loss up to 240 °C (L) is 39% (the equivalent for two bmse molecules 44.8%). The sublimation curve of free bmse shows that the temperature at which the first molecule of this ligand is lost is close to the sublimation temperature of the free ligand. The tppo and tpao complexes behave similarly; they melt at 282 and 295 °C, respectively, and show small first decomposition steps (about 10—12% mass loss) up to 300 °C. This is more than the loss of one chlorine atom per molecule (*ca.* 6%), which could be ascribed to a small amount of ligand degradation due to the chlorine evolved.

Donor strength of a ligand is a dominant factor in the formation of complexes in solution. These solid-state decomposition studies indicated, however, that the volatility of the ligand is important in determining the thermal stability of a solid complex; *e.g.* the order of increasing stability of the phosphine oxide complexes (tdpo, tmorpo, and tppo) is the inverse order of their donor strength. Similarly the F temperature of the tmu (195 °C), dmdap (205 °C), and ipae (210 °C) complexes can be related to the volatility of the free ligand (F temperatures 105, 110, and 125 °C, respectively) whereas the substituted urea, tmu, has the highest donor number.

Decomposition rate studies were performed on various cerium(IV) chloro-complexes in order to determine their thermal stabilities in solution. The reactions were all strictly first order with respect to cerium(IV). For $Cs_2[CeCl_6]$ in concentrated HCl at 0 °C $t_{\frac{1}{2}} = 76$ min, and $k_{obs} = 9.1 \times 10^{-3}$ min^{-1}. At 25 °C the decomposition is much faster so that the solubility of $Cs_2[CeCl_6]$ could not really be evaluated in concentrated HCl at 25 °C, let alone in more dilute hydrochloric acid (as claimed [1]). Solution equilibrium cannot be achieved, owing to relatively fast simultaneous decomposition. $Cs_2[CeCl_6]$ is much more stable in methanol solution, *e.g.* $t_{\frac{1}{2}}$ at 25 °C is 810 min and k_{obs} is 8.6×10^{-4} min^{-1}. $H_2[CeCl_6(dmee)_3]$, used as a starting material, is quite stable in a methanol (5%)-ethyl acetate (95%) mixture at 0 °C ($t_{\frac{1}{2}} = 124$ min, $k_{obs} = 5.6 \times 10^{-3}$ min^{-1}), but much less stable at 25 °C ($t_{\frac{1}{2}} = 35$ min, $k_{obs} = 2.0 \times 10^{-2}$ min^{-1}). The first-order rate constants of

[$CeCl_4(ipae)_2$] and [$CeCl_4(tpao)_2$] in various solvents at 25 °C are given in Table 4. The decomposition rates of the complexes are approximately directly proportional to the donor numbers of the solvents. Hexachlorocerate(IV) species are indefinitely stable in thionyl chloride solution and can be obtained by heating $CeCl_3(H_2O)_7$ in thionyl chloride containing soluble chloride, as recently indicated by us.[8]

Conductometric Behaviour.—Solutions of both UCl_4 and [$UCl_4(ipae)_2$] in cold acetone (0 °C) were titrated with cold acetone solutions of a number of arsine oxide, phosphine oxide, and sulphoxide ligands and their behaviour was followed conductometrically in order to determine to what extent [$UCl_4(ipae)_2$] solutions could be effectively regarded as equivalent to those of UCl_4 itself. Close similarities were found, except in the case of dmso where the auto-ionization [12] of UCl_4 appears to be somewhat suppressed by the presence of ipae. It can therefore be assumed that the behaviour of [$CeCl_4(ipae)_2$] will be very similar to that of the unstable $CeCl_4$ in acetone solution, especially for the stronger ligands. The conductometric behaviours of cold (0 °C) 0.0030 mol dm^{-3} acetone solutions of [$CeCl_4(ipae)_2$] and [$UCl_4(ipae)_2$], when titrated with the same ligands, are almost the same within experimental error. The curves for some of these ligands, *viz.* tpao, tdpo, and dmso, are given in Figure 3. The close similarity between the co-ordination behaviour of the two tetrachlorides is clear, especially if these are compared [12] with those of $ThCl_4$. The lowering of the conductivity up to a metal-to-ligand ratio of 1 : 2 as a result of formation of six-co-ordinate [MCl_4L_2] species (L = tpao or tdpo) followed by varying degrees of ionization,[18] depending on the donor strength of the neutral ligand [14] (*e.g.* As=O or P=O) or auto-ionization, in cases where the [MCl_4L_2] species are not very stable {*e.g.* $[MCl_2(dmso)_6]^{2+}[MCl_6]^{2-}$} applies equally well to $CeCl_4$ and UCl_4. Only the UCl_4 complexes precipitated before metal-to-ligand ratios of 1 : 4 were reached (points where dotted curves stop coincide with precipitation).

Comparison between $CeCl_4$ *and* UCl_4 *Complexes.*—A comparative study of solubility of MCl_4 complexes was made. To each of two separate equimolar methanolic solutions of $[Hpy]_2[MCl_6]$ (py = pyridine) (M = U or Ce) at 20 °C was added an equimolar solution of the same ligand in 5% excess. Both solutions were subsequently cooled in ice. The preparative yields of the UCl_4 complexes, obtained in this way, were always much higher than those of their cerium analogues, *e.g.* for [$MCl_4(tpao)_2$] 90 and 36%, and for [$MCl_4(bmse)_2$] 62 and 42%, respectively. This consistent, significantly greater solvoscopic character of $CeCl_4$ complexes cannot readily be explained in the light of the great similarity in co-ordination properties between UCl_4 and $CeCl_4$, *e.g.* similar tendencies for ionization, auto-ionization, i.r. shifts of complexed ligands, and stoicheiometries of complexes, as well as the apparent similarity in size of U^{4+} and Ce^{4+} in their chloro-complexes. Although differences in ionic radii amongst quadrivalent actinoids are greater [U^{IV} 0.93, Np^{IV} 0.92, Pu^{IV} 0.90 Å] smaller differences are observed in preparative yields and solubilities of their tetrachloro-complexes [19–21] than found between U^{IV} and Ce^{IV}.

In conclusion, the results of this study suggest that the co-ordination chemistries of cerium(IV) and uranium(IV) are as similar as conceivable for tetravalent lanthanoids and actinoids, and that the existing small differences should be interpreted in terms of differences between 4*f* and 5*f* transition-metal character.

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