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Short communication

Synthesis and structure of $[CeF_4(Me_2SO)_2]$—A rare neutral ligand complex of a lanthanide tetrafluoride☆

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ABSTRACT

Hydrated cerium(IV) fluoride dissolves in hot dimethylsulfoxide to form yellow $[CeF_4(Me_2SO)_2]$, the X-ray structure of which reveals a chain polymer with eight-coordinate cerium bound to two terminal and four bridging fluorines and two O-bonded Me_2SO molecules. The complex was also characterised by IR, ^1H and $^{19}F\{^1H\}$ NMR and UV/visible spectroscopies. Attempts to use $[CeF_4(Me_2SO)_2]$ as a synthon to prepare other complexes with phosphine oxides or 2,2′-bipyridyl were unsuccessful. Thorium(IV) fluoride hydrate does not react with boiling dmso.

1. Introduction

Although their study was neglected for many years, recent work has revealed an extensive coordination chemistry of early transition metal fluorides, including TiF_4, ZrF_4, HfF_4, NbF_5, TaF_5 and WF_6 [1]. In marked contrast, the coordination chemistry of lanthanide fluorides is limited to a range of fluorometallate anions, and a few, usually poorly characterised hydrates [1,2]. One crown ether complex has been described, $[Gd_4F_7(15\text{-crown-}5)_4][AsF_6]_5{\cdot}6SO_2$ obtained from $[GdF(AsF_6)_2]$ and 15-crown-5 in liquid SO_2 [3]. Of the three tetrafluorides, PrF_4 and TbF_4 are readily hydrolysed and reduced, but CeF_4 is very stable [2]. We recently reported that although the anhydrous MF_4 (M=Zr or Hf) are intractable inert polymers, the hydrates $MF_4{\cdot}2H_2O$ dissolve easily in hot Me_2SO or dmf (L), to form $[MF_4(L)_2]$ which are suitable synthons to prepare a range of complexes with N- or O-donor ligands [4]. We report here the results of our work attempting to extend this approach to CeF_4 and ThF_4, including the preparation, properties and structures of a rare coordination complex of an f-block tetrafluoride.

2. Results and discussion

Anhydrous CeF_4 is an inert and extensively F-bridged polymer, but by analogy with the Zr/Hf chemistry [4], we proposed that using the hydrate $CeF_4{\cdot}xH_2O$ ($x \leq 1$ and varies with the drying method) [5,6], may offer a possible route into the chemistry. Commercial samples of the hydrate (Alfa) were particularly unreactive, dissolving only very slightly in hot Me_2SO. However, addition of 40% aqueous HF to a hot aqueous solution of $Ce(SO_4)_2$, gave a cream precipitate of $CeF_4{\cdot}xH_2O$ [5], which after separation and drying *in vacuo*, dissolved easily in hot Me_2SO to give a yellow solution. Removal of the solvent from the Me_2SO solution or allowing the solution to stand for some days, produced a bright yellow powder, $[CeF_4(Me_2SO)_2]$. The hydrate, $CeF_4{\cdot}xH_2O$, did not dissolve in boiling thf, *N*,*N*-dimethylformamide (dmf) or MeCN. Powder X-ray diffraction patterns recorded for the commercial and the freshly synthesised samples of $CeF_4{\cdot}xH_2O$ were generally similar to that reported [5], although the former had much sharper diffraction lines, indicative of increased crystallinity. It is likely that the lower crystallinity/particle size of the freshly prepared sample results in its higher reactivity.

Very small crystals of $[CeF_4(Me_2SO)_2]$ were deposited from Me_2SO solutions at room temperature that were left to stand for several days. Several crystals from different batches were examined, and all gave rather poor diffraction patterns, with some evidence of disorder. The crystal structure was solved in the orthorhombic space group $Pca2_1$ and revealed a polymeric chain structure which consists of eight-coordinate cerium coordinated to two terminal and four bridging fluorines, with two *cis*-disposed Me_2SO groups alternating "*anti*" along the zig-zag chain. The asymmetric unit, in which each of the Me_2SO ligands is disordered over two sites, is shown in Fig. 1 and part of the chain in Fig. 2.

The bridging Ce–F distances (2.295(10)–2.385(11) Å) can be compared with those in anhydrous CeF_4, which contains

☆ Added in proof, CeF4(NH3)4.NH3 has been made and structurally characterised. F. Kraus, S. A. Baer, Z. Naturforsch. 66b (2011) 868-870.

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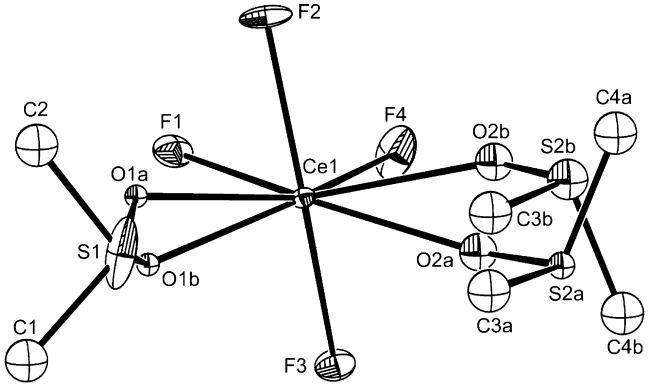

Fig. 1. The structure of $[CeF_4(Me_2SO)_2]$ showing the atom labelling scheme for the asymmetric unit. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. The disordered Me_2SO groups are also shown. Selected bond lengths (Å) and angles (°) Ce1–F1 = 2.114(9), Ce1–F4 = 2.120(9), Ce1–F3a = 2.261(11), Ce1–F2 = 2.295(10), Ce1–F2a = 2.320(10), Ce1–F3 = 2.385(11) Ce1–O = 2.33(4)–2.52(4), F1–Ce1–F4 = 83.0(4), F3–Ce1–F2a = 67.7(3), F3b–Ce1–F2 = 84.6(3).

eight-coordinate cerium in a square antiprismatic environment with vertex sharing fluorines (2.200(3)–2.304(4) Å) [7]. As expected the terminal Ce–F distances are slightly shorter (2.114(9), 2.120(9) Å) with the terminal fluorines disposed *cis* (<F1–Ce1–F4 = 83.0(4)°).

The IR spectrum of $[CeF_4(Me_2SO)_2]$ is simple, showing ν(SO) at 1034 and 993 cm^{-1}, consistent with O-coordinated Me_2SO [8], and bands assigned to stretching modes of the terminal Ce–F at 425(s), 380(m), and bridging Ce–F–Ce at 290(m) cm^{-1}. The ^1H NMR spectra in CD_2Cl_2, d^7-dmf or d^6-dmso show singlet Me resonances, but the $^{19}F\{^1H\}$ NMR spectrum in d^7-dmf contains two singlets of equal intensity at −182.2 and −183.3 ppm, which we tentatively suggest are due to a *pseudo*-octahedral *cis*-$[CeF_4(Me_2SO)_2]$, whereas in d^6-Me_2SO a singlet at −148.7 ppm was observed. The latter would suggest that in the strongly coordinating Me_2SO solution, a higher coordination number complex, possibly eight-coordinate as in $[CeF_4(Me_2SO)_4]$, may be present. A convincing spectrum could not be obtained in (non-coordinating) CD_2Cl_2 due to very poor solubility. The diffuse reflectance UV–visible spectrum

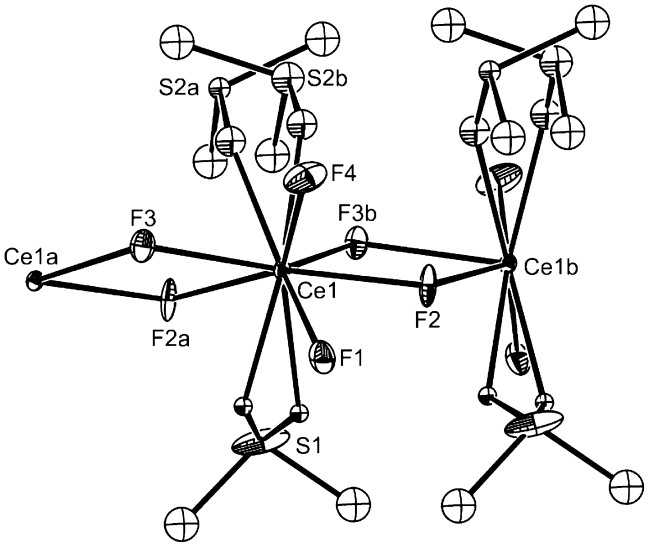

Fig. 2. The structure of $[CeF_4(Me_2SO)_2]$ showing part of the chain in the *z* direction. The disordered Me_2SO groups are also shown. Ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity. Symmetry operations: $a = 1/2 - x, y, z + 1/2$; $b = 1/2 - x, y, z - 1/2$.

of $[CeF_4(Me_2SO)_2]$ contained a broad feature at ~25 000 cm^{-1} which is responsible for the yellow colour. This is assigned as a $O(\pi) \rightarrow Ce(4f)$ charge transfer transition, and there is a band at ~37 000 cm^{-1} corresponding to the $\pi \rightarrow \pi^*$ of the sulfoxide group. The $F(\pi) \rightarrow Ce(4f)$ charge transfer bands are expected to lie in the far UV region [9].

The $[CeF_4(Me_2SO)_2]$ proved to be disappointing as a synthon for other complexes. As might have been expected based on similarity with $[MF_4(Me_2SO)_2]$ (M=Zr or Hf) [4], in Me_2SO solution (*i.e.* in the presence of a large excess of Me_2SO) it did not react with Ph_3PO or 2,2′-bipyridyl, with the $[CeF_4(Me_2SO)_2]$ being recovered unchanged after removal of the solvent. However, unlike the Zr and Hf species, suspensions of $[CeF_4(Me_2SO)_2]$ in CH_2Cl_2 or dmf also failed to react with the phosphine oxide and diimine ligands. Melting Ph_3PO or 2,2′-bipyridyl with $[CeF_4(Me_2SO)_2]$ *in vacuo* also failed to displace the Me_2SO. The $[MF_4(Me_2SO)_2]$ (M=Zr or Hf) form discrete dimers $[(Me_2SO)_2F_3M(\mu\text{-}F)_2MF_3(Me_2SO)_2]$ [4], which contrast with the chain polymer structure evident for $[CeF_4(Me_2SO)_2]$, and the unreactivity of the latter in CH_2Cl_2 or dmf may be due, at least in part, to the much lower solubility resulting from the polymeric structure, whilst in Me_2SO solution, the large excess of strongly competitive Me_2SO prevents its replacement.

Although limited in number, neutral ligand complexes of actinide fluorides are known [1], although none with ThF_4. Hydrated thorium fluoride, $ThF_4{\cdot}xH_2O$, was prepared as described [10,11], by precipitation from a hot aqueous $Th(NO_3)_4$ solution by 40% aqueous HF. However, the $ThF_4{\cdot}xH_2O$ so produced did not dissolve even on prolonged reflux in Me_2SO, the recovered solid showed an unchanged IR spectrum with no evidence for incorporation of Me_2SO. The trend of diminishing reactivity appears to continue: Zr, Hf >> Ce > Th.

3. Conclusions

The first example of a lanthanide tetrafluoride coordinated to a neutral organic ligand, $[CeF_4(Me_2SO)_2]$, has been prepared in good yield and fully characterised, revealing a fluoride-bridged chain polymer with terminal O-coordinated dmso ligands and eight-coordinate Ce(IV). Attempts to extend this approach to other O- or N-donor ligands have been unsuccessful. Studies of the coordination chemistry of transition metal tetrafluorides including TiF_4, ZrF_4 and HfF_4 have shown that the systems often prefer formation of fluoride bridges over coordination to neutral ligands [1,4,12] and this is particularly evident in attempts to prepare complexes of these hard oxophilic Lewis acids with soft donor groups. In the f-block the much reduced covalent contributions to the bonding will also make binding of neutral ligands less favoured. The preference for fluorine bridges even over coordination of hard neutral ligands appears to be greater for CeF_4 and ThF_4 than for the d-block metals, and this is likely to limit their coordination chemistry. In having a readily accessible M(IV) state, cerium is an atypical lanthanide, and the coordination chemistry of the trivalent LnF_3 certainly merit further study.

4. Experimental

$CeF_4{\cdot}xH_2O$ (Alfa), $Ce(SO_4)_2{\cdot}2H_2O$ (BDH), 40% aqueous HF and Me_2SO (Aldrich) and $Th(NO_3)_4{\cdot}xH_2O$ (BDH) were used as received. Infrared spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer Spectrum 100 over the range 4000 – 200 cm^{-1}. ^1H NMR spectra were recorded from CD_2Cl_2, d^7-dmf or d^6-Me_2SO solutions using a Bruker AV300 spectrometer and are referenced to the residual protio-solvent signal. $^{19}F\{^1H\}$ NMR spectra were recorded using a Bruker DPX400 spectrometer and are referenced to external $CFCl_3$. UV–visible spectra were recorded by diffuse reflectance on the neat samples using a Perkin

Elmer Lambda 19 spectrometer. Microanalyses were undertaken by London Metropolitan University.

4.1. $CeF_4{\cdot}xH_2O$

$Ce(SO_4)_2{\cdot}4H_2O$ (1.2 g, 3.0 mmol) was dissolved in hot water (200 mL, ~90 °C) in a Teflon beaker, and 40% aqueous HF (5 mL) added with vigorous stirring. A pale cream precipitate formed immediately, and the solution was allowed to cool and then stand at ambient temperatures for 24 h. The cream precipitate was filtered off, rinsed with cold water (20 mL) and dried in vacuo. Yield: 0.6 g, ~90%. IR spectrum (Nujol/cm^{-1}): 3400(vbr), 1630(m) H_2O, 376(vbr) Ce–F.

4.2. $[CeF_4(Me_2SO)_2]$

Me_2SO (25 mL) was heated to ~90 °C and finely powdered $CeF_4{\cdot}xH_2O$ added with stirring until no more dissolved, producing a clear yellow solution. The hot solution was decanted from any undissolved solid, concentrated *in vacuo* to ~5 mL and allowed to stand undisturbed for 24 h. The yellow powder produced was filtered off and dried *in vacuo*. Yield: ~60%. The compound can also be isolated by pumping the solution to dryness, but is sometimes obtained as a rather sticky solid by this route. Anal: Calc. for $C_4H_{12}CeF_4O_2S_2$ (372.4): C, 12.9; H, 3.3. Found: C, 12.8; H, 3.2%. IR (Nujol/cm^{-1}): 1034(s), 993(m) S–O, 425(s), 380(m) Ce–F, 290(m) Ce–F–Ce. ^1H NMR (CD_2Cl_2, 298 K): 2.56 (s); (d^7-dmf, 298 K): 2.55 (s); (d^6-Me_2SO, 298 K): 2.52 (s). $^{19}F\{^1H\}$ NMR (d^7-dmf, 298 K): −182.2 (s), [F], −183.3 (s), [F]; (d^6-Me_2SO, 298 K): −148.7 (s).

4.3. $ThF_4{\cdot}xH_2O$

This was prepared similarly to the cerium salt and isolated as a white powder, by adding 40% HF to a hot solution of $Th(NO_3)_4$ in water [10]. After standing for 12 h the white solid was filtered off, rinsed with cold water and dried *in vacuo*. IR (Nujol/cm^{-1}): 3500 (vbr,s), 1620(br) H_2O, 355(vbr) Th–F.

4.4. X-ray experimental

Crystals of $[CeF_4(Me_2SO)_2]$ were obtained as described above. Data collection used a Rigaku AFC12 goniometer equipped with an enhanced sensitivity (HG) Saturn724+ detector using a FR-E+ SuperBright molybdenum rotating anode generator with VHF Varimax optics and with the crystal held at 100 K (N_2 cryostream). Data were collected for several different crystals, but were of modest quality; the data analysed appeared the best quality available. Structure solution [13] and refinement [14] presented some problems. The data were collected as orthorhombic and with systematic absences consistent with (non-standard settings) $Pca2_1$ (#29) and Pmca (#57). An attempted solution in Pbcm (#57) gave an encouragingly low CFOM and RE (0.036 and 0.20) and a Ce atom position on a 4d site with mirror symmetry. The model developed showing four F atoms and two disordered Me_2SO ligands where S and O atoms in both ligands appeared in difference electron-density maps as two symmetry related peaks and with rather complicated C atom positions. Looking at the structure showed the Ce chain with bridging F atoms, but the space group symmetry generated four bridging F (sof = 0.5) between adjacent Ce atoms. However, with $R1 = 0.067$ for all data out to 2θ of 55°, the disordered structure looked promising. Repeating the structure determination in $Pca2_1$ (#29) followed a similar path with low CFOM (0.026) and again the disordered Me_2SO ligands, although S1 was only found as a single peak, but with two well-defined C atoms for each of the S atoms. Probably because of the approximate centrosymmetric nature of the crystal, refinement showed quite large correlation coefficients and needed restrictions on the refined parameters and DFIX on S–C distances. The final structure was very similar to the centrosymmetric model, but the bridging F atoms were not disordered. The fit to the data was marginally better ($R1 = 0.064$) and the C atom geometry at S was better. H atoms were added to the model in geometrical positions using the default C–H distance. The three largest Q-peaks were close to the Ce1 (within *ca.* 1 Å). The data are reported in the space group $Pca2_1$.

Crystal data: Formula $C_4H_{12}CeF_4O_2S_2$, formula weight 372.38, crystal system orthorhombic $Pca2_1$ (#29), $a = 13.520(4)$, $b = 10.984(3)$, $c = 7.434(2)$ Å, $\alpha = 90$, $\beta = 90$, $\gamma = 90°$, $V = 104.0(5)$ Å^3, $Z = 4$, $F(0\,0\,0) = 712$, $\mu = 4.525$ mm^{-1}, reflections collected = 3452, Rint = 0.037, unique reflections = 1857, no. of parameters = 97, restraints = 7, final R [$I > 2\sigma(I)$]: $R1 = 0.064$, $wR2 = 0.069$; R (all data): $R1 = 0.152$, $wR2 = 0.158$.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2013.10.014.

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