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Halide-abstraction reactions of tin(IV) and lanthanide(III) chlorides in tetrahydrofuran: crystal and molecular structures of $[LnCl_2(thf)_5][SnCl_5(thf)]$ where Ln = Ce, Gd or Yb

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It has been established that halide abstraction from several lanthanide(III) chlorides can be effected by tin tetrachloride. Direct treatment (1 : 1) of $LnCl_3$ where Ln = Ce, Gd or Yb with $SnCl_4$ in tetrahydrofuran (thf) provided colourless compounds of the generic type $LnSnCl_7(thf)_6$ which have been identified by X-ray crystallography as ionic salts [*trans*-$LnCl_2(thf)_5$][$SnCl_5(thf)$]. The individual seven-co-ordinate cations feature a regular pentagonal-bipyramidal metal geometry in which a *trans*-$LnCl_2$ unit is surrounded by five thf molecules arranged in an equatorial plane. These co-ordinated solvent molecules adopt the familiar 'propeller-like' arrangement indicative of a skew as opposed to envelope ligand conformation. For Ln = Ce, Ce–Cl 2.697(2), Ce–O mean 2.495(5) Å; for Ln = Gd, Gd–Cl 2.608(2), Gd–O mean 2.415(4) Å; for Ln = Yb, Yb–Cl 2.5375(13), Yb–O mean 2.346(4) Å. The six-co-ordinate $[SnCl_5(thf)]^-$ anions common to the series show a two-fold axis of symmetry containing the metal atom, the oxygen (thf) atom and a chloride atom mutually *trans* to the latter. Bond distances for Ln = Ce, *i.e.* Sn–O 2.276(7), Sn–Cl mean 2.399(2) Å, are typical for the series.

In previous studies of halide transfer reactions we have utilized $SbCl_5$ in acetonitrile solution as a convenient abstractor for a range of covalent metal halides, *i.e.*, $MCl_n + SbCl_5 \longrightarrow [MCl_{n-1}][SbCl_6]$. The resulting cation can be stabilized either directly by solvent (L) molecules or, indirectly, following the addition of a suitable oxacrown and/or aza macrocyclic ligand, *e.g.* M = Ti,[1] *fac*-$[TiCl_3(MeCN)_3]^+$; M = Sc,[2] $[ScCl_2L^1]^+$ (L^1 = 18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane); M = Gd,[3] $[GdCl_2(L^2)(MeCN)]^+$ (L^2 = dibenzo-18-crown-6 = 6,7,9,10,18,20,21-octahydrodibenzo[*b*,*k*][1,4,7,10,13,16]hexaoxacyclooctadecane); M = Pr,[4] $[PrCl_2L^2(H_2O)]^+$; M = Sb,[5] $[SbCl_2(Me_3[9]aneN_3)]^+$ ($Me_3[9]aneN_3$ = 1,4,7-trimethyl-1,4,7-triazacyclononane). In several cases involving M = transition metal sequential removal of halide ions has been achieved resulting in the formation of a cation (solvated) series, *e.g.* $(cp)MCl_3 \longrightarrow (cp)MCl_2{}^+ \longrightarrow (cp)MCl^{2+} \longrightarrow (cp)M^{3+}$ where cp = η^5-C_5H_5 and M = Ti, Zr and Hf,[6] Nb[7] or Mo.[8] Equally Sobota and co-workers have shown that $SnCl_4$ in tetrahydrofuran (thf) solution can be used to remove halide ions from early transition-metal(III) chlorides, *e.g.* $MCl_3(thf)_3 + SnCl_4(thf)_2 \longrightarrow$ [*trans*-$MCl_2(thf)_4$][$SnCl_5(thf)$] where M = Ti,[9] V[10] or Cr.[10] For the reaction system $2FeCl_3$–$SnCl_2$–thf the initial redox $2Fe^{III}/Sn^{II} \longrightarrow 2Fe^{II}/Sn^{IV}$ is followed by halide abstraction $Fe^{II} \longrightarrow FeCl^+$ (as initiated by Sn^{IV}) resulting in the formation of the dinuclear confacial bioctahedral cation $[Fe_2(\mu\text{-}Cl)_3(thf)_6]^+$.[10]

The stimulus for this investigation was whether the acceptor properties of $SnCl_4$ would also embrace halide abstraction from the lanthanide elements. Herein we describe the reactions of $SnCl_4$ and $LnCl_3$ where Ln = Ce, Gd or Yb in tetrahydrofuran and the subsequent identification (X-ray crystallography) of the products $LnSnCl_7(thf)_6$ as the ionic salts [*trans*-$LnCl_2(thf)_5$][$SnCl_5(thf)$] respectively.

Experimental

All manipulations were carried out under a dinitrogen and/or argon atmosphere using standard Schlenk, vacuum-line and glove-box techniques. Tetrahydrofuran was predried over sodium wire then distilled from potassium prior to use. Hexane was predried over CaH_2 and also distilled from potassium. The lanthanide trihalide–thf adducts were prepared from commercially available lanthanide trihalide hydrates by heating at reflux with thionyl chloride, in the presence of an excess of tetrahydrofuran.[11] Tin tetrachloride was purchased from Aldrich Chemical Co. and used without further purification. The IR spectra were recorded as Nujol mulls between CsI plates using a Perkin-Elmer 580B instrument, and elemental analyses were carried out using a Leeman Lab Inc., PS 1000 sequential inductively coupled plasma (ICP) spectrometer and a CE 440 elemental (C, H, N) analyser.

Preparations

[$CeCl_2(thf)_5$][$SnCl_5(thf)$]. Dropwise addition of $SnCl_4$ (1.02 g, 3.92 mmol) to tetrahydrofuran (50 cm^3) at 0 °C led to the formation of a brown solution with a large amount of white precipitate. To this chilled, stirred suspension was introduced a solution of $[CeCl_3(thf)_2]$ (1.53 g, 3.92 mmol) in tetrahydrofuran (30 cm^3). The resulting slurry was heated at reflux for 6 h, by which time the bulk of the material had dissolved. Filtration of the still warm reaction mixture and subsequent cooling gave the required compound as a mass of colourless spine crystals. Yield: 3.04 g, 83% (Found: C, 30.92; H, 5.27; Cl, 26.21. Calc. for $C_{24}H_{48}CeCl_7O_6Sn$: C, 30.68; H, 5.15; Cl, 26.41%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1302w, 1257w, 1171w, 1040m, 1003s [ν_{asym}(COC)], 953m, 833s [ν_{sym}(COC)], 677w, 454w (ligand) and 290s (br).

[$GdCl_2(thf)_5$][$SnCl_5(thf)$]. Following the same procedure as above, a mixture of $SnCl_4$ (0.84 g, 3.23 mmol) and $[GdCl_3(thf)_4]$ (1.76 g, 3.08 mmol) in tetrahydrofuran (30 cm^3) was heated at reflux for 6 h. Filtration of the hot reaction liquors and cooling to −15 °C produced a large amount of white microcrystalline solid. This was filtered off, washed with hexane (2 × 25 cm^3) and then pumped to dryness *in vacuo* for 3 h. Recrystallization from tetrahydrofuran in the presence of activated charcoal gave the required compound as colourless cuboid crystals. Yield 2.51 g, 85% (Found: C, 30.38; H, 5.04; Cl, 26.05. Calc. for $C_{24}H_{48}Cl_7GdO_6Sn$: C, 30.13; H, 5.06; Cl, 25.94%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1300w, 1253w, 1170w, 1040m, 1008s, [ν_{asym}(COC)], 953m, 918m, 833s [ν_{sym}(COC)], 680w, 466w (ligand) and 295s (br).

[$YbCl_2(thf)_5$][$SnCl_5(thf)$]. As above, a mixture of $SnCl_4$ (1.13 g, 4.34 mmol) and $[YbCl_3(thf)_3]$ (2.12 g, 4.28 mmol) in tetrahydrofuran (75 cm^3) was heated at reflux for 6 h. The reaction mixture was filtered whilst still hot, then allowed to cool to room temperature to provide a white solid which was filtered off, washed with hexane (3 × 20 cm^3) and pumped to dryness *in vacuo* for 2 h. The required compound was obtained as colourless air-sensitive cuboid crystals, following recrystallization from tetrahydrofuran in the presence of activated charcoal. Yield: 3.30 g, 78% (Found: C, 29.83; H, 4.95; Cl, 25.71. Calc. for $C_{24}H_{48}Cl_7O_6SnYb$: C, 29.64; H, 4.97; Cl, 25.52%). $\tilde{\nu}_{max}/cm^{-1}$ (Nujol) 1300w, 1260w, 1170w, 1040m, 1003s [ν_{asym}(COC)], 918m, 838s [ν_{sym}(COC)], 678w (ligand) and 292s (br).

X-Ray crystallography

Crystal data. [$CeCl_2(thf)_5$][$SnCl_5(thf)$]. $M = 939.58$, $T = 180(2)$ K, $\lambda = 0.710\,73$ Å, monoclinic, space group $P2/c$, $a = 12.4113(6)$, $b = 11.1468(6)$, $c = 13.7330(7)$ Å, $\beta = 104.113(2)°$, $U = 1842.6(2)$ Å^3, $Z = 2$, $D_c = 1.694$ mg m^{-3}, $\mu = 2.438$ mm^{-1}, $F(000) = 934$. Crystal size 0.21 × 0.14 × 0.10 mm; θ range for data collection 1.69–25.50°; index ranges $-16 \leqslant h \leqslant 16, -14 \leqslant k \leqslant 14, -18 \leqslant l \leqslant 7$; reflections collected 9271; independent reflections 3427 [R(int) = 0.075]; data, restraints, parameters 3427, 0, 179; goodness of fit on F^2 1.03; $R(F)$ [$I > 2\sigma(I)$] = 0.054, $wR(F^2) = 0.109$; largest difference peak and hole 0.72 and −0.68 e Å^{-3}.

[$GdCl_2(thf)_5$][$SnCl_5(thf)$]. $M = 956.71$, $T = 200(2)$ K, $\lambda = 0.710\,73$ Å, monoclinic, space group $P2/c$, $a = 12.2924(6)$, $b = 11.1255(5)$, $c = 13.7155(7)$ Å, $\beta = 104.25(2)°$, $U = 1818.0(2)$ Å^3, $Z = 2$, $D_c = 1.748$ mg m^{-3}, $\mu = 3.043$ mm^{-1}, $F(000) = 946$. Crystal size 0.40 × 0.10 × 0.07 mm; θ range for data collection 1.71–26.00°; index ranges $-16 \leqslant h \leqslant 13$, $-14 \leqslant k \leqslant 14$, $-15 \leqslant l \leqslant 18$; reflections collected 9564; independent reflections 3567 [R(int) = 0.0447]; data, restraints, parameters 3567, 0, 179; goodness of fit on F^2 1.03; $R(F)$ [$I > 2\sigma(I)$] = 0.041, $wR(F^2)$ = 0.092; largest difference peak and hole 0.65 and −0.89 e Å^{-3}.

[$YbCl_2(thf)_5$][$SnCl_5(thf)$]. $M = 972.50$, $T = 180(2)$ K, $\lambda = 0.710\,73$ Å, monoclinic, space group $P2/c$, $a = 12.1373(6)$, $b = 11.1000(5)$, $c = 13.7137(6)$ Å, $\beta = 104.220(1)°$, $U = 1790.95(14)$ Å^3, $Z = 2$, $D_c = 1.803$ mg m^{-3}, $\mu = 3.848$ mm^{-1}, $F(000) = 958$. Crystal size 0.50 × 0.18 × 0.14 mm; θ range for data collection 1.73–28.58°; index ranges $-14 \leqslant h \leqslant 15$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 17$; reflections collected 10 401; independent reflections 4170 [R(int) = 0.055]; data, restraints, parameters 4170, 0, 179; goodness of fit on F^2 1.000; $R(F)$ [$I > 2\sigma(I)$] = 0.047, $wR(F^2)$ = 0.084; largest difference peak and hole 0.71 and −0.86 e Å^{-3}.

The crystallographic measurements were made using a Siemens SMART area-detector diffractometer and graphite-monochromated Mo-Kα radiation. The temperature of the crystal was controlled using an Oxford Cryosystem Cryostream Cooler. Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal to detector distance was 5.01 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection; the decay was negligible in each case. Empirical absorption corrections (using SADABS)[12] were applied in all cases. The structures were solved using direct methods (SHELXTL PC)[13] and refined with anisotropic displacement parameters by full-matrix least squares on F^2 (SHELXL 96).[14] Hydrogen atoms were added at calculated positions and refined using a riding model. Siemens SMART[15] and SAINT[16] programs were used to control and integrate data collection.

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Results and Discussion

The reactions of $SnCl_4$ (1 mol) with the anhydrous lanthanide(III) chlorides $LnCl_3$ (1 mol) where Ln = Ce, Gd or Yb proceed smoothly in tetrahydrofuran solution with direct formation of the ionic salts [$LnCl_2(thf)_5$][$SnCl_5(thf)$]. Slow concentration of the mother-liquor with cooling provided colourless crystals of X-ray quality for Ln = Ce, Gd or Yb respectively. These products require careful handling; even under an inert atmosphere there is a tendency for a gradual discolouration and breakdown of crystallinity. The IR spectra of the products are almost identical and show intense bands at 1003–1008 [ν_{asym}-(C–O–C)], 833–838 [ν_{sym}(C–O–C)] and 290–295 cm^{-1} [ν(Sn–Cl)] characteristic for ring stretching of co-ordinated tetrahydrofuran molecules and tin–halogen stretching modes respectively.

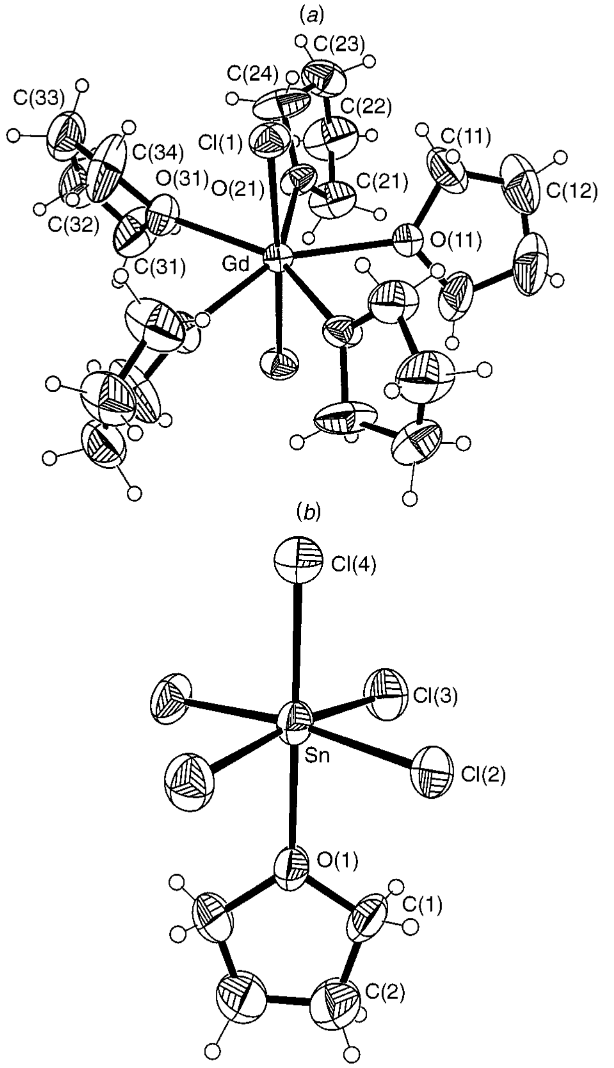

Fig. 1 Views of (*a*) the [$GdCl_2(thf)_5$]$^+$ cation and (*b*) the accompanying [$SnCl_5(thf)$]$^-$ anion. Atoms are represented by thermal vibration ellipsoids at the 50% level

The crystal structures form an isomorphous series with the contraction in unit-cell size following the lanthanide contraction. The structures contain discrete [$LnCl_2(thf)_5$]$^+$ cations and [$SnCl_5(thf)$]$^-$ anions; the molecular structure of the complex cation for Ln = Gd is illustrated in Fig. 1(*a*) (the Ln = Ce or Yb structures are very similar due to the isomorphism) and the molecular structure of the corresponding anion, [$SnCl_5(thf)$]$^-$ (common for the series Ln = Ce, Gd or Yb) is shown in Fig. 1(*b*). Several features emerge that merit comment. Each [$LnCl_2(thf)_5$]$^+$ cation is seven-co-ordinate and contains a *trans*-$LnCl_2$ unit with five solvent (tetrahydrofuran) molecules co-ordinated to the metal centre resulting in a pentagonal-bipyramidal geometry. As noted for similar seven-co-ordinate *trans*-$MCl_2(thf)_5$ units, *e.g.* M = Dy,[17] Y,[18] Tb[19] or Ce,[20] the equatorial quintet of solvent molecules adopt the familiar 'propeller-like' arrangement which is a reflection of a skew as opposed to envelope ligand conformation.

Table 1 Bond dimensions (Å) (mean) of $[LnCl_2(thf)_5]^+$ cations and related lanthanide(III) solvates

Compound*	Co-ordination number	Ln−Cl (terminal)	Ln−O (thf)	Ref.
$[CeCl_2(thf)_5]^+$	7	2.697(2)	2.485(7)–2.501(5) mean 2.495(5)	This work
$[CeCl_2(thf)_5]^+$	7	2.688(8)	2.493(13)	20
$[CeCl(\mu\text{-}Cl)_2(thf)_2]$	7	2.661(1)	2.500(3)	19
$[GdCl_2(thf)_5]^+$	7	2.608(2)	2.400(5)–2.420(4) mean 2.415(4)	This work
$[GdCl_3L^3{}_3]$	6	2.634(3)	—	21
$[GdCl_2L^2(MeCN)]^+$	9	2.632(2), 2.679(2) mean 2.656(2)	—	3
$[GdPhCl_2(thf)_4]$	7	2.650(7), 2.694(9) mean 2.677(8)	2.432(14), 2.584(14) mean 2.508(14)	22
$[GdCl_2(C_9H_7)(thf)_3]\cdot thf$	8	2.581(3), 2.735(4) mean 2.658(4)	2.392(6), 2.513(8) mean 2.429(8)	23
$[YbCl_2(thf)_5]^+$	7	2.5375(13)	2.327(5)–2.357(4) mean 2.346(4)	This work
$[\{YbCl_2(\mu\text{-}Cl)(thf)_2\}_2]$	6	2.490(3)	2.265(8)	24
$[YbCl_3(cap)(thf)_2]$	6	2.527(5)	2.304(6)	19
$[YbCl_3(thf)_3]$	6	2.52(5)	2.272(5)	25
$[YbCl_3(hmpa)_3]$	6	2.588(4)	—	26
$[Yb(\eta^5\text{-}C_5H_4Bu^t)_2Cl(thf)]$	8	2.539(3)	2.333(6)	27

* L^3 = 2,6-Dimethyl-4-pyrone; C_9H_7 = indenyl; cap = ε-caprolactone ($C_6H_{10}O_2$); hmpa = hexamethylphosphoramide $[(Me_2N)_3P{=}O]$.

The equatorial LnO_5 segments are coplanar and show high regularity with interligand bond angles close to the idealized values: *cis* O−Ln−O mean 72.2(1)° and *cis* O−Ln−Cl mean 90.0(1)° for Ln = Ce, Gd or Yb. Least-squares planes taken through the six atoms show root-mean-square deviations of 0.141 (Ln = Ce), 0.120 (Gd) and 0.103 Å (Yb).

The bond dimensions of these cations are remarkably consistent: in summary the Cl−Ln−Cl central unit is uniformly linear and the Ln−O (thf) bond distances show a very narrow range for each particular metal. The data are summarized in Table 1 which also includes relevant bond parameters for a collection of similar lanthanide(III) complexes to allow direct comparison(s). There is a discernible shortening in both the Ln−Cl and the Ln−O bond distances for $Ce^{III} \longrightarrow Gd^{III} \longrightarrow Yb^{III}$ consistent with the recognized atomic size contraction across the series.

For the $[SnCl_5(thf)]^-$ anions, previous examples show some subtle structural variation within the confines of the observed octahedral geometry: for the green salt $[trans\text{-}TiCl_2(thf)_4][SnCl_5(thf)]$ the anion exhibits a mirror plane containing the metal atom, three chlorine atoms and the tetrahydrofuran molecule which is disordered;[9] for the bright yellow $[Fe_2(\mu\text{-}Cl)_3(thf)_6][SnCl_5(thf)]$ there is only C_1 point symmetry;[10] for $[trans\text{-}CrCl_2(thf)_4][SnCl_5(thf)]$ the anion lies on a two-fold axis of symmetry containing the metal atom, the oxygen (thf) atom and the chlorine mutually *trans* to the ligand.[10] However it should be stressed that the actual bond dimensions are closely similar in all three cases. In the present instance a single pattern is observed throughout Ln = Ce, Gd or Yb: *vis-à-vis* the anions show a two-fold axis of symmetry containing the metal atom, the oxygen atom and the chlorine atom located in the mutually *trans* position. Typically for Ln = Ce, Sn−O 2.276(7), Sn−Cl mean 2.399(2) Å, *cis* O−Sn−Cl mean 85.83(6), *cis* Cl−Sn−Cl mean 91.93(7)°; a closely similar picture emerges for the other two cases where Ln = Gd or Yb. For direct comparison we note the dimensions of the anion where M = Ti, *i.e.* Sn−O 2.269(8), Sn−Cl mean 2.399(4) Å, *cis* O−Sn−Cl mean 85.9(2), *cis* Cl−Sn−Cl mean 92.3(1)°.

On the basis of the smooth reactions and high yields (78–85%) observed for the $SnCl_4$–$LnCl_3$–thf system, where Ln = Ce, Gd or Yb, it is clear that Sn^{IV} is a convenient and effective halide abstractor for these lanthanide(III) chlorides. Having established $[LnCl_2(thf)_5][SnCl_5(thf)]$ formation for this representative cross-section of the 4f block it seems most likely that such salt formation will extend across the whole series.

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