

Halide-abstraction reactions of tin(IV) and lanthanide(III) chlorides in tetrahydrofuran: crystal and molecular structures of $[\text{LnCl}_2(\text{thf})_5][\text{SnCl}_5(\text{thf})]$ where $\text{Ln} = \text{Ce}, \text{Gd}$ 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 $\text{Ln} = \text{Ce}, \text{Gd}$ or Yb with SnCl_4 in tetrahydrofuran (thf) provided colourless compounds of the generic type $\text{LnSnCl}_7(\text{thf})_6$ which have been identified by X-ray crystallography as ionic salts $[\text{trans-LnCl}_2(\text{thf})_5][\text{SnCl}_5(\text{thf})]$. 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 $\text{Ln} = \text{Ce}$, Ce-Cl 2.697(2), Ce-O mean 2.495(5) Å; for $\text{Ln} = \text{Gd}$, Gd-Cl 2.608(2), Gd-O mean 2.415(4) Å; for $\text{Ln} = \text{Yb}$, Yb-Cl 2.5375(13), Yb-O mean 2.346(4) Å. The six-co-ordinate $[\text{SnCl}_5(\text{thf})]^-$ 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 $\text{Ln} = \text{Ce}$, *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.*, $\text{MCl}_n + \text{SbCl}_5 \longrightarrow [\text{MCl}_{n-1}]^+[\text{SbCl}_6]^-$. 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.* $\text{M} = \text{Ti}$,¹ *fac*- $[\text{TiCl}_3(\text{MeCN})_3]^+$; $\text{M} = \text{Sc}$,² $[\text{ScCl}_2\text{L}]^+$ ($\text{L}^1 = 18\text{-crown-6} = 1,4,7,10,13,16\text{-hexaoxacyclooctadecane}$); $\text{M} = \text{Gd}$,³ $[\text{GdCl}_2(\text{L}^2)(\text{MeCN})]^+$ ($\text{L}^2 = \text{dibenzo-18-crown-6} = 6,7,9,10,18,20,21\text{-octahydrodibenzo}[b,k][1,4,7,10,13,16]\text{hexaoxacyclooctadecane}$); $\text{M} = \text{Pr}$,⁴ $[\text{PrCl}_2\text{L}^2(\text{H}_2\text{O})]^+$; $\text{M} = \text{Sb}$,⁵ $[\text{SbCl}_2(\text{Me}_3[9]\text{aneN}_3)]^+$ ($\text{Me}_3[9]\text{aneN}_3 = 1,4,7\text{-trimethyl-1,4,7-triazacyclononane}$). In several cases involving $\text{M} = \text{transition metal}$ sequential removal of halide ions has been achieved resulting in the formation of a cation (solvated) series, *e.g.* $(\text{cp})\text{MCl}_3 \longrightarrow (\text{cp})\text{MCl}_2^+ \longrightarrow (\text{cp})\text{MCl}^{2+} \longrightarrow (\text{cp})\text{M}^{3+}$ where $\text{cp} = \eta^5\text{-C}_5\text{H}_5$ and $\text{M} = \text{Ti}, \text{Zr}$ 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.* $\text{MCl}_3(\text{thf})_3 + \text{SnCl}_4(\text{thf})_2 \longrightarrow [\text{trans-MCl}_2(\text{thf})_4][\text{SnCl}_5(\text{thf})]$ where $\text{M} = \text{Ti}$,⁹ V ¹⁰ or Cr .¹⁰ For the reaction system $2\text{FeCl}_3\text{-SnCl}_2\text{-thf}$ the initial redox $2\text{Fe}^{\text{III}}/\text{Sn}^{\text{II}} \longrightarrow 2\text{Fe}^{\text{II}}/\text{Sn}^{\text{IV}}$ is followed by halide abstraction $\text{Fe}^{\text{II}} \longrightarrow \text{FeCl}^+$ (as initiated by Sn^{IV}) resulting in the formation of the dinuclear confacial bioctahedral cation $[\text{Fe}_2(\mu\text{-Cl})_3(\text{thf})_6]^+$.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 $\text{Ln} = \text{Ce}, \text{Gd}$ or Yb in tetrahydrofuran and the subsequent identification (X-ray crystallography) of the products $\text{LnSnCl}_7(\text{thf})_6$ as the ionic salts $[\text{trans-LnCl}_2(\text{thf})_5][\text{SnCl}_5(\text{thf})]$ 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

$[\text{CeCl}_2(\text{thf})_5][\text{SnCl}_5(\text{thf})]$. Dropwise addition of SnCl_4 (1.02 g, 3.92 mmol) to tetrahydrofuran (50 cm³) 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 $[\text{CeCl}_3(\text{thf})_2]$ (1.53 g, 3.92 mmol) in tetrahydrofuran (30 cm³). 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 $\text{C}_{24}\text{H}_{48}\text{CeCl}_7\text{O}_6\text{Sn}$: C, 30.68; H, 5.15; Cl, 26.41%). $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (Nujol) 1302w, 1257w, 1171w, 1040m, 1003s [$\nu_{\text{asym}}(\text{COC})$], 953m, 833s [$\nu_{\text{sym}}(\text{COC})$], 677w, 454w (ligand) and 290s (br).

$[\text{GdCl}_2(\text{thf})_5][\text{SnCl}_5(\text{thf})]$. Following the same procedure as above, a mixture of SnCl_4 (0.84 g, 3.23 mmol) and $[\text{GdCl}_3(\text{thf})_4]$ (1.76 g, 3.08 mmol) in tetrahydrofuran (30 cm³) 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 ($2 \times 25 \text{ cm}^3$) 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 $\text{C}_{24}\text{H}_{48}\text{Cl}_7\text{GdO}_6\text{Sn}$: C, 30.13; H, 5.06; Cl, 25.94%). $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (Nujol) 1300w, 1253w, 1170w, 1040m, 1008s, [$\nu_{\text{asym}}(\text{COC})$], 953m, 918m, 833s [$\nu_{\text{sym}}(\text{COC})$], 680w, 466w (ligand) and 295s (br).

$[\text{YbCl}_2(\text{thf})_5][\text{SnCl}_5(\text{thf})]$. As above, a mixture of SnCl_4 (1.13 g, 4.34 mmol) and $[\text{YbCl}_3(\text{thf})_3]$ (2.12 g, 4.28 mmol) in tetrahydrofuran (75 cm³) 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 ($3 \times 20 \text{ cm}^3$) 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 $\text{C}_{24}\text{H}_{48}\text{Cl}_7\text{O}_6\text{SnYb}$: C, 29.64; H, 4.97; Cl, 25.52%). $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (Nujol) 1300w, 1260w, 1170w, 1040m, 1003s [$\nu_{\text{asym}}(\text{COC})$], 918m, 838s [$\nu_{\text{sym}}(\text{COC})$], 678w (ligand) and 292s (br).

X-Ray crystallography

Crystal data. $[\text{CeCl}_2(\text{thf})_5][\text{SnCl}_5(\text{thf})]$. $M = 939.58$, $T = 180(2) \text{ K}$, $\lambda = 0.710 73 \text{ \AA}$, monoclinic, space group $P2_1/c$, $a = 12.4113(6)$, $b = 11.1468(6)$, $c = 13.7330(7) \text{ \AA}$, $\beta = 104.113(2)^\circ$, $U = 1842.6(2) \text{ \AA}^3$, $Z = 2$, $D_c = 1.694 \text{ mg m}^{-3}$, $\mu = 2.438 \text{ mm}^{-1}$, $F(000) = 934$. Crystal size $0.21 \times 0.14 \times 0.10 \text{ mm}$; θ range for data collection $1.69\text{--}25.50^\circ$; index ranges $-16 \leq h \leq 16$, $-14 \leq k \leq 14$, $-18 \leq l \leq 7$; reflections collected 9271; independent reflections 3427 [$R(\text{int}) = 0.075$]; 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 \AA^{-3} .

$[\text{GdCl}_2(\text{thf})_5][\text{SnCl}_5(\text{thf})]$. $M = 956.71$, $T = 200(2) \text{ K}$, $\lambda = 0.710 73 \text{ \AA}$, monoclinic, space group $P2_1/c$, $a = 12.2924(6)$, $b = 11.1255(5)$, $c = 13.7155(7) \text{ \AA}$, $\beta = 104.25(2)^\circ$, $U = 1818.0(2) \text{ \AA}^3$, $Z = 2$, $D_c = 1.748 \text{ mg m}^{-3}$, $\mu = 3.043 \text{ mm}^{-1}$, $F(000) = 946$. Crystal size $0.40 \times 0.10 \times 0.07 \text{ mm}$; θ range for data collection $1.71\text{--}26.00^\circ$; index ranges $-16 \leq h \leq 13$, $-14 \leq k \leq 14$, $-15 \leq l \leq 18$; reflections collected 9564; independent reflections 3567 [$R(\text{int}) = 0.0447$]; 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 \AA^{-3} .

$[\text{YbCl}_2(\text{thf})_5][\text{SnCl}_5(\text{thf})]$. $M = 972.50$, $T = 180(2) \text{ K}$, $\lambda = 0.710 73 \text{ \AA}$, monoclinic, space group $P2_1/c$, $a = 12.1373(6)$, $b = 11.1000(5)$, $c = 13.7137(6) \text{ \AA}$, $\beta = 104.220(1)^\circ$, $U = 1790.95(14) \text{ \AA}^3$, $Z = 2$, $D_c = 1.803 \text{ mg m}^{-3}$, $\mu = 3.848 \text{ mm}^{-1}$, $F(000) = 958$. Crystal size $0.50 \times 0.18 \times 0.14 \text{ mm}$; θ range for data collection $1.73\text{--}28.58^\circ$; index ranges $-14 \leq h \leq 15$, $-14 \leq k \leq 14$, $-16 \leq l \leq 17$; reflections collected 10 401; independent reflections 4170 [$R(\text{int}) = 0.055$]; 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 \AA^{-3} .

The crystallographic measurements were made using a Siemens SMART area-detector diffractometer and graphite-monochromated Mo-K α 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 SMART¹⁵ and SAINT¹⁶ 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 $\text{Ln} = \text{Ce}$, Gd or Yb proceed smoothly in tetrahydrofuran solution with direct form-

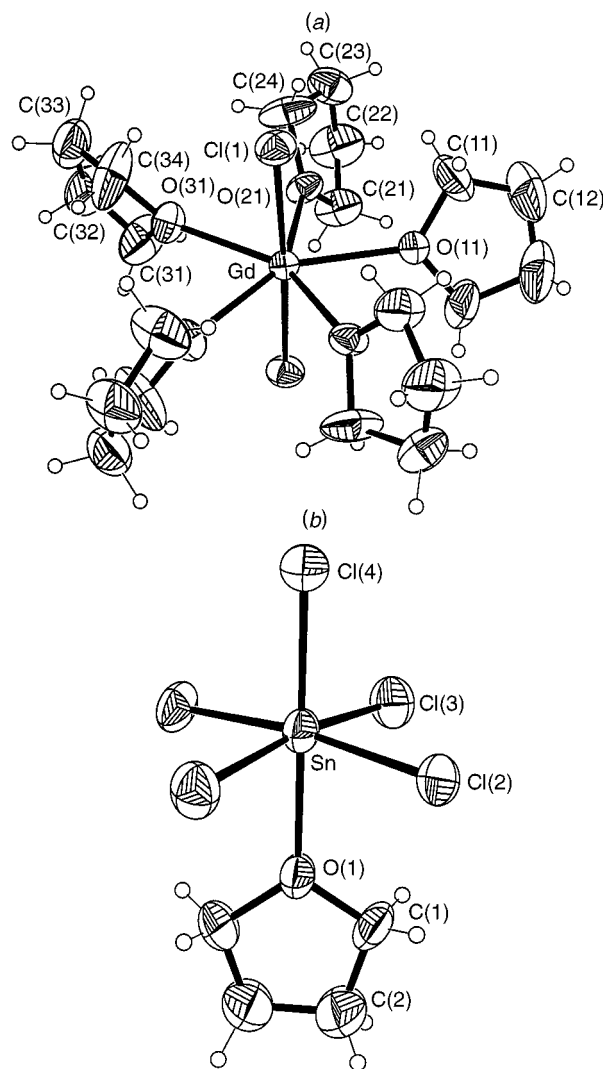


Fig. 1 Views of (a) the $[\text{GdCl}_2(\text{thf})_5]^+$ cation and (b) the accompanying $[\text{SnCl}_5(\text{thf})]^-$ anion. Atoms are represented by thermal vibration ellipsoids at the 50% level

ation of the ionic salts $[\text{LnCl}_2(\text{thf})_5][\text{SnCl}_5(\text{thf})]$. Slow concentration of the mother-liquor with cooling provided colourless crystals of X-ray quality for $\text{Ln} = \text{Ce}$, 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 [$\nu_{\text{asym}}(\text{C-O-C})$], 833–838 [$\nu_{\text{sym}}(\text{C-O-C})$] and 290–295 cm^{-1} [$\nu(\text{Sn-Cl})$] characteristic for ring stretching of co-ordinated tetrahydrofuran molecules and tin-halogen stretching modes respectively.

The crystal structures form an isomorphous series with the contraction in unit-cell size following the lanthanide contraction. The structures contain discrete $[\text{LnCl}_2(\text{thf})_5]^+$ cations and $[\text{SnCl}_5(\text{thf})]^-$ anions; the molecular structure of the complex cation for $\text{Ln} = \text{Gd}$ is illustrated in Fig. 1(a) (the $\text{Ln} = \text{Ce}$ or Yb structures are very similar due to the isomorphism) and the molecular structure of the corresponding anion, $[\text{SnCl}_5(\text{thf})]^-$ (common for the series $\text{Ln} = \text{Ce}$, Gd or Yb) is shown in Fig. 1(b). Several features emerge that merit comment. Each $[\text{LnCl}_2(\text{thf})_5]^+$ 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*- $\text{MCl}_2(\text{thf})_5$ units, e.g. $\text{M} = \text{Dy}$,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 [LnCl₂(thf)₃]⁺ cations and related lanthanide(III) solvates

Compound*	Co-ordination number	Ln–Cl (terminal)	Ln–O (thf)	Ref.
[CeCl ₂ (thf) ₃] ⁺	7	2.697(2)	2.485(7)–2.501(5) mean 2.495(5)	This work
[CeCl ₂ (thf) ₃] ⁺	7	2.688(8)	2.493(13)	20
[CeCl(μ-Cl) ₂ (thf) ₂]	7	2.661(1)	2.500(3)	19
[GdCl ₂ (thf) ₃] ⁺	7	2.608(2)	2.400(5)–2.420(4) mean 2.415(4)	This work
[GdCl ₃ L ³] ₃	6	2.634(3)	—	21
[GdCl ₂ L 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 ₉ H ₇)(thf) ₃]. 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) ₃] ⁺	7	2.5375(13)	2.327(5)–2.357(4) mean 2.346(4)	This work
[{YbCl ₂ (μ-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(η ³ -C ₅ H ₄ Bu') ₂ Cl(thf)]	8	2.539(3)	2.333(6)	27

* L³ = 2,6-Dimethyl-4-pyrone; C₉H₇ = indenyl; cap = ε-caprolactone (C₆H₁₀O₂); hmpa = hexamethylphosphoramide [(Me₂N)₃P=O].

The equatorial LnO₅ 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} → Gd^{III} → Yb^{III} consistent with the recognized atomic size contraction across the series.

For the [SnCl₅(thf)][−] anions, previous examples show some subtle structural variation within the confines of the observed octahedral geometry: for the green salt [*trans*-TiCl₂(thf)₄][SnCl₅(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 [Fe₂(μ-Cl)₃(thf)₆][SnCl₅(thf)] there is only C₁ point symmetry;¹⁰ for [*trans*-CrCl₂(thf)₄][SnCl₅(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 SnCl₄–LnCl₃–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 [LnCl₂(thf)₃][SnCl₅(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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