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Lanthanide(III)chloride–tetrahydrofuran solvates: structural patterns within the series $LnCl_3(THF)_n$, where $n = 2$, 3, 3.5 and 4: crystal and molecular structures of $[PrCl(\mu\text{-}Cl)_2(THF)_2]_n$, $[Nd(\mu\text{-}Cl)_3(H_2O)(THF)]_n$ and $GdCl_3(THF)_4$

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Abstract—Praseodymium(III), neodymium(III) and gadolinium(III) chloride adducts with tetrahydrofuran (THF) have been prepared and structurally characterized by X-ray crystallography. Removal of water from the corresponding hexahydrate $LnCl_3(H_2O)_6$ using thionyl chloride in the presence of excess THF provides light-green cubic crystals of $[PrCl_3(THF)_2]_n$ (**1**), blue block crystals of $[NdCl_3(H_2O)(THF)]_n$ (**2**) and colourless needle crystals of $GdCl_3(THF)_4$ (**3**). In **1** each praseodymium atom is seven-coordinate and is linked to (two) adjacent metal centres by double $(\mu\text{-}Cl)_2$ halogen bridging units, resulting in a polymeric chain structure. The metal geometry approximates to distorted pentagonal bipyramidal with Pr—Cl_{bridge} 2.852(6)–2.891(5), Pr—$Cl_{terminal}$ 2.668(6), Pr—O_{THF} 2.51(1) (axial), 2.53(2) Å (equatorial). In **2** the structure is a two-dimensional cross-linked polymer in which each neodymium atom is connected to (three) others *via* double $(\mu\text{-}Cl)_2$ halogen bridge bonds. The coordination sphere of each metal centre comprises six chlorine atoms [Nd—Cl_{bridge} 2.816(3)–2.938(3) Å] and two oxygen atoms belonging to a THF molecule [Nd—O, 2.548(6) Å] and a water molecule [Nd—O, 2.490(7) Å], respectively. Hydrogen bonding interactions involving halogen atoms and coordinated water molecules from adjacent metal units (intermolecular) are observed, O—H···Cl 3.147–3.350 Å. In **3** the molecular structure is based on a seven-coordinate pentagonal bipyramidal metal geometry in which two chlorides occupy the axial positions with the other chloride and the four solvate (THF) molecules making up the equatorial plane. Gd—Cl 2.60(2)–2.66(2), Gd—O 2.40(2)–2.52(3) Å. In addition, general comments concerning structural relationships within the series $LnCl_3(THF)_n$, where $n = 2$, 3, 3.5 and 4, are discussed. © 1997 Elsevier Science Ltd

Keywords: praseodymium(III); tetrahydrofuran; neodymium(III); adducts; gadolinium(III); (X-ray) structures.

The anhydrous chlorides $LnCl_3$ (Ln = Ce···Lu) are extensively used as precursors to a wide selection of lanthanide coordination compounds. Removal of water from the commercially available hydrates $LnCl_3 \cdot xH_2O$ ($x \geqslant 6$) using thionyl chloride as a dehydrating agent remains a convenient route to these important compounds [1]. Other dehydrating agents that have been used include alkyl formates [2] and 2,2-dimethoxypropane [3]. When the dehydration is carried out in the presence of a strong donor solvent (S), such as tetrahydrofuran (THF) or acetonitrile (MeCN), this leads to the formation of the appropriate adducts $LnCl_3(S)_n$, which are invariably well-defined crystalline materials; an alternative approach to these solvates involves recrystallization of the anhydrous chloride directly from the donor solvent. Specifically for the tetrahydrofuran adducts $LnCl_3(THF)_n$, representatives are known for the range $n = 1.5$, 2, 3, 3.5 and 4. A list of compounds is given in Table 1 covering those which have been characterized by analytical data and those which have been

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Table 1. Summary of LnCl$_3$(THF)$_n$ compounds (references)

Element \ n	1.5	2	3	3.5	4
Sc			⑪ $\boxed{17}$		
Y		⑫	$\boxed{17}$	⑫ $\boxed{13(a)(c)}$ ⑱	
La	$\boxed{13(a)(c)}$ ⑱	$\boxed{9}$			
Ce	$\boxed{13(a)}$	⑤ $\boxed{18}$			
Pr		◬ $\boxed{13(a)}$ $\boxed{18}$			
Nd	$\boxed{14}$	⑤ $\boxed{9}$ $\boxed{13(a)(c)}$ $\boxed{15}$			⑥
Pm					
Sm		$\boxed{9}$ $\boxed{13(a)(c)}$ $\boxed{14}$ $\boxed{18}$		$\boxed{13(c)}$	⑦
Eu		$\boxed{13(c)}$		$\boxed{13(c)}$	⑧
Gd		$\boxed{13(a)}$	$\boxed{9}$	$\boxed{13(c)}$	◬
Tb		$\boxed{13(c)}$		⑤ $\boxed{13(c)}$	
Dy		$\boxed{13(c)}$		④ $\boxed{13(a)(c)}$ $\boxed{18}$	
Ho				$\boxed{13(a)(c)}$	
Er				$\boxed{9}$ $\boxed{13(a)(c)}$ $\boxed{14}$ $\boxed{16}$	
Tm				$\boxed{13(c)}$	
Yb		⑨	$\boxed{9}$ $\boxed{13(a)(c)}$ $\boxed{14}$ $\boxed{16}$ $\boxed{18}$ ⑲		
Lu			⑩ $\boxed{13(c)}$		

○ X-ray crystal structure determinations; □ analytical data; ◬ this work.

identified structurally following X-ray diffraction studies. For comparison, examples of the prelanthanide elements of Group 3 (Sc, Y, La) are also included.

LnCl$_3$(THF)$_{1.5}$

Several examples of this particular group have been noted, but without structural recognition. In passing we note that examples of this stoichiometry for transition-metal elements are limited to the divalent compounds MCl$_2$(THF)$_{1.5}$, where M = Fe [20], Co [21], which feature a centrosymmetric tetrameric structure in which there are two different metal environments, i.e. octahedral MCl$_4$(THF)$_2$ and trigonal bipyramidal MCl$_4$(THF) centres.

LnCl$_3$(THF)$_2$

The two structural types that have been identified are dimeric [LnCl$_3$(THF)$_2$]$_2$ and polymeric [LnCl$_3$(THF)$_2$]$_n$; the former is based on edge–edge fused twin octahedra involving a central (μ-Cl)$_2$ halogen bridged unit, whereas the latter has a chain structure again with (μ-Cl)$_2$ units but with a seven-coordinate pentagonal bipyramidal metal geometry.

LnCl$_3$(THF)$_3$

The "classic" structure for this group is the mononuclear six-coordinate octahedral arrangement with possible *fac–mer* isomers. Other variations such as trigonal prismatic have not been observed.

LnCl$_3$(THF)$_{3.5}$

Structural characterization of this "unusual" stoichiometry reveals ion-pair formation involving pentasolvated LnCl$_2^+$ cations (CN = 7, pentagonal bipyramid) and disolvated LnCl$_4^-$ anions (CN = 6, octahedral).

$LnCl_3(THF)_4$

The preferred coordination polyhedron for this mononuclear seven-coordinate series is pentagonal bipyramidal with two of the halogen atoms occupying the *trans*-axial positions.

In this paper we report the isolation and X-ray crystal structures of three new THF solvates, *viz.* $GdCl_3(THF)_4$, $[NdCl_3(H_2O)(THF)]_n$ and $[PrCl_3(THF)_2]_n$ and present an overview of the structural vagaries that emerge for the series $LnCl_3(THF)_n$, $n = 2, 3, 3.5$ and 4.

EXPERIMENTAL

All manipulations were carried out under dinitrogen and/or argon using standard Schlenk, vacuum-line and glovebox techniques, with the rigorous exclusion of air and moisture. All solvents were predried over CaH_2 and distilled from potassium/benzophenone prior to use. The lanthanide hydrates were used as commercially supplied (Aldrich). IR spectra were recorded as Nujol mulls sandwiched between CsI plates using a Perkin–Elmer 580B spectrophotometer.

Synthesis of $[PrCl_3(THF)_2]_n$

$SOCl_2$ (21.0 cm^3, 287.9 mmol) was introduced dropwise to a stirred, cooled (0°C) suspension of $PrCl_3 \cdot (H_2O)_6$ (3.51 g, 9.88 mmol) in tetrahydrofuran (60 cm^3). The resulting mixture was heated at reflux for 48 h. The subsequent green solution was concentrated *in vacuo* to one-third volume, affording a large amount of microcrystalline precipitate. This solid was collected by filtration, washed with ether (3 x 20 cm^3) and hexane (2 x 20 cm^3), then pumped to dryness for several hours. Following recrystallization from tetrahydrofuran in the presence of activated charcoal, the title compound was obtained as light green cubic crystals. Yield: 3.26 g, 84.3%. Found: C, 24.1; H, 4.3; Cl, 27.0; Pr, 35.7. Calc. for $C_8H_{16}O_2PrCl_3$: C, 24.5; H, 4.1; Cl, 27.2; Pr, 36.0%. $\bar{\nu}_{max}/cm^{-1}$ (Nujol): 1343(m), 1184(m), 1037(m), 1012(vs) $\nu_{as}(COC)$, 924(m), 860(vs) $\nu_s(COC)$, 670(w), 576(w) (ligand); 272(s) br, 238(s) br, $\nu(PrCl)$.

Synthesis of $[NdCl_3(OH_2)(THF)]_n$

To a stirred cooled (0°C) suspension of $NdCl_3 \cdot (H_2O)_6$ (3.40 g, 9.48 mmol) in tetrahydrofuran (60 cm^3) was added $SOCl_2$ (20.0 cm^3, 273.8 mmol) dropwise over 30 min. This caused the dissolution of the residual solid, giving a blue solution which was heated at reflux for 36 h. At this point the solvent was removed *in vacuo* and the resulting blue solid washed with ether (4 x 20 cm^3) and hexane (2 x 15 cm^3). Recrystallization from tetrahydrofuran in the presence of activated charcoal gave the title compound as large blue chunks. Yield: 2.51 g, 77.8%. Found: C, 14.4; H, 3.0; Cl, 31.1; Nd, 42.8. Calc. for $C_4H_{10}O_2NdCl_3$: C, 14.1; H, 3.0; Cl, 31.2; Nd, 42.3%. $\bar{\nu}_{max}/cm^{-1}$ (Nujol): 3348(w) br $\nu(OH)$, 1615(w) $\nu(OH)$, 1300(m), 1184(w), 1037(m), 1012(vs) $\nu_{as}(COC)$, 924(m), 860(vs), $\nu_s(COC)$, 670(m) ligand; 270(s), 240(s) $\nu(NdCl)$.

Synthesis of $GdCl_3(THF)_4$

$SOCl_2$ (15.0 cm^3, 206.1 mmol) was added dropwise to a stirred chilled (0°C) suspension of $GdCl_3 \cdot (H_2O)_6$ (2.52 g, 6.78 mmol) in tetrahydrofuran (75 cm^3). The solid dissolved, giving a yellow solution which was heated at reflux for 72 h. The orange solution was concentrated *in vacuo* to one-third volume and a large amount of solid precipitate collected by filtration. This solid was washed with ether (3 x 20 cm^3) and hexane (3 x 20 cm^3) then pumped to dryness *in vacuo*. Recrystallization from hot tetrahydrofuran, in the presence of activated charcoal gave colourless needle crystals. Yield: 3.15 g, 84.2%. Found: C, 34.6; H, 5.8; Cl, 19.4; Gd, 28.9. Calc. for $C_{16}H_{32}O_4GdCl_3$: C, 34.8; H, 5.8; Cl; 19.3; Gd, 28.5%. $\bar{\nu}_{max}/cm^{-1}$ (Nujol): 1344(m), 1300(m), 1183(w), 1120(w), 1039(s), 1011(s) $\nu_{as}(COC)$, 925(m), 864(vs) $\nu_s(COC)$, 673(w) ligand; 274(vs), 240(m), br $\nu(GdCl)$.

X-ray crystallography

Crystal data are given in Table 2, together with refinement details. Data for the three crystals were collected with Mo-K_α radiation using the MAR-research Image Plate System. The crystals were positioned at 75 mm from the Image Plate. 95 frames were measured at 2° intervals with a counting time of 2 min. Data analysis was carried out with the XDS program [22]. The structures were all solved by heavy-atom methods using the SHELX86 program [23]. For structures **1** and **2** all non-hydrogen atoms were refined with anisotropic thermal parameters, but in structure **3**, only the metal and chlorine atoms were so treated and the thf atoms were given isotropic thermal parameters. In all three structures, the hydrogen atoms bonded to carbon were included in geometric positions. The hydrogen atoms on the water molecule in **2** could not be located and were omitted. An empirical absorption correction was carried out for all three structures using DIFABS [24]. The structures were finally refined on F^2 using SHELX [25]. All calculations were carried out on a Silicon Graphics R4000 Workstation at the University of Reading. Selected bond dimensions of compounds **1**, **2** and **3** are provided in Table 3. Supplementary material including atomic coordinates, a complete listing of all bond lengths and angles, and thermal parameters has been deposited at the Cambridge Crystallographic Data Centre.

Table 2. Crystal data and structure refinement for **1**, **2** and **3**

Compound	**1**	**2**	**3**
Formula	$[PrCl(\mu\text{-}Cl_2)(THF)_2]_n$	$[Nd(\mu\text{-}Cl)_3(H_2O)(THF)]_n$	$GdCl_3(THF)_4$
Empirical formula	$C_8H_{16}Cl_3O_2Pr$	$C_4H_{10}Cl_3NdO_2$	$C_{16}H_{32}Cl_3GdO_4$
Formula weight	391.481	340.721	552.02
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	Cc
Unit cell dimensions (Å, °) a	8.470(9)	6.722(8)	9.552(9)
b	8.781(10)	7.465(9)	16.674(12)
c	10.191(11)	10.252(11)	15.488(14)
α	82.56(1)	83.03(1)	(90)
β	69.91(1)	76.85(1)	107.95(1)
γ	85.15(1)	74.40	(90)
Volume (Å^3)	705.2	481.5	2347
Z	2	1	4
Density (calculated) (Mg m^{-3})	1.84	2.350	1.562
Absorption coefficient (mm^{-1})	4.00	6.169	3.182
$F(000)$	380	322	1100
Crystal size (mm)	0.25 × 0.30 × 0.30	0.20 × 0.20 × 0.15	0.25 × 0.30 × 0.30
θ range for data collection	2.56 to 25.24	3.21 to 24.99	2.44 to 25.11
Index ranges	$0 < = h < = 10$, $-9 < = k < = 9$, $-11 < = 1 < = 12$	$0 < = h < = 7$ $-8 < = k < = 8$ $-11 < = l < = 12$	$0 < = h < = 11$ $-19 < = k < = 19$ $-18 < = l < = 17$
Reflections collected	2113	1261	3118
Independent reflections	2113	1261	1970 ($R_{int} = 0.0786$)
Data/parameters	2113/127	1261/92	1970/123
Goodness-of-fit on F^2	0.698	1.165	0.988
Final R indices $[I > 2\sigma(I)]$ R_1	0.0872	0.0499	0.1013
wR_2	0.2282	0.1377	0.2580
R indices (all data) R_1	0.1161	0.0502	0.1338
wR_2	0.2850	0.1382	0.3331
Largest difference peak, hole (e Å^{-3})	1.176, −2.954	2.078, −2.055	2.619, −1.361

RESULTS AND DISCUSSION

$[PrCl(\mu\text{-}Cl)_2(THF)_2]_n$

The polymeric structure of this bis-solvate is depicted in Fig. 1, together with the atom notation used. Each metal centre is seven-coordinated and is flanked by two others *via* halogen bridging $(\mu\text{-}Cl)_2$ units resulting in a one-dimensional polymeric chain. In addition to the four bridging chlorine atoms (equatorial), a further two THF molecules (one axial, one equatorial) and one terminal chlorine atom (axial) complete each metal coordination sphere to give a geometry that approximates to distorted pentagonal bipyramidal with $Pr—Cl_{bridge}$ 2.852(6)–2.891(5), $Pr—Cl_{terminal}$ 2.668(6), $Pr—O_{THF}$ 2.51(1)(axial), 2.53(2)(equatorial) Å. For the axial ligands the nonlinear deformation is small $Cl—Pr—O_{THF}$ 176.1(4)° and within the equatorial girdle the interligand angles fall within the range 71.9(3)–73.5(3) mean 72.7(3)°, close to the idealized 72°. A least squares plane taken through these equatorial atoms shows significant deviations from planarity (maximum deviation 0.43 Å) with the metal atom 0.13 Å from this plane. Comparable bond dimensions include those of $PrCl_3(HMPA)_3$ [26] (six-coordinate), Pr—Cl 2.706(3), 2.725(3), 2.733(3), mean 2.721(3), Pr—O 2.351(6), 2.356(6), 2.352(6), mean 2.353(6) Å, and $PrCl_3$ (15-crown-5) [27] (eight-coordinate), Pr—Cl, 2.707(3), 2.724(4), 2.736(4), mean 2.722(4) Å; clearly there is little variation over the coordination number range CN 6–8.

A similar one-dimensional chain arrangement has been noted for $[NdCl(\mu\text{-}Cl)_2(THF)_2]_n$ [5] $[CeCl(\mu\text{-}Cl)_2(THF)_2]_n$ and $[LaCl(\mu\text{-}Cl)_2(C_7H_8O_2)(H_2O)]_n$ [28], where $C_7H_8O_2$ = 2,6-dimethyl-4-pyrone, thereby emphasizing the fact that this structure is perhaps the most viable for the earlier (and larger) lanthanide ions.

$[Nd(\mu\text{-}Cl)_3(H_2O)(THF)]_n$

Perspective views of the polymeric structure of the title compound are shown in Fig. 2 to include the

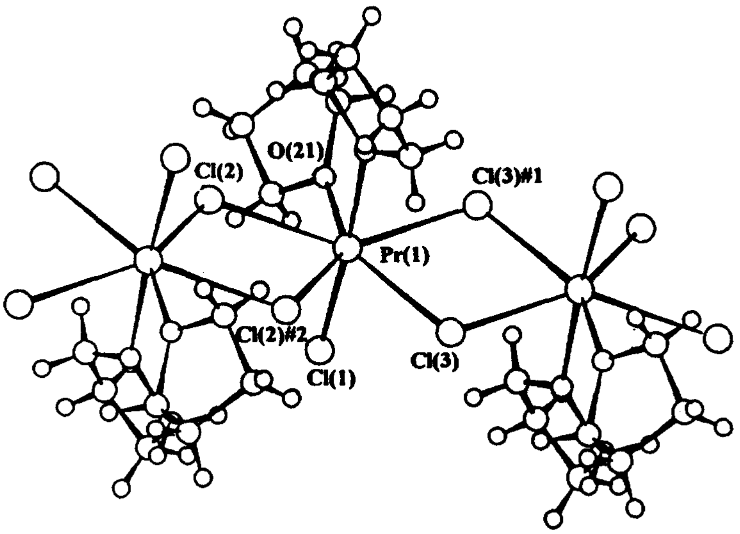

Fig. 1. The one-dimensional polymeric structure of **1** with the atomic numbering scheme.

atom labelling used. For the $NdCl_3 \cdot 6H_2O/SOCl_2$/THF system dehydration is incomplete and there is retention of one water molecule per metal centre. What is immediately clear about this "mixed solvate" is that whereas it is identified with the polymeric $[LnCl_3(solvent)_2]_n$ group, the structure is quite different. Not only has the metal geometry changed, the coordination number is now 8, but there is extensive two-dimensional cross-linking, i.e. each metal centre is linked to three others by $(\mu\text{-}Cl)_2$ halogen bridges, resulting in a two-dimensional net polymer. The metal environment comprises the six chlorine atoms and two oxygen atoms arising from coordinated tetrahydrofuran and water molecules, respectively, and the resulting geometry is quite close to square anti-prismatic. The $Nd—Cl_{bridge}$ distances are all similar lying in the range 2.816(3)–2.938(3) Å and Nd—O bond distances are 2.548(6) (THF) and 2.490(7) (H_2O) Å. For comparison we note that the bond dimensions for the seven-coordinate variant $[NdCl(\mu\text{-}Cl)_2(THF)_2]_n$ [5] are $Nd—Cl_{terminal}$ mean 2.630(1), $Nd—Cl_{bridging}$ mean 2.81(1), $Nd—O_{THF}$ mean 2.469(8) Å. Interestingly the seven-coordinate pentagonal bipyramidal structure reported for the discrete mononuclear $NdCl_3(THF)_4$ species [6] shows $Nd—Cl_{terminal}$ mean 2.674 and $Nd—O_{THF}$ mean 2.498 Å. In the present polymeric structure the shortest Nd· · ·Nd separation distance is 4.54 Å, signifying that no direct metal–metal bonding interactions are present. Very recently Hubert-Pfalzgraf *et al.* [29] and, independently, Evans *et al.* [30] have reported the crystal structure of $[Ce(\mu\text{-}Cl)_3(THF)(H_2O)]_n$, which is closely similar to that of the Nd^{III} analogue under discussion here. The inclusion of coordinated water molecules is the key; their presence gives rise to an intricate hydrogen bonding network e.g. there are two close contacts (3.147, 3.350 Å) with chlorine atoms in other coordination spheres and this may well presage the observed structural change away from the linear chain polymeric arrangement that distinguishes the "authentic" solvates $[MCl(\mu\text{-}Cl)_2(THF)_2]$ based on CN = 7. As the "exception" to this arbitrary subclassification we note that the "mixed" solvate $[LaCl(\mu\text{-}Cl)_2(C_7H_8O_2)(H_2O)]_n$ [28] has a linear chain structure; perhaps the steric imposition of the lactone with respect to tetrahydrofuran mitigates against the build-up of extensive hydrogen-bonding interactions and thus outlaws the two-dimensional web structure with its higher coordination geometry.

$GdCl_3(THF)_4$

The structure of the title compound is shown in Fig. 3 together with the atom notation used. Each discrete molecule has a central gadolinium atom which is seven-coordinate; this is based on a regular pentagonal bipyramidal geometry involving two chlorine atoms in the axial positions, with the remaining halogen atom and the four tetrahydrofuran solvent molecules in the equatorial sector. Interestingly, occupancy of the axial (*trans*) sites by halogen atoms rather than solvent molecules is the common structural feature for this seven-coordinate $LnCl_3S_4$ series, e.g. $NdCl_3(THF)_4$ [6] and $EuCl_3(THF)_4$ [8], presumably reflecting the greater steric bulk of the chlorine atom over the oxygen of a coordinated tetrahydrofuran ligand. In the present structure the metal to chlorine bond distances are $Gd—Cl_{axial}$ 2.60(2), 2.64(2) and $Gd—Cl_{equatorial}$ 2.66(2) Å. These compare with 2.632(4), 2.625(4) (axial) and 2.629(4) Å (equatorial) in $GdCl_3(dme)_2$ [31]. The Gd—O distances lie in the range 2.40(2)–2.52(3), mean 2.47(3) Å, and can be compared with those in $GdCl_3(dme)_2$

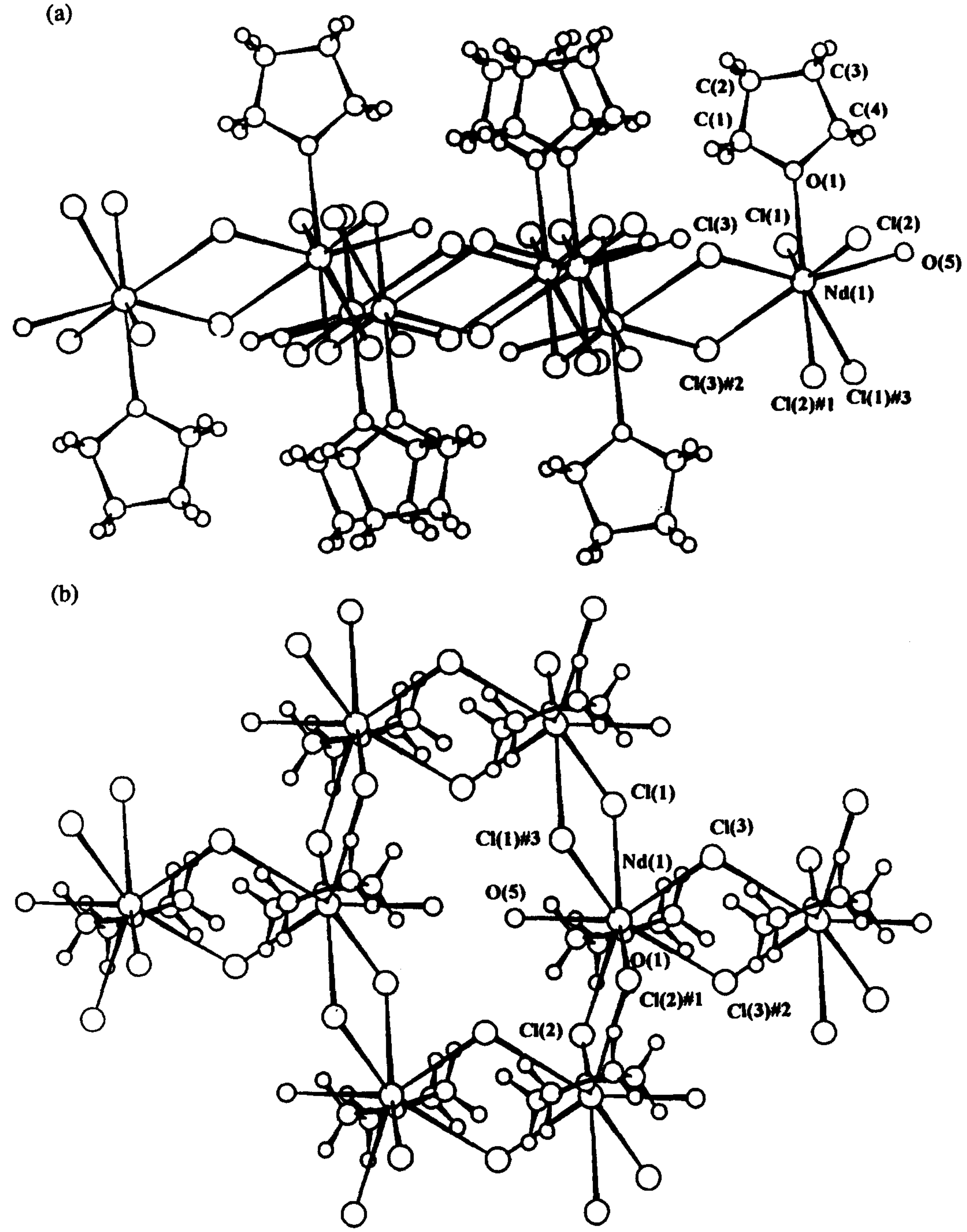

Fig. 2. Two views, (a) and (b), of the two-dimensional polymeric structure of **2** with the atomic numbering scheme. The hydrogen atoms of the water molecule are not included. All chlorine atoms are bridging.

[31], mean 2.461(4) Å, and $GdCl_3$ (2,6-dimethyl-4-pyrone)$_3$ [32], mean 2.338(5) Å. The axial Cl—Gd—Cl unit is almost linear, 175.2(8)°, and the interligand angles within the pentagonal plane approach the ideal 72°. A least-squares plane taken through the equatorial ligands shows minor deviations from planarity ±0.09 Å. The metal is displaced 0.024 Å from the plane containing the three chlorine atoms.

General discussion

As can be seen from Table 1 there is no single dominant value for n in the series of solvates $LnCl_3(THF)_n$, where $n = 1.5, 2, 3, 3.5$ and 4. Even for individual elements there is often a range in classification, e.g. $NdCl_3(THF)_2$ [5], $NdCl_3(THF)_4$ [6] and $NdCl_3(THF)_{1.5}$ [14]. Since the variation in atomic size from Ce → Lu is relatively small, it would seem

Table 3. Bond lengths (Å) and angles (°) in the metal coordination spheres

In (**1**)	
Pr(1)—O(11)	2.508(12)
Pr(1)—O(21)	2.53(2)
Pr(1)—Cl(1)	2.668(6)
Pr(1)—Cl(2)	2.852(6)
Pr(1)—Cl(3)	2.869(6)
Pr(1)—Cl(3)^1	2.870(5)
Pr(1)—Cl(2)^2	2.891(5)
O(11)—Pr(1)—O(21)	95.0(5)
O(11)—Pr(1)—Cl(1)	176.1(4)
O(21)—Pr(1)—Cl(1)	82.4(4)
O(11)—Pr(1)—Cl(2)	80.5(4)
O(21)—Pr(1)—Cl(2)	73.4(3)
Cl(1)—Pr(1)—Cl(2)	101.4(2)
O(11)—Pr(1)—Cl(3)	85.0(5)
O(21)—Pr(1)—Cl(3)	143.9(3)
Cl(1)—Pr(1)—Cl(3)	95.4(2)
Cl(2)—Pr(1)—Cl(3)	141.3(2)
O(11)—Pr(1)—Cl(3)^1	81.6(4)
O(21)—Pr(1)—Cl(3)^1	71.9(3)
Cl(1)—Pr(1)—Cl(3)^1	94.9(2)
Cl(2)—Pr(1)—Cl(3)^1	139.1(2)
Cl(3)—Pr(1)—Cl(3)^1	72.4(2)
O(11)—Pr(1)—Cl(2)^2	95.3(4)
O(21)—Pr(1)—Cl(2)^2	141.9(3)
Cl(1)—Pr(1)—Cl(2)^2	88.5(2)
Cl(2)—Pr(1)—Cl(2)^2	72.4(2)
Cl(3)—Pr(1)—Cl(2)^2	73.5(2)
Cl(3)^1—Pr(1)—Cl(2)^2	146.0(2)
Pr(1)—Cl(2)—Pr(1)^2	107.6(2)
Pr(1)—Cl(3)—Pr(1)^1	107.6(2)

Symmetry transformations used to generate equivalent atoms: (1) $-x, -y+1, -z$; (2) $-x, -y, -z$.

In **2**	
Nd(1)—O(5)	2.490(7)
Nd(1)—O(1)	2.548(6)
Nd(1)—Cl(2)^1	2.816(3)
Nd(1)—Cl(2)	2.850(3)
Nd(1)—Cl(3)^2	2.857(4)
Nd(1)—Cl(3)	2.863(3)
Nd(1)—Cl(1)	2.882(3)
Nd(1)—Cl(1)^3	2.938(3)
O(5)—Nd(1)—O(1)	79.9(2)
O(5)—Nd(1)—Cl(2)^1	106.3(2)
O(1)—Nd(1)—Cl(2)^1	143.13(14)
O(5)—Nd(1)—Cl(2)	71.6(2)
O(1)—Nd(1)—Cl(2)	74.2(2)
Cl(2)^1—Nd(1)—Cl(2)	73.65(8)
O(5)—Nd(1)—Cl(3)^2	143.2(2)
O(1)—Nd(1)—Cl(3)^2	74.5(2)
Cl(2)^1—Nd(1)—Cl(3)^2	80.76(9)
Cl(2)—Nd(1)—Cl(3)^2	76.34(8)
O(5)—Nd(1)—Cl(3)	144.5(2)
O(1)—Nd(1)—Cl(3)	117.1(2)
Cl(2)^1—Nd(1)—Cl(3)	79.11(9)
Cl(2)—Nd(1)—Cl(3)	140.82(8)
Cl(3)^2—Nd(1)—Cl(3)	71.89(6)
O(5)—Nd(1)—Cl(1)	80.4(2)
O(1)—Nd(1)—Cl(1)	71.19(14)
Cl(2)^1—Nd(1)—Cl(1)	145.25(5)
Cl(2)—Nd(1)—Cl(1)	138.56(7)
Cl(3)^2—Nd(1)—Cl(1)	114.55(9)
Cl(3)—Nd(1)—Cl(1)	76.95(9)
O(5)—Nd(1)—Cl(1)^3	72.1(2)
O(1)—Nd(1)—Cl(1)^3	137.1(2)
Cl(2)^1—Nd(1)—Cl(1)^3	77.26(10)
Cl(2)—Nd(1)—Cl(1)^3	123.81(7)
Cl(3)^2—Nd(1)—Cl(1)^3	143.19(6)
Cl(3)—Nd(1)—Cl(1)^3	75.19(8)
Cl(1)—Nd(1)—Cl(1)^3	72.52(9)
Nd(1)—Cl(1)—Nd(1)^3	107.48(9)
Nd(1)^1—Cl(2)—Nd(1)	106.35(8)
Nd(1)^2—Cl(3)—Nd(1)	108.11(6)

Symmetry transformations used to generate equivalent atoms: (1) $-x+1, -y, -z+1$; (2) $-x, -y, -z+1$; (3) $-x, -y+1, -z+1$.

In **3**	
Gd(1)—O(3)	2.43(3)
Gd(1)—O(1)	2.40(2)
Gd(1)—O(4)	2.52(3)
Gd(1)—O(2)	2.52(3)
Gd(1)—Cl(1)	2.60(2)
Gd(1)—Cl(3)	2.66(2)
Gd(1)—Cl(2)	2.64(2)
O(3)—Gd(1)—O(1)	65.8(13)
O(3)—Gd(1)—O(4)	158.4(10)
O(1)—Gd(1)—O(4)	135.8(14)
O(3)—Gd(1)—O(2)	135.2(11)
O(1)—Gd(1)—O(2)	69.8(12)
O(4)—Gd(1)—O(2)	66.2(11)
O(3)—Gd(1)—Cl(1)	89.3(9)
O(1)—Gd(1)—Cl(1)	89.5(9)
O(4)—Gd(1)—Cl(1)	90.8(7)
O(2)—Gd(1)—Cl(1)	84.6(9)
O(3)—Gd(1)—Cl(3)	79.1(8)
O(1)—Gd(1)—Cl(3)	144.8(11)
O(4)—Gd(1)—Cl(3)	79.3(8)
O(2)—Gd(1)—Cl(3)	145.3(9)
Cl(1)—Gd(1)—Cl(3)	92.3(7)
O(3)—Gd(1)—Cl(2)	91.2(7)
O(1)—Gd(1)—Cl(2)	86.4(9)
O(4)—Gd(1)—Cl(2)	90.5(9)
O(2)—Gd(1)—Cl(2)	91.6(9)
Cl(1)—Gd(1)—Cl(2)	175.2(8)
Cl(3)—Gd(1)—Cl(2)	92.5(7)

reasonable to expect a smooth variation in structural type to emerge for such a simple solvate system [33] such that the earlier lanthanides would enjoy high coordination environment(s) with a mandatory tailing off across the series. To some extent this is true; there is a gradual reduction in coordination number across the series from 8 → 7 → 6, despite the fluctuations in stoichiometry. A cursory look at Table 1 reveals two main classes, *viz.* $n = 2$ and 3.5. For the $n = 2$ class there are reports for the majority of elements ranging from the largest (La) to two of the

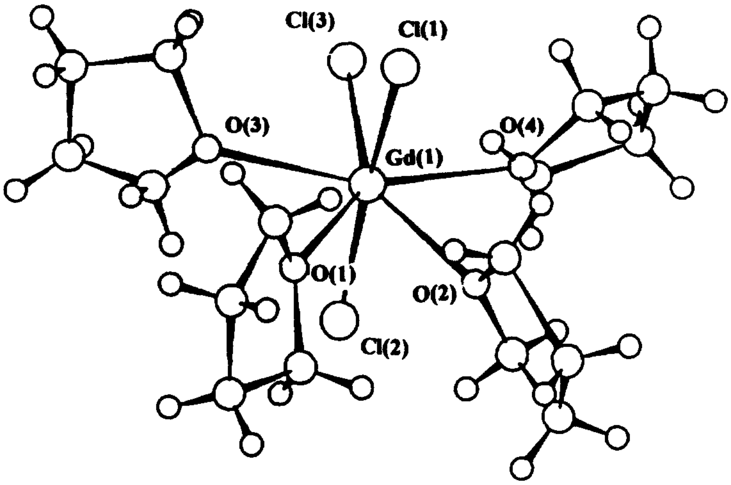

Fig. 3. The structure of **3** with the atomic numbering scheme.

smallest (Y and Yb); for $n = 3.5$ this appears to be a general classification for the middle group of elements (Sm → Tm) and also includes Y.

In terms of reported structures those for the early members Ce → Gd inclusive embrace seven- and eight-coordination with the distinction that n may be either 2 or 4. For $n = 2$ there are subtle subdivisions. As noted in the Introduction, the structure for the homoleptic $[LnCl_3(THF)_2]_n$ is polymeric with bridging (μ-Cl)$_2$ linkages to seven-coordinate metal centres, e.g. Ln = Ce [5], Nd [5]. The introduction of coordinated water molecules to give the "mixed" type $[LnCl_3(THF)(H_2O)]_n$ provides a startlingly different type of polymeric structure based on an eight-coordinate metal geometry Ln = Pr (this work) and Ce [29,30]. However, when $n = 4$ the adducts are discrete mononuclear seven-coordinate compounds as typified by Nd [6], Sm [7], Eu [8] and Gd (this work). Moving to the late lanthanides, strictly Yb and Lu, the adducts are six-coordinate with, again, a split into two subgroups, *viz.* the dimeric $[YbCl_3(THF)_2]_2$, and the discrete mononuclear "classical" systems based on $LnCl_3(THF)_3$ as represented by Ln = Yb [9] and Lu [10]. Scandium(III) is conspicuously smaller in size than the other members of Group 3 and it is no surprise that the sole adduct *mer*-$ScCl_3(THF)_3$ shows six-coordinate octahedral metal geometry.

Turning to the $n = 3.5$ class this represents a "crossover" point between 8/7 and 6 coordination and coincides with the autoionization:

$$LnCl_3(THF)_{3.5} \overset{THF}{\rightleftharpoons} [LnCl_2(THF)_5][LnCl_4(THF)_2] \qquad (1)$$

featuring seven-coordinate (pentagonal bipyramidal) cations and six-coordinate anions (octahedral) as witnessed for Ln = Tb [5] and Dy [4]. Yttrium sits alongside holmium and erbium in terms of relative size and is a prime candidate for autoionisation [eqn (1)]. This is indeed the case as confirmed by Sobota *et al.* [12]. As yet there is no reported lanthanum(III)chloride solvate structure; on the basis of its very large (relative) size either a seven-coordinate structure based on polymeric $[LaCl_3(THF)_2]_n$ or mononuclear $LaCl_3(THF)_4$ and/or an eight-coordinate structure involving a "mixed solvate" of the type $[LaCl_3(THF)(H_2O)]_n$ (*ca* the Ce, Nd analogues described above) are distinct possibilities.

The one significant "gap" in Table 1 is the lack of structural identification of the $n = 1.5$ class (La, Ce, Nd). On size strictures alone seven- and/or eight-coordinate structure(s) would seem the most likely. On the other hand, the authenticity of $n = 1.5$ species as a separate structural category may prove ephemeral, especially since it is known that the final stoichiometry of these solvates appears susceptible to the extent and degree of the washing and drying conditions used. The early work by Rossmanith [13] details the preparation of the several classes $n = 1.5$, 2, 3 and 3.5 (interestingly, not $n = 4$) and also includes some thermal decomposition studies. Under severe degradation conditions $LnCl_3(THF)_2$ (Ln = Pr, Nd, Sm, Dy, Er) provide the stoichiometric class $LnCl_3(THF)_{0.5}$ with release of THF and there is evidence for the existence of a further intermediate phase $LnCl_3(THF)$ for Ln = Dy, Er. Using the more gentle conditions of heating at reflux in the absence of THF (benzene or ether) Rossmanith observed a class change $LnCl_3(THF)_{3.5} \rightarrow LnCl_3(THF)_2$ for the series Ln = Sm, Eu, Gd, Tb, Dy, Y, Ho, Er and Tm. Evidently, the choice of solvent is of paramount importance in the structural chemistry of these lanthanide(III)chloride solvates. Interestingly Sobota *et al.* [12] have reported that recrystallization of $YCl_3(THF)_{3.5}$ from neat CH_2Cl_2 affords the polymeric $[YCl_3(THF)_2]_n$ involving seven-coordinate pentagonal bipyramidal metal centres with (μ-Cl)$_2$ linkages (see the Introduction); clearly there is no reason to exclude similar

$$n = 2 \underset{-THF}{\overset{+THF}{\rightleftharpoons}} n = 3.5 \text{ (autoionization)}$$

interconversions for the other members of the list. Bearing in mind that Yb has been structurally characterized for $n = 2$, i.e. treatment of $YbCl_3(THF)_3$ with pentane results in the formation of $[YbCl_3(THF)_2]_2$ [9], which in this particular instance is the *trans*-octahedral dimer rather than a halogen-bridged polymeric structure, similar identification ($n = 2$) in the case of Ln = Ho, Er, Tm seems eminently reasonable given the size similarities. To date no structural data for solvates of this "trio" of late lanthanides are available.

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