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Polymeric Aquatri-μ-chloro-(tetrahydrofuran-*O*)lanthanum(III)

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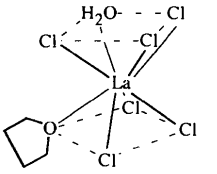
Abstract

The structure of the title compound, $[La(\mu\text{-}Cl)_3(C_4H_8O)(H_2O)]_n$, is based on a bidimensional mesh-like polymer. The metal is eight-coordinate with distorted square antiprismatic geometry; each $[LaCl_3(thf)(H_2O)]$ unit is linked to three others *via* pairs of chloride bridges.

Comment

The title compound, (I), was isolated as a partial dehydration product from the reaction system $LaCl_3(H_2O)_6/SOCl_2$/THF (Taylor, 1962). The La atom is eight-coordinate, with the ligands providing a distorted square antiprismatic environment (Fig. 1). The atoms in the square faces of the antiprism have r.m.s. deviations of 0.083 (Cl3, Cl1, O2, Cl3*A*; see Fig. 1) and 0.100 Å (Cl2, O1, Cl1*A*, Cl2*A*; see Fig. 1), while the dihedral angle between these faces is 2.8 (1)°. Each La atom is linked to three others *via* $(\mu_2\text{-}Cl)_2$ halogen bridging to produce polymeric layers. A single layer as viewed down the *c* axis (Fig. 2) shows that the tetrahydrofuran molecules coordinated to adjacent La atoms lie on opposite sides of the polymeric layer. The water molecules are located within the La–Cl layers. The shortest water O to Cl distance is 3.295 (10) Å; this is about the same as the sum of the respective van der Waals radii and thus there is no strong evidence for hydrogen bonding.



(I)

The title compound is isostructural with the Ce and Nd analogues, *i.e.* $[Ce(\mu\text{-}Cl)_3(thf)(H_2O)]_n$ (Hubert-Pfalzgraf, Machado & Vaissermann, 1996; Evans, Feldman & Ziller, 1996) and $[Nd(\mu\text{-}Cl)_3(thf)(H_2O)]_n$ (Willey, Woodman & Drew, 1997).

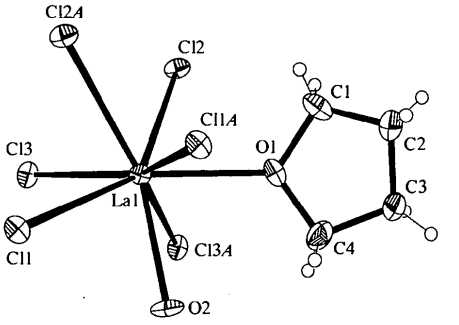


Fig. 1. View of the environment of one metal centre showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level. H atoms are drawn as small spheres of arbitrary radii; water H atoms are not shown. Atoms Cl1*A*, Cl2*A* and Cl3*A* have been generated by the symmetry operations $(-x, 1-y, 2-z)$, $(-x, -y, 2-z)$ and $(1-x, -y, 2-z)$, respectively.

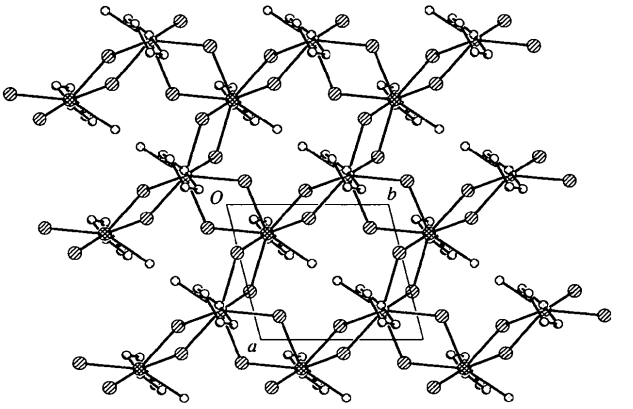


Fig. 2. Packing diagram viewed down the *c* axis.

Two other polymeric lanthanum(III) chloride (solvate) species are known, namely $[La(\mu\text{-}Cl)_3(2,6\text{-dimethyl-4-pyrone})_2]_n$ (Castellani & Coda, 1985) and $[LaCl(\mu\text{-}Cl)_2(2,6\text{-dimethyl-4-pyrone})(H_2O)]_n$ (Castellani & Tazzoli, 1984). In the present structure, there are six La—Cl(bridging) bond distances in the range 2.854 (2)–2.952 (2) Å. Eight-coordinate $[La(\mu\text{-}Cl)_3(2,6\text{-dimethyl-4-pyrone})_2]_n$ has La—Cl(bridging) bond distances in the range 2.845 (2)–3.018 (3) Å, whereas seven-

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coordinate [$LaCl(\mu$-$Cl)_2$(2,6-dimethyl-4-pyrone)$(H_2O)]_n$ has La—Cl(terminal) 2.72 (1) Å and La—Cl(bridging) 2.90 (1) and 2.92 (1) Å. The La—O(water) bond distance of 2.518 (6) Å in the present structure compares favourably with that in [$La(\mu$-$Cl)_3$(2,6-dimethyl-4-pyrone$)_2]_n$ [2.50 (2) Å].

Experimental

Synthesis was by dehydration of $LaCl_3(H_2O)_6$ with an excess of $SOCl_2$ (molar ratio 1:25) in refluxing THF under an atmosphere of dinitrogen for 12 h. Recrystallization was from THF.

Crystal data

[$LaCl_3(C_4H_8O)(H_2O)$]
M_r = 335.38
Triclinic
$P\bar{1}$
a = 6.7468 (7) Å
b = 7.4849 (8) Å
c = 10.1537 (10) Å
α = 84.349 (2)°
β = 76.610 (1)°
γ = 74.816 (2)°
V = 481.01 (9) Å^3
Z = 2
D_x = 2.316 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 1858 reflections
θ = 2.06–25.0°
μ = 5.219 mm^{-1}
T = 180 (2) K
Block
0.10 × 0.04 × 0.02 mm
Colourless

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.623, T_{max} = 0.903
2433 measured reflections

1652 independent reflections
1430 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 25°
h = −5 → 8
k = −8 → 8
l = −12 → 12

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.109
S = 1.042
1652 reflections
94 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0571P)^2 + 2.2385P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.97 e Å^{-3}
$\Delta\rho_{min}$ = −1.75 e Å^{-3} (1.01 Å from La1)
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

La1—O2	2.518 (6)	La1—Cl2	2.885 (2)
La1—O1	2.561 (6)	La1—Cl2^{ii}	2.902 (2)
La1—Cl3	2.854 (2)	La1—Cl1^{iii}	2.914 (2)
La1—Cl3^{i}	2.867 (2)	La1—Cl1	2.952 (2)
O2—La1—O1	79.1 (2)	O1—La1—Cl2^{ii}	118.22 (15)
O2—La1—Cl3	108.43 (17)	Cl3—La1—Cl2^{ii}	77.61 (6)
O1—La1—Cl3	142.42 (16)	Cl2—La1—Cl2^{ii}	72.49 (7)
O2—La1—Cl3^{i}	70.87 (16)	Cl2^{ii}—La1—Cl1^{iii}	76.63 (6)
O1—La1—Cl3^{i}	74.28 (15)	O2—La1—Cl1	71.74 (16)
Cl3—La1—Cl3^{i}	73.93 (7)	O1—La1—Cl1	136.57 (16)
O2—La1—Cl2	142.91 (16)	Cl3—La1—Cl1	78.59 (6)
O1—La1—Cl2	74.33 (15)	Cl2^{ii}—La1—Cl1	75.19 (6)
Cl3—La1—Cl2	79.56 (7)	La1^{iii}—Cl1—La1	106.64 (7)
Cl3^{i}—La1—Cl2	77.26 (6)	La1—Cl2—La1^{ii}	107.51 (7)
O2—La1—Cl2^{ii}	144.18 (16)	La1—Cl3—La1^{i}	106.07 (7)

Symmetry codes: (i) 1 − x, −y, 2 − z; (ii) −x, −y, 2 − z; (iii) −x, 1 − y, 2 − z.

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). 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. Coverage of the unique set was over 90% complete to at least 25° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analyzing the duplicate reflections; no significant decay was observed. Tetrahydrofuran H atoms were added at calculated positions and refined using a riding model; one of the H atoms in the coordinated water molecule was located from the electron-density map, but the location of the second could neither be detected nor calculated in a satisfactory manner. Anisotropic displacement parameters were used for all non-H atoms; each H atom was given an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of the atom to which it is attached.

Data collection: *SMART* (Siemens, 1994*b*). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Siemens, 1994*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher, McMeeking & Parkin, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1180). Services for accessing these data are described at the back of the journal.

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A Chromium(III) 2,2′-Bipyrimidine (bipym) Complex, $(Et_4N)[Cr(NCS)_4(bipym)]$

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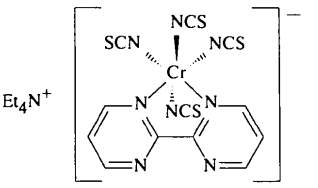
Abstract

The title structure, tetraethylammonium tetrakis(isothiocyanato)(2,2′-bipyrimidine-*N*,*N*′)chromium(III), $[(C_2H_5)_4N][Cr(NCS)_4(C_8H_6N_4)]$, consists of discrete $[Cr(NCS)_4(bipym)]^-$ and $[(C_2H_5)_4N]^+$ ions. The Cr^{3+} ion lies on a mirror plane and has a regular octahedral coordination polyhedron. The bipym group is planar, with unexceptional bond distances and angles.

Comment

2,2′-Bipyrimidine (bipym) is a versatile ligand able to coordinate in a bidentate mode or in a bis(bidentate) bridging mode to yield mono- or polynuclear complexes (De Munno & Julve, 1996). Structural data for bipym-containing complexes of first-row transition metal ions are essentially limited to the 2+ oxidation state and mainly concern, for their intrinsic magnetic properties, copper (Julve *et al.*, 1993; Decurtins *et al.*, 1996) and manganese derivatives (De Munno *et al.*, 1996; Cortes *et al.*, 1996; Hong *et al.*, 1996). The present work concerns a bipyrimidine complex with a paramagnetic Cr^{III} cation, (I). As far as we know, the structural data presented here are the first example of an M^{III}–bipym system.



(I)

The structure consists of discrete units of $[Cr(NCS)_4(bipym)]^-$ (Fig. 1) and $[(C_2H_5)_4N]^+$ ions. In the anionic complex, the metal coordination geometry can be described as octahedral, bisected by the space-group mirror plane through the metal center and two of the NCS^- groups. The geometry is regular, the main departure being the small N1—Cr—N1 angle [78.5 (2)°] constrained by the bidentate character of the bipym ligand. The two heterocycles in the bipym moiety are planar within experimental error [maximum deviation: 0.006 (4) Å for C3] and so is the resulting bicyclic ligand [rotation around the C4—C4(x, $\frac{1}{2}-y$, z) bond being 0.30 (15)°]. The four Cr—N(CS) bonds average 1.986 (5) Å and are slightly shorter than Cr—N(bipym) bonds [2.072 (3) Å]. The isolated counterion, also bisected by the mirror plane, is unusually well behaved, with reasonable displacement parameters, and bonds and angles within normal ranges. The packing of the structure viewed along the monoclinic axis, shows 'cationic' and 'anionic' planes which are clearly seen evolving perpendicular to the c axis, at c = 0.0 and c = 0.5, respectively. A few long non-bonding contacts connecting both types of planes [C31—H31*A*···N2(x, y, $1+z$) 2.544 (4) and C3—H3*A*···S1*C*($-x$, $1-y$, $1-z$) 2.942 (4) Å], stabilize the crystal structure.

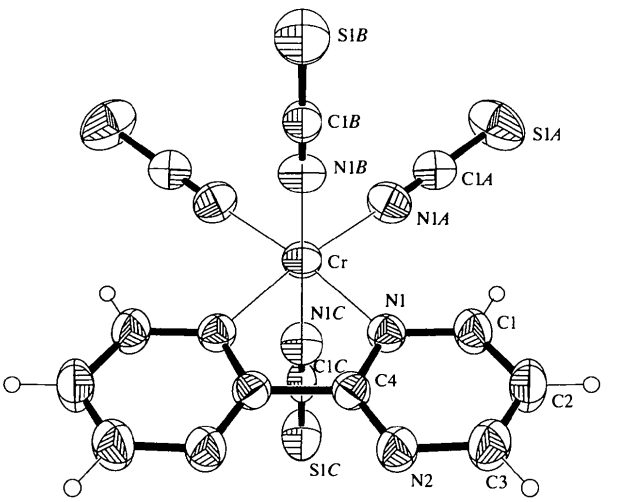


Fig. 1. View of the Cr coordination sphere, showing the labeling scheme used. Displacement ellipsoids are shown at the 50% probability level.

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