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1,4-Diazoniabicyclo[2.2.2]octane tetraaquatetrachlorolanthanate(III) chloride

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The title compound, $(C_6H_{14}N_2)[LaCl_4(H_2O)_4]Cl$, is built up from organic cations, $[La(H_2O)_4Cl_4]^-$ complex anions and uncoordinated chloride ions. The previously unseen rare-earth-containing complex ion is irregular in shape. A network of O—H···Cl and N—H···Cl hydrogen bonds helps to establish the structure. Prominent among these are two well defined trifurcated N—H···(Cl,Cl,Cl) interactions. The La atom, one Cl atom, two N atoms and two C atoms possess site symmetry *m*.

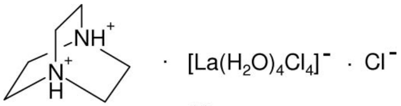
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.020
wR factor = 0.044
Data-to-parameter ratio = 32.5

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The title compound, (I), which contains a new La/Cl/H_2O complex ion, complements known adducts of lanthanum chloride with O-donor ligands such as the polymeric $[LaCl_3(C_7H_8O_2)_2]_n$ ($C_7H_8O_2$ is 2,6-dimethyl-4-pyrone; Bisi Castellani & Coda, 1985) and the dimeric $[La_2(H_2O)_6Cl_8(C_6H_8N)_2]$ (C_6H_8N is 4-picoline; Mackenstedt & Urland, 1993). Although various materials containing $[LaCl_6]^{3-}$ (Matsumoto *et al.*, 2002), $[La(H_2O)_8]^{3+}$ (Hardie *et al.*, 2001) and $[La(H_2O)_9]^{3+}$ complex ions (Harrowfield *et al.*, 1983) have been described, the only monomeric La/Cl/H_2O complex reported in version 5.27 of the Cambridge Structural Database (Allen, 2002) contains $[La(H_2O)_6Cl_2]^+$ ions (Urland, 1985), although no atomic coordinates are available.



(I)

The $[La(H_2O)_4Cl_4]^-$ species in (I) (Fig. 1) is generated from the unique atoms by mirror symmetry, with La1 and Cl1 lying on the reflecting plane. Refinements placing Cl2 on the plane led to a highly anisotropic displacement ellipsoid for this atom, and the final refinement cycles placed it just off the mirror plane, disordered over two symmetry-related positions [Cl2···Cl2^i = 0.530 (4) Å; symmetry code: (i) $x, \frac{1}{2} - y, z$]. The resulting LaO_4Cl_4 polyhedron is irregular in shape, although the mean La—O and La—Cl bond lengths of 2.547 (2) and 2.8960 (9) Å, respectively, are normal. The geometrical parameters for the 1,4-diazoniabicyclo[2.2.2]octane cation are also unexceptional (Bremner & Harrison, 2003).

As well as electrostatic forces, the component species in (I) are held together by a network of O—H···Cl and N—H···Cl hydrogen bonds (Table 2). The most distinctive of these are two trifurcated N—H···(Cl,Cl,Cl) interactions, one from each NH group of the $C_6H_{14}N_2^{2+}$ cation. This results (Fig. 2) in (001) sheets in which [100] columns of cations and anions

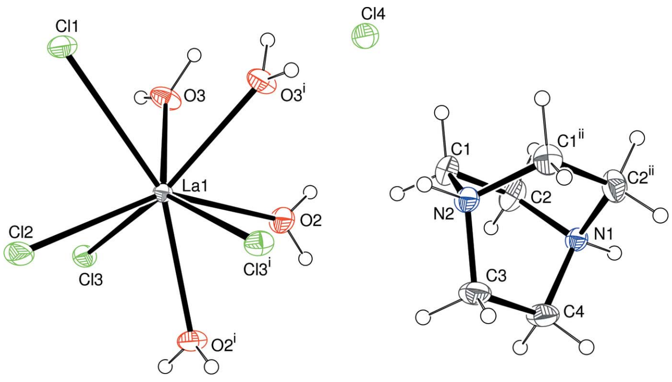


Figure 1
View of (I), showing 30% probability displacement ellipsoids (arbitrary spheres for the H atoms). Only one orientation of the disordered atom Cl2 is shown. [Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $x, \frac{3}{2} - y, z$.]

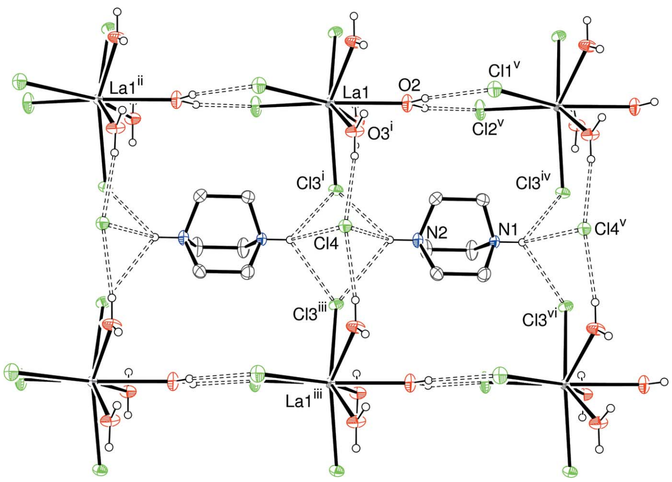


Figure 2
View down [001] of part of a $(C_6H_{14}N_2)\cdot[La(H_2O)_4Cl_4]\cdot Cl$ layer in (I), with hydrogen bonds shown as dashed lines. C-bound H atoms have been omitted for clarity and only one orientation of the disordered atom Cl2 is shown. [Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $x + 1, y, z$; (iii) $x, y + 1, z$; (iv) $x - 1, \frac{1}{2} - y, z$; (v) $x - 1, y, z$; (vi) $x - 1, y + 1, z$.]

alternate with respect to the [010] direction. Every trio of acceptor chloride ions (two Cl3 atoms bound to different La atoms and one free Cl4 species) accepts a trifurcated hydrogen bond from both N1/H6 and N2/H7. The average bond angles at H6 and H7 are 108 and 107°, respectively.

The [100] columns of $[La(H_2O)_4Cl_4]^-$ anions interact by way of two hydrogen bonds from the O2 water molecule to two chloride ion acceptors. Crystal symmetry results in all the anions in one (001) layer pointing in the same direction. The uncoordinated chloride ion participates in an O—H···Cl···H—O bridge between adjacent anion columns (Fig. 2). Still further O—H···Cl hydrogen bonds help to consolidate the inter-layer packing, to result in a dense three-dimensional network (Fig. 3).

Experimental

0.1 *M* $LaCl_3$, 1 *M* HCl and solid 1,4-diazabicyclo[2.2.2]octane ($C_6H_{12}N_2$) were mixed in a Petri dish in a 1:1:1 molar ratio, resulting in a clear solution. Small block-like crystals of (I) appeared as the water slowly evaporated over a few days.

Crystal data

$(C_6H_{14}N_2)[LaCl_4(H_2O)_4]Cl$
$M_r = 502.42$
Orthorhombic, *Pnma*
$a = 7.5005$ (3) Å
$b = 9.1759$ (4) Å
$c = 25.0388$ (10) Å
$V = 1723.27$ (12) Å^3
$Z = 4$
$D_x = 1.937$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 3.26$ mm^{-1}
$T = 293$ (2) K
Block, colourless
0.35 × 0.21 × 0.16 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.395$, $T_{max} = 0.624$
18229 measured reflections
3279 independent reflections
2971 reflections with $I > 2\sigma(I)$
$R_{int} = 0.020$
$\theta_{max} = 32.5°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.044$
$S = 1.14$
3279 reflections
101 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0199P)^2 + 0.3724P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.58$ e Å^{-3}
$\Delta\rho_{min} = -0.43$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00056 (9)

Table 1
Selected bond lengths (Å).

La1—O2	2.5240 (18)	La1—Cl2	2.8310 (8)
La1—O3	2.5492 (11)	La1—Cl3	2.8524 (4)
La1—O1	2.5650 (16)	La1—Cl1	3.0482 (6)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···Cl3^i	0.83	2.49	3.2429 (14)	151
O2—H2···Cl2^{ii}	0.84	2.28	3.1035 (19)	166
O2—H2···Cl2^{iii}	0.84	2.28	3.1035 (19)	166
O2—H3···Cl1^{ii}	0.82	2.41	3.1834 (19)	159
O3—H4···Cl4^{iv}	0.83	2.33	3.1542 (12)	173
O3—H5···Cl1^v	0.93	2.26	3.1765 (12)	173
N1—H6···Cl3^{iii}	0.91	2.67	3.2930 (15)	127
N1—H6···Cl3^{vi}	0.91	2.67	3.2930 (15)	127
N1—H6···Cl4^{ii}	0.91	2.71	3.3086 (19)	125
N2—H7···Cl4	0.91	2.54	3.208 (2)	131
N2—H7···Cl3^{vii}	0.91	2.80	3.3962 (17)	125
N2—H7···Cl3^{viii}	0.91	2.80	3.3962 (17)	125

Symmetry codes: (i) $-x + 1, -y, -z + 1$; (ii) $x - 1, y, z$; (iii) $x - 1, -y + \frac{1}{2}, z$; (iv) $x, y - 1, z$; (v) $x - \frac{1}{2}, y, -z + \frac{3}{2}$; (vi) $x - 1, y + 1, z$; (vii) $x, y + 1, z$; (viii) $x, -y + \frac{1}{2}, z$.

The O-bound H atoms were located in difference maps and refined as riding in their as-found relative locations. The C- and N-bound H atoms were placed in idealized locations (C—H = 0.97 and N—H = 0.91 Å) and refined as riding. The constraint $U_{iso}(H) = 1.2U_{eq}$(carrier) was applied in all cases.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997; molecular graphics:

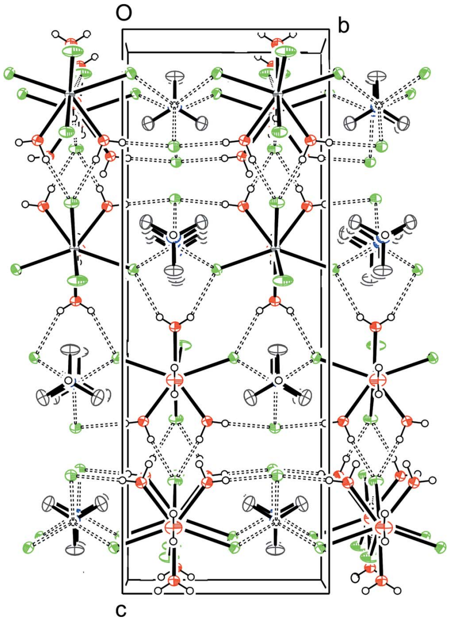


Figure 3
The packing in (I), viewed down [100]. Drawing conventions as in Fig. 2.

ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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