The three molecules of dmp, as far as bond distances and bond angles are concerned, are essentially equivalent; the carbonyl bond length is a little longer than that found in the uncoordinated ligand (Brown, Norment & Levy, 1957); this result is consistent with the shift to lower frequencies of the carbonyl stretching mode found in the IR spectrum of $[GdCl_3(dmp)_3]$ relative to dmp. The other bond lengths and angles are in very good agreement with those found in the uncoordinated ligand and in the complex $[Er(dmp)_7](ClO_4)_3$ (Castellani Bisi, Coda & Tazzoli, 1981). In $[Gd(dmp)_7](ClO_4)_3$, gadolinium is coordinated by seven molecules of dmp. The larger size of the chloride ion compared to oxygen is consistent with the lower coordination number, six, in the title compound.

The minimum intermolecular distance (excluding H's) is Cl(2)—O(6^{i}) = 3·39 (1) Å [(i) = 1+x, y, z].

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catena-Aqua-di-μ-chloro-chloro(2,6-dimethyl-4-pyrone)lanthanum(III), $[LaCl_3(C_7H_8O_2)(H_2O)]_n$

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Abstract. $M_r = 387·42$, monoclinic, $P2_1/m$, $a = 7·255$ (5), $b = 9·152$ (5), $c = 9·781$ (6) Å, $\beta = 103·82$ (3)°, $V = 630·6$ (7) Å^3, $Z = 2$, $D_x = 2·040$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 40·6$ cm^{-1}, $F(000) = 368$, $T = 293$ K, final $R = 7·9\%$ for 1734 unique observed reflections. Each La^{III} is coordinated by four equivalent Cl and a water O, which form the equatorial corners of a pentagonal bipyramid; the axial positions are occupied by a terminal Cl and the $C_7H_8O_2$ carbonyl O. The coordination polyhedra form polymeric chains by sharing equatorial edges of Cl atoms. La—O($C_7H_8O_2$) 2·33 (2); La—O(H_2O) 2·50 (2); La—Cl(eq.) 2·90, 2·92 (1); La—Cl(ax.) 2·72 (1) Å.

Introduction. As part of a study on the coordination number of lanthanoids and its variations with decreasing ionic radius of the cation, some years ago the series of complexes $[LnCl_3(dmp)_3]$ (dmp = 2,6-dimethyl-4-pyrone; Ln = all lanthanoids except Pm) (Castellani Bisi, 1970) was prepared. The crystal structure of $[GdCl_3(dmp)_3]$, typical of the series, was determined and the metal ion was found to have octahedral coordination geometry (Bisi Castellani & Tazzoli, 1984).

By operating with a deficiency of the ligand, for La only, the complex $[LaCl_3(dmp)_2]$ was also obtained for which a polymeric structure involving Cl bridges was supposed, since a monomeric form would imply five coordination which is exceedingly rare for lanthanoids. Its crystal structure determination was not possible, since it has been invariably isolated as a powder. However, during repeated preparations a novel complex with formula $[LaCl_3(dmp)(H_2O)]$ was obtained, probably due to imperfect drying of the ethanol.

Experimental. A few crystals of the title compound were grown after mixing equimolar saturated ethanolic solutions of dmp and $LaCl_3$ without excluding atmospheric moisture and slowly evaporating the solvent at room temperature. Unfortunately, several subsequent trials no longer yielded the crystals; thus, at the

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moment, the controlled conditions that produce them cannot be settled. The diffraction profile of the intensity peaks was of rather poor quality; thus the goal of accuracy was not attainable. Nevertheless, the structure determination was carried out, and is presented here as the crystal network is unusual for lanthanoids.

Colourless irregular fragments, roughly equidimensional with average diameter 0·024 cm, sealed in a capillary under nitrogen in order to avoid moisture-induced decomposition. Philips PW 1100 diffractometer, $\lambda_{Mo} = 0{\cdot}71069$ Å (graphite-monochromatized radiation); 25 reflections for lattice-parameter measurements in the range $7 \le \theta \le 10°$; refinement with a Philips routine (*LAT*) that takes into account a 2θ-circle zero correction by measuring very accurate profiles on the positive and negative range of 2θ; seven rows in the range $2 \le \theta \le 30°$ were used; 1950 independent reflections with $\theta \le 30°$ [$(\sin\theta/\lambda \le 0{\cdot}70$ Å^{-1}], $\pm h, k, l$ set (*i.e.* no equivalent data) with max. absolute values 10, 12, 13 respectively; no significant intensity deterioration of standard reflections (600, 080, 006); Lp correction, no absorption correction; Patterson structure determination; full-matrix least-squares refinement with F magnitudes by *ORFLS* (Busing, Martin & Levy, 1962); 216 F's with magnitude $\le 2\sigma(F)$ not used in the refinement; unit weights for all reflections; anisotropic thermal parameters for all atoms; H atoms not taken into consideration; atomic scattering factors with anomalous-dispersion coefficients from *International Tables for X-ray Crystallography* (1974); final $R = 0{\cdot}079$ ($R = 0{\cdot}085$ including unobserved reflections with $|F| = 0{\cdot}67|F_{min,obs}|$ in their zone), $R_w = 0{\cdot}088$, goodness of fit $S = 1{\cdot}33$; $(\Delta/\sigma)_{max} = 0{\cdot}13$; $\Delta\rho$ peaks between $-1{\cdot}12$ and $+1{\cdot}43$ e Å^{-3}.

Discussion. Table 1 shows the atomic parameters,* Table 2 the bond distances and angles. The structure (Fig. 1) is characterized by the occurrence of infinite polymeric chains with symmetry $2_1/m$ running along 2_1, two equivalent Cl atoms being shared by each pair of nearest La atoms. The La coordination polyhedron is a pentagonal bipyramid with symmetry m; the equatorial corners are occupied by the four equivalent bridging Cl atoms and a water O; the axial positions are taken by a terminal Cl atom and the dmp carbonyl O.

The coordination number seven is not rare for lanthanoids, and the pentagonal-bipyramidal geometry has been found in some monomeric complexes with monodentate ligands (Kepert, 1974; Mattos, Surcouf & Mornon, 1977; Pinkerton & Schwarzenbach, 1976; Castellani Bisi, Coda & Tazzoli, 1981). However, heptacoordination is preferred by smaller cations, while the La coordination number is normally eight or higher.

Table 1. *Fractional atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters,* B_{eq}, *with e.s.d.'s in parentheses*

B_{eq} is according to Hamilton (1959); m is the site-occupation factor.

	m	x	y	z	B_{eq}(Å^2)
La	0·5	854 (2)	2500	125 (2)	1·77 (2)
Cl(1)	0·5	1349 (11)	2500	2973 (6)	4·4 (2)
Cl(2)	1	−2313 (4)	483 (4)	−229 (4)	3·1 (1)
O(1)	0·5	43 (26)	2500	−2331 (15)	4·5 (6)
O(2)	0·5	−3266 (19)	2500	−6271 (16)	3·6 (5)
O(3)	0·5	4250 (20)	2500	−27 (24)	4·6 (6)
C(1)	0·5	−1095 (27)	2500	−3590 (21)	2·9 (6)
C(2)	1	−1665 (20)	1158 (20)	−4281 (16)	3·1 (4)
C(3)	1	−2745 (19)	1222 (21)	−5614 (16)	3·3 (4)
C(4)	1	−3491 (26)	−85 (26)	−6508 (21)	4·9 (6)

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

The integer before any bond or distance denotes the multiplicity within the same La coordination polyhedron. Key for symmetry transformations: (i) $-x, \frac{1}{2}+y, -z$; (ii) $-x, -y, -z$; (iii) $x, \frac{1}{2}-y, z$.

1	La–Cl(1)	2·72 (1)	1	La–O(1)	2·33 (2)
2	La–Cl(2)	2·90 (1)	1	La–O(3)	2·50 (2)
2	La–Cl(2^i)	2·92 (1)			
1	Cl(1)–La–O(1)	173 (1)	1	Cl(2^i)–La–Cl(2^{ii})	138·3 (3)
2	Cl(1)–La–Cl(2)	91·7 (3)	2	Cl(2)–La–O(1)	83 (1)
2	Cl(1)–La–Cl(2^i)	90·4 (3)	2	Cl(2^i)–La–O(1)	92·1 (5)
1	Cl(1)–La–O(3)	100 (1)	2	Cl(2)–La–O(3)	139·0 (3)
2	Cl(2)–La–Cl(2^i)	150·3 (2)	2	Cl(2^i)–La–O(3)	69·4 (2)
2	Cl(2)–La–Cl(2^{ii})	71·3 (3)	1	O(1)–La–O(3)	87 (1)
1	Cl(2)–La–Cl(2^{iii})	79·0 (3)	4	La–Cl(2)–La^{ii}	108·7 (2)
1	O(1)–C(1)	1·31 (4)	2	C(3)–C(4)	1·50 (4)
2	C(1)–C(2)	1·41 (4)	2	C(3)–O(2)	1·34 (4)
2	C(2)–C(3)	1·35 (4)			
1	La–O(1)–C(1)	156 (1)	2	C(2)–C(3)–O(2)	122 (3)
2	O(1)–C(1)–C(2)	120 (2)	2	O(2)–C(3)–C(4)	113 (3)
2	C(1)–C(2)–C(3)	117 (3)	1	C(2)–C(1)–C(2^{iii})	120 (3)
2	C(2)–C(3)–C(4)	125 (3)	1	C(3)–O(2)–C(3^{iii})	121 (3)
2	La–O(1)–C(1)–C(2)–92 (4)				

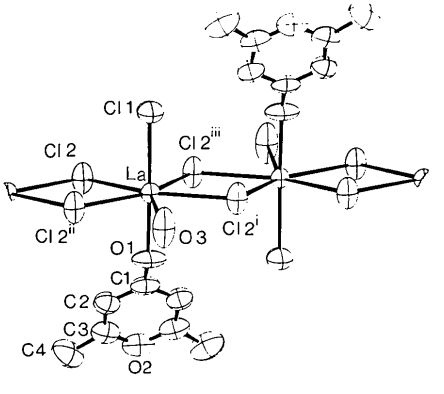

Fig. 1. A perspective view of the title complex.

* Lists of structure factors and anisotropic thermal parameters and details of the dmp least-squares plane have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39662 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Moreover, this type of polymeric structure, although quite common among halogen metal complexes with monodentate organic ligands, has not previously been described for a lanthanoid chloride.

In the title compound Cl bridges are symmmetrical, as found in di-μ-chloro-bis[di-η-cyclopentadienylscandium(III)] (Atwood & Smith, 1973) and the Yb analogue (Baker, Brown & Raymond, 1975), whereas in a previously described dimeric Ce complex containing the cyclooctatetraene ligand (Hodgson & Raymond, 1972) the Cl bridges are definitely asymmetrical. The asymmetry in the Ce complex was attributed to the radius of Ce, large compared to that of Sc and Yb, and to the corresponding increase in metal–metal distance, which does not allow the Cl^- ion to span the gap. However, this explanation is not consistent with the symmetry of the Cl bridges in the title compound, with the La–La distance of 4·732 (3) Å still longer than Ce–Ce, 4·642 (3) Å.

The La–Cl(1) bond, with a terminal Cl, is shorter than the La–Cl(2) bonds with bridge Cl atoms, which is consistent with the usual lengthening of a bond with a bridge halide (Atwood & Smith, 1973). The La–O(carbonyl) distance is shorter than all the La–O distances found in $[La(dmp)_8](ClO_4)_3$ (Castellani Bisi, Della Giusta, Coda & Tazzoli, 1974); this could reflect the crowded environment about La in $[La(dmp)_8](ClO_4)_3$. Bond lengths and angles of dmp compare well with those found in the uncoordinated ligand (Brown, Norment & Levy, 1957) and in the lanthanoid complexes containing it.

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Structure of Bis(1,3-propanediamine)mercury(II) Sulphate Dihydrate, $[Hg(C_3H_{10}N_2)_2]SO_4.2H_2O$

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Abstract. $M_r = 480·90$, monoclinic, $P2$, $a = 13·830$ (2), $b = 6·023$ (1), $c = 8·250$ (1) Å, $\beta = 97·45$ (3)°, $V = 681·4$ (2) Å^3, $Z = 2$, $D_x = 2·343$, $D_m = 2·34$ g cm^{-3}, λ(Mo $K\alpha$) = 0·7107 Å, $\mu = 116·9$ cm^{-1}, $F(000) = 464$, room temperature, final $R = 0·033$ for 1914 independent observed reflections. The structure is built up of the polymeric $[Hg(1,3\text{-propanediamine})_2]_n^{2n+}$ cations with the Hg^{2+} ions bridged by the 1,3-propanediamine ligands and tetrahedrally coordinated by the N atoms. The sulphate ions do not belong to the mercury coordination sphere but are connected in chains with the water molecules through hydrogen bonds.

Introduction. The great majority of metal complexes with 1,3-propanediamine (tn) contain tn as the bidentate chelating ligand. A similar chelating property of tn was expected for mercury complexes, analogously to the mercury complexes with ethylenediamine (Duplančić, Grdenić, Kamenar, Matković & Sikirica, 1976; Grdenić, Sikirica & Vicković, 1977).

Experimental. Title compound prepared by the procedure described for the preparation of the analogous perchlorate complex $[Hg(tn)_2][ClO_4]_2$ (Pfeiffer, Schmitz & Böhm, 1952). Density measured by flotation in methylene iodide and benzene. Crystal 0·23 × 0·36 ×

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