Acta Cryst. (1990). C**46**, 984–985

Structure of Lanthanum Chloride Oxalate Trihydrate

By P. Baker* and A. J. Smith

Department of Chemistry, University of Sheffield, Sheffield S3 7HF, England

(*Received* 26 *September* 1988; *accepted* 2 *June* 1989)

Abstract. Triaquachloro-$\mu_{2,4}$-oxalato-lanthanum(III), $LaCl(C_2O_4).3H_2O$, $M_r = 316·426$, monoclinic, $P2_1/n$, $a = 8·489$ (6), $b = 16·187$ (10), $c = 5·880$ (3) Å, $\beta = 104·14$ (5)°, $V = 783·4$ Å^3, $Z = 4$, $D_x = 2·682$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 58·44$ cm^{-1}, $F(000) = 671·91$, room temperature, final $R = 0·072$ for 1356 unique observed reflections. The La atoms are 9-coordinated in a tricapped trigonal prism arrangement by two independent chelating oxalates (each lying across an inversion centre), one Cl, three waters, and one O from a symmetry-related oxalate. The oxalates link the metal atoms into sheets perpendicular to [010] and the hydrogen bonds, which run to oxalate oxygens and to chlorines, join the structure into a three-dimensional framework.

Introduction. Job (1898) obtained a mixed ligand complex of lanthanum, which he formulated as $2La(C_2O_4)Cl.5H_2O$, by recrystallizing lanthanum oxalate from hot concentrated hydrochloric acid. It seems to have received little attention since. We obtained good crystals (Baker & Smith, 1985) by following Job's method of preparation, though we found the composition to be $La(C_2O_4)Cl.3H_2O$.

Experimental. X-ray reflexion data from a small (approx. 0·3 × 0·2 × 0·4 mm) crystal were collected on a Nicolet *R*3*M* four-circle automatic diffractometer operating in the ω-scan mode and using Mo $K\alpha$ radiation (graphite monochromator, $\lambda = 0·71069$ Å). The unit-cell parameters were determined by least squares from the ω measurements of 13 well centred reflexions in the range $7 < 2\theta < 27°$. Reflexion data in the range $3·5 < 2\theta < 55°$ and having h, k, l in the ranges 0 to 12, 0 to 22, and −8 to 8 respectively, were collected. Two check reflexions were monitored every 100 reflexions and showed no evidence of decay. 2066 measurements were made giving 1990 unique reflexions, of which 1356 were accepted as observed [$|F| > 3\sigma(F)$]. $R_{\rm int}$ was 0·0143. No absorption correction was applied. The structure was solved by Patterson and difference Fourier methods and refined by cascade blocked-diagonal least squares (88 refined parameters) with weights $w = 1/[\sigma^2(F) + 0·00362F^2]$ (the weighting parameter was refined) to a final R of 0·0716 ($wR = 0·0977$). H atoms were found from a difference Fourier map and were constrained to ride each on its neighbouring O atom at calculated distances. The (isotropic) hydrogen thermal parameters were each fixed at 1·2 times $U_{\rm eq}$ for the adjacent heavy atom.

The shifts on the final cycle of refinement were all less than 0·001 of the corresponding e.s.d.'s; the final difference Fourier map showed no peak which could be interpreted as an atom. Analysis of variance against $\sin\theta$ and against $|F|$ showed no unusual features; neither did the normal probability plot. Atomic scattering factors, linear absorption coefficients, and f' and f'' values were taken from *International Tables for X-ray Crystallography* (1974). The *SHELXTL* suite of crystallographic programs (Sheldrick, 1983) was used throughout on a NOVA3 computer.

The atomic parameters are listed in Table 1 and principal bond lengths and angles are in Table 2; the hydrogen bonds are listed in Table 3.† The structure is illustrated in Fig. 1 and 2.

Discussion. There are two distinct oxalate groups, each spanning a crystallographic inversion centre, and each chelating two La atoms. In addition one of the oxalates [C(2), O(5), and O(6)] is coordinated *via* O(6) to a third metal atom [and *via* O(6′) to a fourth]. This oxalate thus generates double chains of La atoms parallel to [001]. The other, C(1), oxalate joins the chains with links parallel to [100], so forming sheets. The six H atoms of the water molecules [represented by O(2), O(3) and O(7)] are all involved in hydrogen bonds, two to oxalate oxygens and the other four to chlorines.

The La atom is 9-coordinate (five oxalate oxygens, three water oxygens, and one Cl) with approximate

---

* Present address: 165 Kingshayes Road, Aldridge, Walsall WS9 8RZ, England.

† Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52305 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

0108-2701/90/060984-02$03.00

Table 1. *Atom coordinates* (× 10^4) *and equivalent isotropic temperature factors* ($Å^2 \times 10^3$)

Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
La(01)	3293 (1)	1057 (1)	223 (2)	18 (1)
Cl(01)	2818 (5)	2652 (3)	2229 (8)	29 (1)
O(1)	576 (15)	944 (8)	1350 (24)	32 (4)
O(2)	4234 (15)	2186 (8)	− 2252 (23)	31 (4)
O(3)	6268 (14)	1454 (8)	2144 (25)	33 (4)
O(4)	1746 (14)	− 259 (8)	− 967 (24)	30 (4)
O(5)	5078 (15)	− 237 (7)	2133 (20)	25 (4)
O(6)	3555 (17)	791 (9)	4522 (22)	34 (4)
O(7)	987 (15)	1418 (9)	− 3355 (23)	33 (4)
C(1)	− 297 (23)	359 (8)	687 (30)	23 (5)
C(2)	5462 (17)	− 306 (9)	4313 (26)	16 (4)

Table 2. *Bond lengths* (Å) *and angles* (°)

La(01)—Cl(01)	2·908 (4)	La(01)—O(1)	2·557 (14)
La(01)—O(2)	2·581 (14)	La(01)—O(3)	2·583 (12)
La(01)—O(4)	2·511 (12)	La(01)—O(5)	2·667 (11)
La(01)—O(6)	2·520 (13)	La(01)—O(7)	2·567 (11)
La(01)—O(5*a*)	2·555 (13)	O(1)—C(1)	1·208 (19)
O(4)—C(1*a*)	1·291 (24)	O(5)—C(2)	1·248 (19)
O(5)—La(0*a*)	2·555 (13)	O(6)—C(2*a*)	1·225 (19)
C(1)—O(4*a*)	1·291 (24)	C(1)—C(1*a*)	1·566 (33)
C(2)—O(6*a*)	1·225 (19)	C(2)—C(2*a*)	1·601 (32)
Cl(01)—La(01)—O(1)	74·6 (3)	Cl(01)—La(01)—O(2)	72·1 (3)
O(1)—La(01)—O(2)	128·3 (4)	Cl(01)—La(01)—O(3)	79·6 (3)
O(1)—La(01)—O(3)	138·7 (4)	O(2)—La(01)—O(3)	70·5 (4)
Cl(01)—La(01)—O(4)	138·7 (3)	O(1)—La(01)—O(4)	64·4 (4)
O(2)—La(01)—O(4)	131·0 (4)	O(3)—La(01)—O(4)	136·2 (4)
Cl(01)—La(01)—O(5)	130·3 (3)	O(1)—La(01)—O(5)	106·9 (4)
O(2)—La(01)—O(5)	124·8 (4)	O(3)—La(01)—O(5)	67·5 (4)
O(4)—La(01)—O(5)	69·9 (4)	Cl(01)—La(01)—O(6)	74·4 (3)
O(1)—La(01)—O(6)	65·9 (4)	O(2)—La(01)—O(6)	136·3 (4)
O(3)—La(01)—O(6)	76·5 (5)	O(4)—La(01)—O(6)	92·7 (5)
O(5)—La(01)—O(6)	62·7 (4)	Cl(01)—La(01)—O(7)	88·7 (3)
O(1)—La(01)—O(7)	70·9 (4)	O(2)—La(01)—O(7)	69·9 (4)
O(3)—La(01)—O(7)	140·4 (4)	O(4)—La(01)—O(7)	73·9 (4)
O(5)—La(01)—O(7)	139·9 (4)	O(6)—La(01)—O(7)	136·4 (5)
Cl(01)—La(01)—O(5*a*)	145·9 (3)	O(1)—La(01)—O(5*a*)	138·2 (4)
O(2)—La(01)—O(5*a*)	77·2 (4)	O(3)—La(01)—O(5*a*)	76·5 (4)
O(4)—La(01)—O(5*a*)	74·0 (4)	O(5)—La(01)—O(5*a*)	59·6 (5)
O(6)—La(01)—O(5*a*)	121·9 (4)	O(7)—La(01)—O(5*a*)	94·6 (4)
La(01)—O(1)—C(1)	119·6 (13)	La(01)—O(4)—C(1*a*)	121·4 (10)
La(01)—O(5)—C(2)	118·8 (10)	La(01)—O(5)—La(O*a*)	120·4 (5)
C(2)—O(5)—La(O*a*)	118·0 (10)	La(01)—O(6)—C(2*a*)	123·5 (12)
O(1)—C(1)—O(4*a*)	125·8 (17)	O(1)—C(1)—C(1*a*)	119·9 (22)
O(4*a*)—C(1)—C(1*a*)	114·2 (16)	O(5)—C(2)—O(6*a*)	127·1 (16)
O(5)—C(2)—C(2*a*)	115·2 (15)	O(6*a*)—C(2)—C(2*a*)	117·7 (16)

Table 3. *Hydrogen-bond lengths* (Å) *and angles* (°)

	H···X	O···X	O—H···X
O(2)—H(1)···Cl	2·41	3·26	148
O(2)—H(2)···Cl	2·24	3·14	157
O(3)—H(3)···O(4)	1·88	2·76	151
O(3)—H(4)···Cl	2·68	3·29	122
O(7)—H(5)···O(6)	2·25	2·95	128
O(7)—H(6)···Cl	2·87	3·17	99

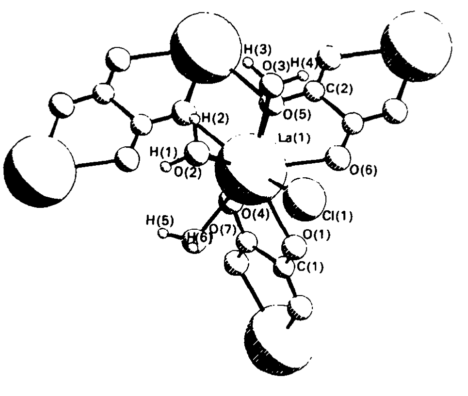

Fig. 1. The surroundings of the one La atom. To avoid confusion the coordination polyhedron is not drawn. It is defined by O(3), Cl(1), and O(6) (top triangle), O(2), O(1), and O(5) (equatorial triangle), and by O(5′) (unlabelled), O(7), and O(4) (bottom triangle).

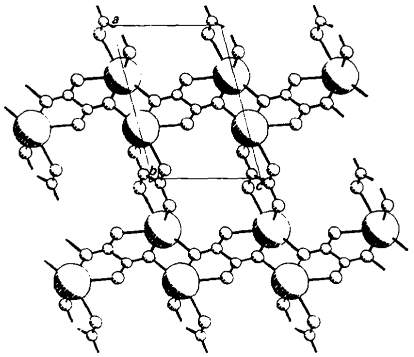

Fig. 2. Lanthanum atoms and oxalates forming a (010) sheet.

D_{3h} local symmetry (3/3/3). The θ angle of the idealized polyhedron obtained from a least-squares fit (Smith, 1990) is 44·35° with a σ of 6·84°. (θ is the angle between the principal symmetry axis and a metal–ligand bond, in this case a non-equatorial bond.) This last figure is somewhat larger than usual because of the large radius of the Cl. The chelate oxalates span two of the pyramid edges, with their non-equatorial oxygens at opposite ends of the same prism edge. The three water oxygens span opposite pyramid edges in the other pyramid. [O(2) is the equatorial one.] This leaves two non-equatorial positions (on opposite ends of the polyhedron, but not on the same prism edge) for the Cl and the O of the bridging oxalate.

References

Baker, P. & Smith, A. J. (1985). IX Eur. Crystallogr. Meet., Torino, Italy, pp. 235–236.

International Tables for X-ray Crystallography (1974). Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Job, A. (1898) *C. R. Acad. Sci.* **126**, 246–248.

Sheldrick, G. M. (1983). *SHELXTL* (Revision 4). Univ. of Göttingen, Federal Republic of Germany.

Smith, A. J. (1990). In preparation.