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Lanthanum(III) Chlorite Trihydrate, $La(ClO_2)_3.3H_2O$: A Redetermination

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Abstract. $M_r = 395·34$, $P\bar{6}2c$, $a = 8·077$ (1), $c = 8·296$ (1) Å, $V = 468·7$ (1) Å^3, $Z = 2$, $D_x = 2·80$, $D_m = 2·8$ Mg m^{-3}, $\lambda = 0·71069$ Å, μ(Mo $K\alpha$) = 5·51 mm^{-1}, $F(000) = 372$, $T = 295$ K, $R = 0·029$ for 263 unique diffractometer reflections. The La coordination polyhedron is a trigonal prism of ClO_2^- [Cl—O = 1·540 (8) Å, O—Cl—O = 114·0 (7)°] O atoms [La—O = 2·547 (7) Å] tricapped by three water O atoms [La—OH_2 = 2·550 (11) Å]. The ClO_2^- anions connect two different La polyhedra. Hydrogen bonding involving the water O atoms also bridges the La polyhedra.

Introduction. The structure of the title compound was solved by Coda, Giuseppetti & Tadini (1965), who encouraged the author to revise and refine this structure, as the unavailability of a good sample at that time and the paucity of the diffraction data prevented them from producing accurate bond lengths and angles (the main goal in the structural study of a simple inorganic compound such as this). Moreover, the number of chlorite structures so far studied is small; thus, it seemed worthwhile searching for a better crystal and redetermining the structure.

Experimental. Sample obtained as described by Castellani Bisi & Clerici (1963). Suitable hexagonal bipyramid 0·192 × 0·192 × 0·368 mm, the last along **c**. Philips PW 1100 diffractometer, graphite-monochromatized Mo $K\alpha$ radiation, 25 reflections for lattice-parameter measurements refined by Philips *LAT* procedure, $11 < \theta < 23°$. Absorption correction for sphere of equal volume, plus North, Phillips & Mathews (1968) empirical ψ-scan correction based on four reflections with $87° \leq \chi \leq 88°$; max. and min. absorption corrections 1·275, 0·988. 293 independent reflections with $\theta_{Mo} \leq 30°$ [max. $(\sin\theta)/\lambda = 0·704$ Å^{-1}] after averaging of 570 hkl and $hk\bar{l}$ measurements ($R_{int} = 4·8\%$). Three standards (300, 030, 004): crystal deterioration, 18% max. intensity variation; linear correction applied. Lp correction. Full-matrix F least-squares refinement (Busing, Martin & Levy, 1962) of coordinates from Coda *et al.* (1965), on 263 observations with $I > 3\sigma(I)$ and $w = 1$. Atomic scattering factors with anomalous-dispersion contributions (*International Tables for X-ray Crystallography*, 1974). Secondary-extinction factor (Zachariasen, 1963) refined to final $g = 0·0046$ (3). H atoms clearly detected as the highest peaks in the final ΔF synthesis, not refined. Anisotropic thermal parameters for all other atoms. Final $R = 0·0290$, $wR = 0·0372$ [with $w = 1/\sigma^2(F)$]; $S = 1·42$; $(\Delta/\sigma)_{max} = 0·005$, final $\Delta\rho$ excursions $\leq 0·3$ e Å^{-3}.* Other programs locally developed; Honeywell DPS8/44 computer.

Discussion. Table 1 shows the atomic parameters, Table 2 the bond distances and angles. The structure is confirmed, particularly the details that cooperate to cause the pseudo extinctions reported by Coda *et al.* (1965) and that needed a careful check: water oxygens with x and y nearly identical, associated with ClO_2^- oxygens almost at $z = 0$. The La coordination consists (Fig. 1) of a trigonal prism of six symmetry-equivalent ClO_2^- oxygens, with every face capped by a water oxygen (coordination number 9). In this refinement all the La—O distances become identical: 2·55 (1) Å. The ClO_2^- anions connect two different La polyhedra; the H-bonding system also bridges La polyhedra as shown in Fig. 1. The O—Cl—O angle is wider than in the previous determination: 114·0 (7)° [against 110 (3)°]. Compare the other O—Cl—O values in the literature: 110·5° in NH_4ClO_2 (Gillespie, Sparks & Trueblood, 1959); 111 (3)° in $AgClO_2$ (Cooper & Marsh, 1961); 108·2 (1)° in $NaClO_2.3H_2O$ (Tarimci, Schempp & Chang, 1975; Tazzoli, Riganti, Giuseppetti & Coda, 1975); 108·6 (1)° in $NaClO_2$ (Tarimci, Rosenstein & Schempp, 1976); 111·4 (1)° in $Zn(ClO_2)_2.2H_2O$ (Pakkanen & Pakkanen, 1979). The present Cl—O bond distance, 1·540 (8) Å, compares, in the same order, with: 1·57 (3), 1·55 (5), 1·557 (1), 1·564 (3) and 1·580 (3) Å.

The diffraction data have been collected on the diffractometer of the Centro di Studio per la Cristallografia Strutturale del CNR, Pavia; the author is grateful for the use of this facility.

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* Lists of structure factors, anisotropic thermal parameters and an analysis of the thermal ellipsoids have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39341 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates and B_{eq} values (B_{iso} for H) according to Hamilton (1959), with e.s.d.'s in parentheses*

m is the site-occupation factor.

	m	x	y	z	B_{eq}(Å^2)
La	$\frac{1}{6}$	$\frac{2}{3}$	$\frac{1}{3}$	$\frac{1}{4}$	1·42 (2)
Cl	$\frac{1}{2}$	0·7600 (4)	0	0	3·7 (1)
O	1	0·4358 (12)	0·2520 (11)	0·0149 (9)	3·3 (3)
Aq	$\frac{1}{2}$	0·5574 (19)	0·5798 (17)	$\frac{1}{4}$	3·5 (5)
H	1	0·560	0·659	0·153	2·3

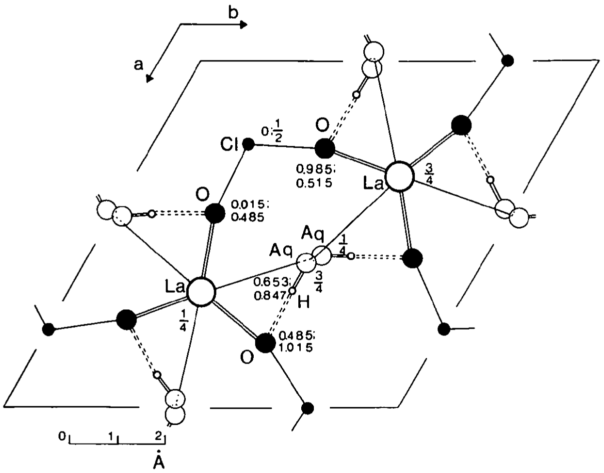

Fig. 1. Projection of one cell along **c**. The double lines denote two superimposed bonds running upwards and downwards respectively. Similarly each of the double-dashed lines represents a pair of hydrogen bonds.

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°), *e.s.d.'s in parentheses*

La–O	2·547 (7)	Aq(–H···)–O^{iii}	2·89 (1)
La–Aq	2·550 (11)	Aq–H	1·02
Cl^{i}–O	1·540 (8)	H–Aq–H^{iv}	104·0
O–Cl^{i}–O^{ii}	114·0 (7)	Aq–H–O^{iii}	176·1

Symmetry code
(i) $1 - x, y - x + 1, \bar{z}$
(ii) $y, x, \bar{z}$
(iii) $y - x + 1, 1 - x, z$
(iv) $x, y, \frac{1}{2} - z$

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The Deuterium-Atom Positions in Deuterated Molybdic Acid, $MoO_3.2D_2O$, by Powder Neutron Diffraction

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Abstract. $M_r = 184{\cdot}0$, monoclinic, $P2_1/n$, $a = 10{\cdot}487\,(1)$, $b = 13{\cdot}850\,(1)$, $c = 10{\cdot}617\,(1)$ Å, $\beta = 91{\cdot}62\,(9)^\circ$, $V = 1541{\cdot}5$ Å^3, $Z = 16$, $D_x = 3{\cdot}17$ g cm^{-3}, $\lambda = 1{\cdot}909$ Å, $\mu = 0{\cdot}032$ cm^{-1}, $T = 298$ K. The D-atom positions in $MoO_3.2D_2O$ have been obtained from profile analysis of powder neutron diffraction data. The profile, arising from 1530 overlapping reflections, was refined to $R_{wp} = 9{\cdot}8$ using the Rietveld method. It was not found necessary to apply a linear absorption correction.

Introduction. $MoO_3.2H_2O$ is one of three stoichiometric hydrates of MoO_3 collectively known as molybdic acids. The two remaining phases are the yellow and white forms of the monohydrate, $MoO_3.H_2O$.

Single-crystal X-ray studies on $MoO_3.2H_2O$ (Krebs, 1972; Åsbrink & Brandt, 1971) have shown that the structure consists of infinite layers of distorted MoO_6 octahedra, each sharing four vertices with neighbouring octahedra. Of the two terminal O atoms in each octahedron, one is replaced by a coordinated

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