inorganic papers

Calcium chlorite, Ca(ClO$_2$)$_2$, from X-ray powder diffraction data

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Key indicators

Powder X-ray study
T = 293 K
Mean σ(Cl–O) = 0.003 Å
R factor = 0.127
wR factor = 0.145
Data-to-parameter ratio = 6.77

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

The structure of calcium chlorite, Ca(ClO$_2$)$_2$, has been refined from X-ray powder diffraction data using the Rietveld method. The compound crystallizes in the orthorhombic space group *Ccca* (*Ccce*), with Z = 4. The structure is based on separate layers parallel to the *ac* plane, consisting of calcium cations that are coordinated by chlorite anions; the O atoms form almost ideal square antiprisms. Within the layers, each anion bridges four metal cations. The Ca atoms are located on special positions of 222 symmetry, the Cl atoms lie on twofold axes and the O atoms are in general positions. The compound is isostructural with strontium chlorite, Sr(ClO$_2$)$_2$, and lead chlorite, Pb(ClO$_2$)$_2$.

Comment

Recently, we carried out the crystal structure determination of barium chlorite hydrate, Ba(ClO$_2$)$_2$·3.5H$_2$O (Smolentsev & Naumov, 2005*a*). To continue our systematic structural characterization of alkaline earth metal chlorites, the present investigation has been performed. Furthermore, obtaining crystal data for calcium chlorite seemed appropriate because it was investigated previously (together with the strontium salt) by Riganti & Garrini (1960), who could not index the X-ray powder pattern satisfactorily and only proposed a pseudo-cubic cell with a lattice parameter of 5.80 Å (5.97 Å for the strontium salt). The results of our study are reported here.

Ca(ClO$_2$)$_2$ is isostructural with Sr(ClO$_2$)$_2$ (Smolentsev & Naumov, 2005*d*) and Pb(ClO$_2$)$_2$ (Okuda *et al.*, 1990). The experimental and calculated powder profiles, as well as the difference plot, are shown in Fig. 1. The structure of the title
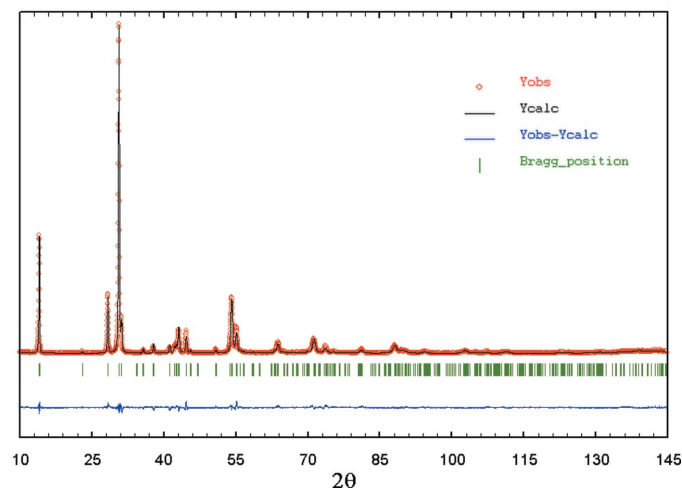

Figure 1
Experimental and calculated powder profiles of Ca(ClO$_2$)$_2$, with difference plot.

2005), which have almost identical positional relationships of structure building units – metal cations M^{2+} (M = Sr, Ba and Pb) and anions with similar shape. Barium hypophosphite is closely related to the title compound. The two compounds have the same space group and similar lattice and positional parameters. This fact confirms the assumption that the ClO_2^- and $H_2PO_2^-$ anions may perform similar structural roles in many cases, which is the result of their geometry and electronic configuration.

Experimental

Polycrystalline $Ca(ClO_2)_2$ was synthesized at room temperature by reacting an aqueous suspension of calcium peroxide with an excess of chlorine dioxide, followed by precipitation from solution by adding a 3:1 mixture of ethanol and diethyl ether. A white crystalline powder resulted.

Crystal data

$Ca(ClO_2)_2$	Cu $K\alpha$ radiation
$M_r = 174.98$	Wavelength of incident radiation:
Orthorhombic, *Ccca* (*Ccce*)	1.54178 Å
$a = 5.7434\ (7)$ Å	$T = 293\ (2)$ K
$b = 12.6002\ (9)$ Å	Specimen shape: flat sheet
$c = 5.7405\ (7)$ Å	$10 \times 10 \times 0.1$ mm
$V = 415.43\ (8)$ Å^3	Particle morphology: plate-like,
$Z = 4$	white
$D_x = 2.798$ Mg m^{-3}	

Data collection

Philips PW1700 powder diffractometer	Specimen mounted in reflection mode
Specimen mounting: drifted powder on standard quartz sample holder	Scan method: step
	$2\theta_{min} = 5.0$, $2\theta_{max} = 145.0°$
	Increment in $2\theta = 0.02°$

Refinement

$R_p = 0.127$	$(\Delta/\sigma)_{max} = 0.01$
$R_{wp} = 0.145$	Preferred orientation correction:
$R_{exp} = 0.080$	$I_{corr} = I_{obs}[G_2 + (1 - G_2) \times$
$R_B = 0.043$	$\exp(G_1\alpha^2)]$, where α is the acute
$S = 1.81$	angle between the scattering
Profile function: split pseudo-Voigt	vector and the normal to the
210 reflections	crystallites, $G_1 = -2.69\ (2)$, $G_2 =$
31 parameters	$0.102\ (1)$, axis [010] (Rietveld,
$w = 1/[\sigma^2(Y_i)]$	1969)

Table 1
Selected geometric parameters (Å, °).

Ca—O	2.481 (3)	Cl—O	1.585 (3)
Ca—O^i	2.499 (3)		
O—Cl—O^{ii}	115.3 (3)		

Symmetry codes: (i) $-x + \frac{1}{2}, y, z + \frac{1}{2}$; (ii) $-x + 1, y, -z + \frac{1}{2}$.

The list of peak positions was obtained from the X-ray raw data using the program *WINPLOTR* (Roisnel & Rodriguez-Carvajal, 2005) and used for indexing by the *CRYSFIRE* suite (Shirley, 2000). An orthorhombic cell was selected as that best corresponding to the observed diffractogram. The calculated cell parameters, *a* and *c*, are in agreement with the pseudo-cubic parameter reported by Riganti & Garrini (1960). In fact, the cell metric is extremely close to tetragonal. Probably this was the reason why previous authors had difficulty in indexing the powder patterns. Systematic absences, *hkl* with *h* + *k*

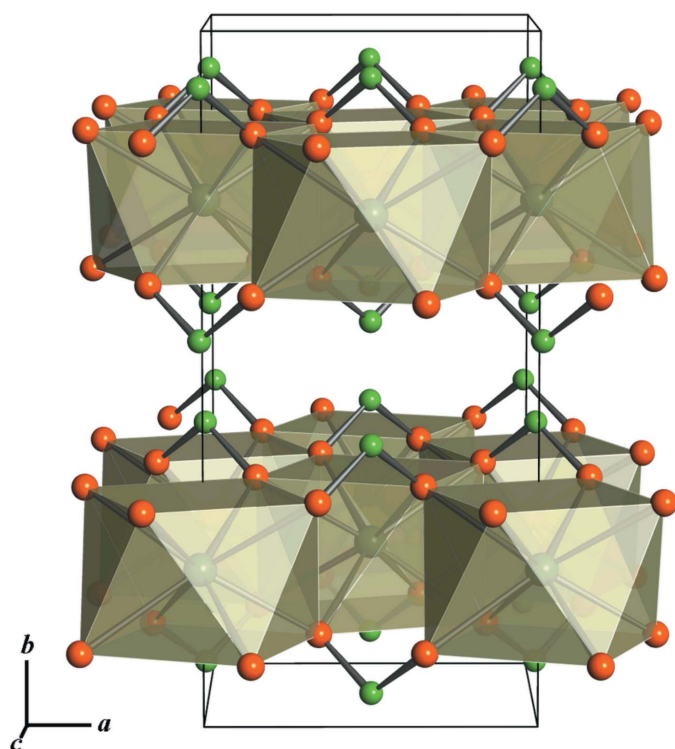**Figure 2**
Layers of metal cations and chlorite anions in the $Ca(ClO_2)_2$ structure.

compound is layered. Separate layers are parallel to the *ac* plane and consist of calcium cations coordinated by chlorite anions. The full coordination sphere of the cation includes eight chlorite O atoms forming an almost ideal square antiprism. Within a layer these square antiprisms share four edges. Each ClO_2^- anion serves as a tetradentate bridging ligand bonding four metal cations (Fig. 2). The shortest Cl···Cl distance between adjacent layers is 3.541 (1) Å. Satisfactory geometric parameters of the ClO_2^- anion (*i.e.* corresponding to those in other chlorites) were obtained through a weak restraint of the Cl—O distance to 1.57 (2) Å, which is the average value of the most accurate distances reported by Tarimci & Schempp (1975), Tarimci *et al.* (1976), Pakkanen (1979), Castellani Bisi (1984), Okuda *et al.* (1990), Marsh (1991), and Smolentsev & Naumov (2005a,b,c). At the same time, the O—Cl—O angle of 115.3 (3)° is comparable to the average of 110 (2)° found in the literature.

In the previously studied $Ba(ClO_2)_2 \cdot 3.5H_2O$, a layered structure is also realized, but in this compound, layers are formed with the participation of water molecules. Nevertheless, general details of the layer construction are similar to those in the title chlorite. Unfortunately, comparison with anhydrous $Ba(ClO_2)_2$ cannot be made because of difficulties with indexing and structure solution (caused either by a non-monophase pattern or high texture), but analysis of the diffractogram showed that $Ba(ClO_2)_2$ most probably belongs to a different crystal system than the calcium member. Among the compounds with comparable anions of other acids, the most similarity is observed for some hypophosphites, *viz.* $Pb(H_2PO_2)_2$, $Sr(H_2PO_2)_2$ and $Ba(H_2PO_2)_2$ (Kuratieva *et al.*,

odd, $hk0$ with h or k odd, $h0l$ with h or l odd, and $0kl$ with k or l odd, showed that the space group is $Ccca$ ($Ccce$). Proceeding from this information, the $Pb(ClO_2)_2$ structure [$Ccca$ ($Ccce$), $Z = 4$, $a = 6.004$ (1) Å, $b = 12.504$ (2) Å, $c = 6.010$ (1) Å; Okuda *et al.*, 1990] was chosen as a trial model for the full-profile Rietveld refinement. The Rietveld refinement was performed in two general steps. First, the validity of cell parameters and space group was confirmed using the profile-matching method (split pseudo-Voigt peak-shape function). At this stage, only the zero shift, background polynomial coefficients, cell parameters, peak-shape and FWHM variables were varied. In subsequent refinements, the scale factor, and positional and isotropic displacement parameters for all atoms were refined. The Cl—O distances were weakly restrained to 1.57 (2) Å. This also improved the O—Cl—O angles. No other restraints were used. Since the structure is layered in the [010] direction, refinement of preferred orientation coefficients was also applied.

Data collection: *APD1700 Software* (Philips, 1989); cell refinement: *FULLPROF2k* (Rodriguez-Carvajal, 2004); program(s) used to refine structure: *FULLPROF2k*; molecular graphics: *WINPLOTR* (Roisnel & Rodriguez-Carvajal, 2005) and *BS* (Ozawa & Kang, 2004); software used to prepare material for publication: *WINPLOTR*.

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