

Barium chlorite hydrate,
 $\text{Ba}(\text{ClO}_2)_2 \cdot 3.5\text{H}_2\text{O}$

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The structure of barium chlorite hydrate, $\text{Ba}(\text{ClO}_2)_2 \cdot 3.5\text{H}_2\text{O}$, has been determined by single-crystal X-ray analysis at 150 K. The structure is monoclinic, space group $C2/c$, with $Z = 8$. It contains layers of Ba^{2+} cations coordinated by ClO_2^- anions and water molecules. There are also solvate water molecules involved only in hydrogen bonding of the layers. Three solvate water O atoms are on sites of twofold symmetry, while all other atoms are in general positions. The full coordination environment of the Ba^{2+} cation consists of ten O atoms belonging to six chlorites and three water molecules, forming a bicapped square antiprism.

Comment

The anhydrous alkaline earth metal chlorites, $\text{Ca}(\text{ClO}_2)_2$, $\text{Sr}(\text{ClO}_2)_2$ and $\text{Ba}(\text{ClO}_2)_2$, were first investigated crystallographically by Riganti & Garrini (1960). Because these compounds were obtained as microcrystalline powders, only powder diffraction patterns were obtained, which were not indexed. These authors proposed that $\text{Ca}(\text{ClO}_2)_2$ and $\text{Sr}(\text{ClO}_2)_2$ are isomorphic and have pseudo-cubic cells with similar parameters. However, the complete structures of all anhydrous alkaline earth metal chlorites are still unknown. They also reported that barium chlorite may form a hydrate with 3.5 water molecules (unlike Ca and Sr chlorites), but its crystal structure was not determined because of its very low stability.

The purpose of the present investigation was to obtain structural data for the title hydrate. As the crystal structures of only some chlorites have been determined to date, a new contribution to the crystal chemistry of these simple compounds seemed useful. The present paper continues our research on chlorous acid salts, which has included LiClO_2 and KClO_2 (Smolentsev & Naumov, 2005*a*) and the redetermined structure of NH_4ClO_2 (Smolentsev & Naumov, 2005*b*).

In the structure of $\text{Ba}(\text{ClO}_2)_2 \cdot 3.5\text{H}_2\text{O}$, the coordination sphere of the Ba^{2+} cation includes ten O atoms (Fig. 1); seven of these belong to the chlorite anions and the other three to the water molecules. The resultant coordination is a distorted

bicapped square antiprism. By sharing edges, the antiprisms form layers parallel to the bc plane (Fig. 2). The layers are stacked in such way that adjacent layers are shifted along the b axis by half a unit translation.

The structure contains both water molecules coordinated to the Ba^{2+} cations and solvate water molecules, which are involved only in hydrogen bonding of the layers. Non-coordinated water of crystallization has not been found in other hydrated chlorites studied so far, *viz.* $\text{NaClO}_2 \cdot 3\text{H}_2\text{O}$ (Tarimci & Schempp, 1975), $\text{Mg}(\text{ClO}_2)_2 \cdot 6\text{H}_2\text{O}$ (Okuda *et al.*, 1990; Marsh, 1991), $\text{Zn}(\text{ClO}_2)_2 \cdot 2\text{H}_2\text{O}$ (Pakkanen, 1979) and $\text{La}(\text{ClO}_2)_3 \cdot 3\text{H}_2\text{O}$ (Castellani Bisi, 1984), in which all water molecules are coordinated to the metal cations. In this regard, $\text{Mg}(\text{ClO}_2)_2 \cdot 6\text{H}_2\text{O}$ is outstanding: the water molecules form the

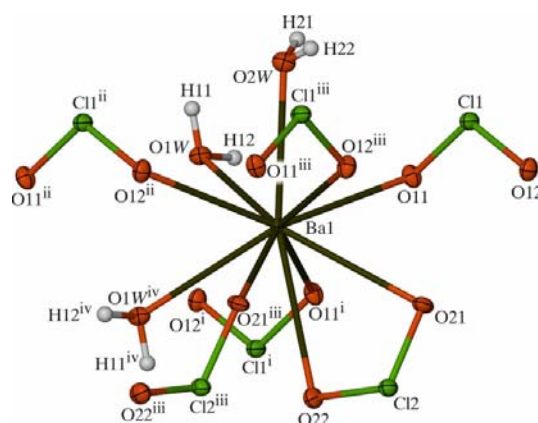


Figure 1

The coordination environment of the Ba^{2+} cation. Displacement ellipsoids are plotted at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (ii) $x, y, 1 + z$; (iii) $x, -y, \frac{1}{2} + z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, 2 - z$.]

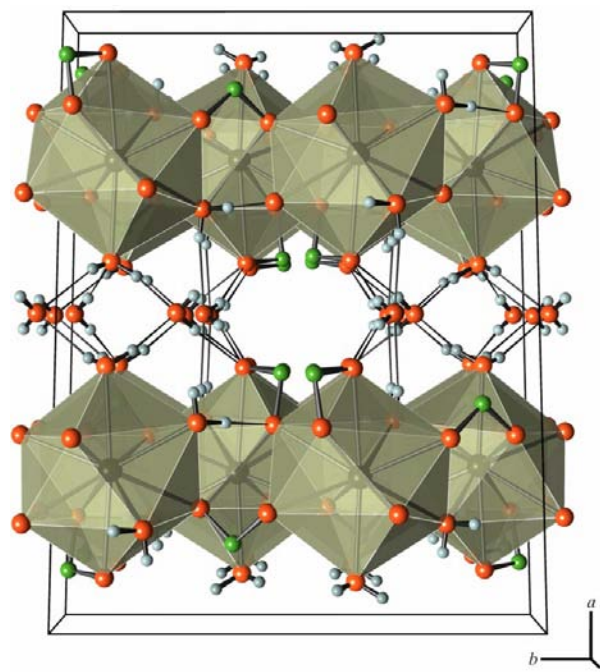


Figure 2

A perspective packing diagram of the $\text{Ba}(\text{ClO}_2)_2 \cdot 3.5\text{H}_2\text{O}$ structure, viewed along the c axis. Thin lines represent hydrogen bonds.

complex cation $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$, which is then hydrogen bonded to ClO_2^- anions. A layered structure is found in $\text{Zn}(\text{ClO}_2)_2 \cdot 2\text{H}_2\text{O}$, while the sodium salt contains chains, and the magnesium and lanthanum salts both have three-dimensional frameworks. Unlike these other hydrated chlorites, the title compound has one more feature, *i.e.* two independent ClO_2^- groups with symmetry non-equivalent O atoms. Anions of the first type (O11—Cl1—O12) serve as tetradentate bridging ligands between the Ba^{2+} cations and are not included in the hydrogen-bond system. The O atoms of the second anion type (O21—Cl2—O22) have different environments. They are both coordinated to the same Ba^{2+} cation and involved in hydrogen bonding. However, atom O21 is also coordinated to the neighbouring cation and forms a hydrogen bond with only one coordinated water molecule within the layer, while atom O22 is hydrogen bonded to two interlayer water molecules.

Due to the non-equivalence of the ClO_2^- anions, their geometric parameters are slightly different. Nevertheless, they are in good agreement with the values determined for other chlorites. Comparison can be made with the average Cl—O distance and O—Cl—O angle calculated from the corresponding values reported previously (Tarimci & Schempp, 1975; Tarimci *et al.*, 1976; Pakkanen, 1979; Castellani Bisi, 1984; Okuda *et al.*, 1990; Marsh, 1991; Smolentsev & Naumov, 2005*a,b*), which are 1.571 (14) Å and 110 (2)°, respectively.

Experimental

The title compound appears as a thin crystalline film on the surface of a concentrated aqueous solution of barium chlorite during evaporation at room temperature. Thus, the main difficulty is in selecting a crystal suitable for X-ray diffraction. It is also necessary to note that this hydrate is very unstable and, without the mother solution, it completely decomposes to the anhydrous salt in a few minutes. In contrast, at low temperatures the crystals are quite stable. Anhydrous $\text{Ba}(\text{ClO}_2)_2$ was previously synthesized by reacting an aqueous suspension of BaO_2 with chlorine dioxide, followed by precipitation from solution by adding a 3:1 mixture of ethanol and diethyl ether. Unlike the hydrate, it is one of the most stable salts of chlorous acid.

Crystal data

$\text{Ba}(\text{ClO}_2)_2 \cdot 3.5\text{H}_2\text{O}$	$D_x = 2.797 \text{ Mg m}^{-3}$
$M_r = 335.30$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 3491 reflections
$a = 18.4801 (5) \text{ \AA}$	$\theta = 2.3\text{--}33.5^\circ$
$b = 13.5715 (4) \text{ \AA}$	$\mu = 5.65 \text{ mm}^{-1}$
$c = 6.6904 (2) \text{ \AA}$	$T = 150 (2) \text{ K}$
$\beta = 108.364 (1)^\circ$	Plate, colourless
$V = 1592.52 (8) \text{ \AA}^3$	$0.15 \times 0.13 \times 0.02 \text{ mm}$
$Z = 8$	

Table 1 Selected geometric parameters (Å, °).

Ba1—O12 ⁱ	2.7741 (14)	Ba1—O22	3.0210 (15)
Ba1—O11	2.7781 (13)	Cl1—O11	1.5728 (13)
Ba1—O2W	2.8330 (15)	Cl1—O12	1.5737 (14)
Ba1—O1W	2.9241 (14)	Cl2—O21	1.5753 (13)
Ba1—O21	2.9450 (14)	Cl2—O22	1.5787 (15)
O11—Cl1—O12	110.77 (8)	O21—Cl2—O22	107.22 (8)

Symmetry code: (i) $x, y, z + 1$.

Data collection

Bruker–Nonius X8 APEX CCD area-detector diffractometer	2821 independent reflections
φ scans	2321 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (SADABS; Bruker, 2004)	$R_{\text{int}} = 0.022$
$T_{\text{min}} = 0.484, T_{\text{max}} = 0.895$	$\theta_{\text{max}} = 32.6^\circ$
7807 measured reflections	$h = -27 \rightarrow 27$
	$k = -20 \rightarrow 12$
	$l = -9 \rightarrow 8$

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.020$	$wR(F^2) = 0.051$
$S = 1.05$	$w = 1/[\sigma^2(F_o^2) + (0.0234P)^2]$
2821 reflections	where $P = (F_o^2 + 2F_c^2)/3$
118 parameters	$(\Delta/\sigma)_{\text{max}} = 0.002$
	$\Delta\rho_{\text{max}} = 1.55 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.54 \text{ e \AA}^{-3}$

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

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
O1W—H11 ⁱ ···O5W ⁱ	0.83 (2)	2.27 (2)	3.0913 (14)	168 (2)
O1W—H12 ⁱ ···O21 ⁱⁱ	0.83 (2)	2.06 (2)	2.8929 (19)	176 (2)
O2W—H21 ⁱ ···O3W	0.83 (2)	1.92 (2)	2.735 (2)	166 (2)
O2W—H22 ⁱ ···O4W ⁱⁱⁱ	0.82 (2)	2.01 (2)	2.798 (2)	161 (2)
O3W—H3 ⁱ ···O22 ^{iv}	0.82 (2)	1.91 (2)	2.730 (2)	173 (2)
O4W—H4 ⁱ ···O2W ^v	0.82 (2)	1.92 (2)	2.7352 (18)	168 (2)
O5W—H5 ⁱ ···O22 ⁱⁱ	0.82 (2)	1.98 (2)	2.7851 (17)	166 (3)

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

The H atoms were located in difference electron-density maps and refined with O—H distances restrained to 0.82 (1) Å.

Data collection: APEX2 (Bruker, 2004); cell refinement: SAINT (Bruker, 2004); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2004); program(s) used to refine structure: SHELXTL; molecular graphics: BS (Ozawa & Kang, 2004) and POV-Ray (Cason, 2002); software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1204). Services for accessing these data are described at the back of the journal.

References

Bruker (2004). APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11) and SHELXTL (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.

Cason, C. J. (2002). POV-Ray for Windows. Version 3.5. URL: <http://www.povray.org>.

Castellani Bisi, C. (1984). Acta Cryst. C40, 1120–1121.

Marsh, R. E. (1991). Acta Cryst. C47, 1775.

Okuda, M., Ishihara, M., Yamanaka, M., Ohba, S. & Saito, Y. (1990). Acta Cryst. C46, 1755–1759.

Ozawa, T. C. & Kang, S. J. (2004). Balls & Sticks (BS). Version 1.51. URL: <http://www.softbug.com/toycrate/bs>.

Pakkanen, T. (1979). Acta Cryst. B35, 2670–2672.

Riganti, V. & Garrini, E. (1960). Gazz. Chim. Ital. 90, 321–327.

Smolentsev, A. I. & Naumov, D. Y. (2005a). Acta Cryst. C61, i17–i19.

Smolentsev, A. I. & Naumov, D. Y. (2005b). Acta Cryst. E61, i38–i40.

Tarimci, C., Rosenstein, R. D. & Schempp, E. (1976). Acta Cryst. B32, 610–612.

Tarimci, C. & Schempp, E. (1975). Acta Cryst. B31, 2146–2149.