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The double-layered hydroxide $3CaO \cdot Al_2O_3 \cdot 0.5CaBr_2 \cdot 0.5CaCl_2 \cdot 10H_2O$

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The title compound, calcium oxide–dialuminium trioxide–calcium dibromide–calcium dichloride hydrate (3/1/0.5/0.5/10), also formulated as $Ca_2Al(OH)_6Br_{0.478}Cl_{0.522} \cdot 2H_2O$ (dicalcium aluminium hydroxide hemibromide hemichloride dihydrate), is a double-layered hydroxide which belongs to the solid solution $Ca_2Al(OH)_6Br_xCl_{1-x} \cdot 2H_2O$, where x can vary from 0 to 1. Chloride and bromide anions of the negatively charged interlayer $[Br_{0.5}Cl_{0.5} \cdot 2H_2O]^-$ share statistically the same crystallographic site. Al^{3+} and Ca^{2+} cations are coordinated by six and seven O atoms, respectively. All water molecules are bonded to Ca^{2+} cations and assume the seventh coordination position. Anions in the interlayer are surrounded by ten H atoms. Br^- and Cl^- are therefore connected to the main layer by ten hydrogen bonds, six of 2.74 (2) Å and four of 2.52 (5) Å, where the donors are hydroxyl groups and water molecules, respectively. Like the chloride equivalent, the title compound is a $6R$ polytype with trigonal space group $R\bar{3}c$ and lattice parameters a = 5.7537 (4) Å and c = 48.108 (4) Å.

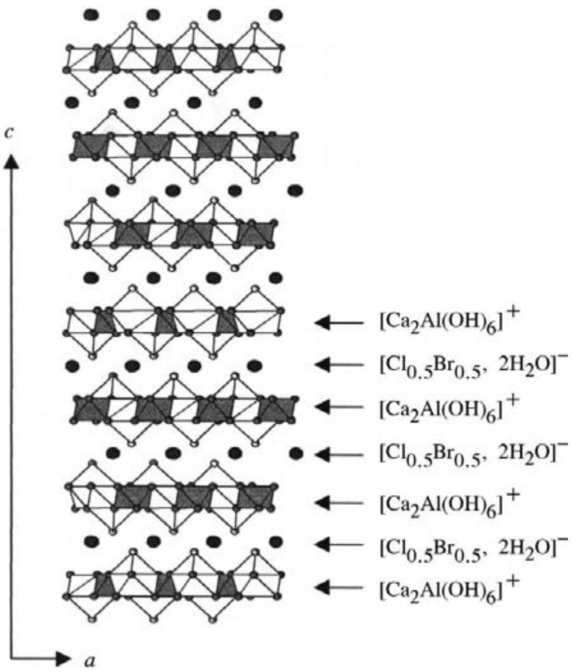

Figure 1
The projection of the layered structure of the title compound along [110]. The polyhedral AlO_6 (shaded) and CaO_7 (unshaded) representation is produced using *ATOMS* (Dowty, 1995).

Comment

The title compound was studied in the course of our investigations on the phases called AFm, which are hydrated compounds formed in cementitious pastes. Their structures are layered and constituted by positively charged $[Ca_2Al(OH)_6]^+$ main layers and negatively charged $[X^-, nH_2O]^-$ interlayers, where X is one monovalent or half of a divalent anion and where n depends on the humidity. The chlorinated compound or Friedel's salt is of monoclinic symmetry (space group $C2/c$) at room temperature. It undergoes a structural transition at 308 K and becomes rhombohedral, with space group $R\bar{3}c$ and lattice parameters a = 5.724 Å and c = 46.689 Å (Renaudin *et al.*, 1999). The c parameter corresponds to six interlayers which are spaced at 7.78 Å ($6R$ polytype). This transition is presumably related to the size of the inserted halide [r = 1.81, 1.96 and 2.20 Å for Cl^-, Br^- and I^-, respectively (Shannon, 1976)]. Indeed, the AFm–Br transforms at 223 K, while AFm–I does not present structural change above 77 K. The structures of AFm–Br (Rapin, Mohamed Noor *et al.*, 1999) and AFm–I (Rapin, Walcarius *et al.*, 1999) have been determined by single-crystal diffraction experiments at room temperature. They are isostructural with space group $R\bar{3}$ and their c parameters correspond to three interlayers spacing ($3R$ polytypes). In order to check the size effect of halide on the transition, the solid solution $[Ca_2Al(OH)_6][Br_xCl_{1-x} \cdot 2H_2O]$ was studied. The transition temperature decreases linearly from 308 to 223 K when x increases from 0 to 1. In particular, the phase corresponding to x = 0.5 changes at 263 K. The single crystals of this phase are not twinned at room temperature, contrary to those of the pure chlorinated phase. The structure of the rhombohedral phase could thus be determined from a single crystal at room temperature. Cl^- and Br^- anions share in a statistical

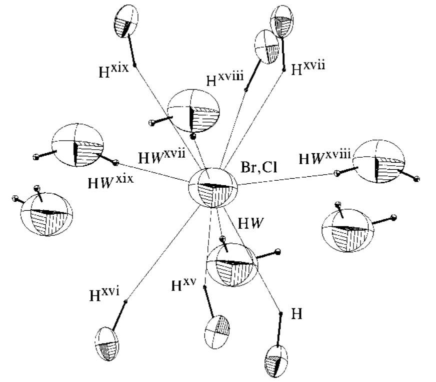

Figure 2
View of the halide hydrogen environment. HW atoms of water molecules are represented in an ordered way. Displacement ellipsoids of (Cl, Br) and H atoms are drawn at the 70% probability level (*ATOMS*; Dowty, 1995). [Symmetry codes: (i) $-y, x-y, z$; (ii) $-x+y, -x, z$; (iii) $-x, -y, -z$; (iv) $x-y, x, -z$; (v) $y, -x+y, -z$; (vi) $-x+y, 1-x, z$; (vii) $1-y, 1+x-y, z$; (viii) $y, 1-x+y, -z$; (ix) $1-x, 1-y, -z$.]

disorder in the same crystallographic site. The increase of the interlayer spacing from 7.78 (1) to 8.02 (1) Å on going from $x = 0$ to $x = 0.5$, corresponds to the increase of the anionic radii tabulated by Shannon (1976) when Cl^- is replaced by the larger halide Br^-. The structure is represented in Fig. 1. The main layers of composition $[Ca_2Al(OH)_6]^+$ are brucite-like layers with an octahedral environment for Al^{3+} and a coordination up to seven for the Ca^{2+} cations. The seventh coordination is occupied by water molecules. In the interlayer spacing of composition (Br0.5, Cl0.5, $2H_2O$), the Cl^- and Br^- anions are surrounded by ten H atoms, of which six belong to hydroxyl groups and four to water molecules (see Fig. 2). The anions are therefore connected to the main layer by ten hydrogen bonds, six of 2.74 (2) Å and four of 2.52 (5) Å, where the donors are hydroxyl groups and water molecules, respectively.

Experimental

Single crystals of the title compound were prepared by hydrothermal synthesis. The starting powders $Ca(OH)_2$, $Al(OH)_3$, $CaCl_2{\cdot}6H_2O$ and $CaBr_2{\cdot}2H_2O$ (molar proportion 2/1/0.5/0.5) are mixed with water (ratio solid/water = 0.5), loaded in a silver capsule (length: 100 mm; diameter: 5 mm; thickness: 0.1 mm) and sealed under argon. The experiment was performed over a period of 60 d at 393 K and 2 Kbar (1 bar = 10^5 Pa).

Crystal data

$Ca_2Al(OH)_6Br_{0.478}Cl_{0.522}{\cdot}2H_2O$
$M_r = 302.01$
Trigonal, $R\bar{3}c$
$a = 5.7537$ (4) Å
$c = 48.108$ (4) Å
$V = 1379.21$ (18) Å^3
$Z = 6$
$D_x = 2.182$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 25$–$50°$
$\mu = 3.58$ mm^{-1}
$T = 293$ (2) K
Plate, colorless
0.20 × 0.15 × 0.04 mm

Data collection

Nonius diffractometer
CCD scans
Absorption correction: empirical fitted by spherical harmonic functions (*SORTAV*; Blessing, 1995)
$T_{\min} = 0.48$, $T_{\max} = 0.86$
8579 measured reflections
516 independent reflections

390 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.035$
$\theta_{\max} = 31.38°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 8$
$l = 0 \rightarrow 70$
3 standard reflections every 600 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.090$
$S = 1.050$
516 reflections
29 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0151P)^2 + 6.1190P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.55$ e Å^{-3}
$\Delta\rho_{\min} = -0.76$ e Å^{-3}

Table 1
Selected bond distances (Å).

Al—O	1.9105 (16)	Ca—O*W*	2.492 (5)
Ca—O	2.3568 (18)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O—H···Br	0.92 (2)	2.74 (2)	3.547 (3)	146 (5)
O*W*—H*W*···Br	0.94 (2)	2.52 (5)	3.449 (3)	167 (9)

Cl and Br atoms were located on the same site. The sum of their occupancy factors was fixed at unity. H atoms of the hydroxyl groups and water molecules were located from a difference Fourier map. The O—H distance was restrained to 0.95 Å, with a fixed individual isotropic displacement parameter $U_{\rm iso} = 1.2U_{\rm eq}$(O). The O atom (O*W*) of the water molecule was located on a special site 12(*c*), whereas its H atom occupies the general site 36(*f*) with an occupancy of 2/3.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor 1997); data reduction: *HKL DENZO and SCALEPACK*; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1995); software used to prepare material for publication: *WINWORD* (Version 5.0).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ1005). Services for accessing these data are described at the back of the journal.

References

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Dowty, E. (1995). *ATOMS for Windows*. Version 3.1. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.
Nonius (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
Rapin, J. P., Mohamed Noor, N. & François, M. (1999). *Acta Cryst.* C**55**, IUC9900092.
Rapin, J. P., Walcarius, A., Lefévre, G. & François, M. (1999). *Acta Cryst.* C**55**, 1957–1959.
Renaudin, G., Kubel, F., Rivera, J.-P. & François, M. (1999). *Cem. Concr. Res.* **29**, 1937–1942.
Shannon, R. D. (1976). *Acta Cryst.* A**32**, 751–767.
Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.