

## INORGANIC COMPOUNDS

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## A double-layered hydroxide, 3CaO·Al<sub>2</sub>O<sub>3</sub>·CaI<sub>2</sub>·10H<sub>2</sub>O

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### Abstract

The title compound, calcium oxide–dialuminium trioxide–calcium iodide hydrate (3/1/1/10), also formulated as Ca<sub>2</sub>Al(OH)<sub>6</sub>I·2H<sub>2</sub>O (dicalcium aluminium hydroxide iodide dihydrate), belongs to the AFm family of phases, which are hydrated products commonly encountered in cement paste. It also belongs to the more general category of compounds called lamellar double hydroxides (HDL). Its structure can be considered very close to that of the equivalent disordered sulfate compound, with the ordered I<sup>−</sup> anions replacing the disordered SO<sub>4</sub><sup>2−</sup> groups. It consists of positively charged main layers, [Ca<sub>2</sub>Al(OH)<sub>6</sub>]<sup>+</sup>, and negatively charged interlayers, [I<sup>−</sup>·2H<sub>2</sub>O], where I and O atoms occupy ordered sites. Al<sup>3+</sup> and Ca<sup>2+</sup> cations are six- and seven-coordinate, respectively, and all water molecules are bonded to Ca<sup>2+</sup> cations to assume the seventh coordination position. I<sup>−</sup> anions are surrounded by ten H atoms, six from hydroxyl groups and four from water molecules. These anions are therefore connected to the main layers by ten I—H hydrogen bonds, six of 3.10 (4) Å and four of 2.78 (8) Å, where the donors are hydroxyl groups and water molecules, respectively.

### Comment

The title compound, 3CaO·Al<sub>2</sub>O<sub>3</sub>·CaI<sub>2</sub>·10H<sub>2</sub>O, belongs to the related basic salts called AFm phases, which are important in cement chemistry because they occur on hydration. They form positively charged brucite-like layers, [Ca<sub>2</sub>(Al,Fe)(OH)<sub>6</sub>]<sup>+</sup>, with negatively charged [X<sub>z</sub>·nH<sub>2</sub>O]<sup>−</sup> interlayers to assume electroneutrality; X is a monovalent anion (OH<sup>−</sup>, Cl<sup>−</sup>, NO<sub>3</sub><sup>−</sup> or AlO<sub>2</sub><sup>−</sup>), with z = 1, or a bivalent anion (CO<sub>3</sub><sup>2−</sup> or SO<sub>4</sub><sup>2−</sup>), with z = 1/2, and n can vary depending on the humidity and on the nature of the inserted anions. A com-

plete structural determination based on single crystal data has been determined earlier for the monosulfate 3CaO·Al<sub>2</sub>O<sub>3</sub>·CaSO<sub>4</sub>·12H<sub>2</sub>O (*R*3̄) (Allmann, 1977) and the chloride 3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCl<sub>2</sub>·10H<sub>2</sub>O (*C2/c*) at room temperature (Terzis *et al.*, 1987). More recently, structural determinations have been described for the monocarbonate 3CaO·Al<sub>2</sub>O<sub>3</sub>·CaCO<sub>3</sub>·10H<sub>2</sub>O, for which there are two modifications depending on the synthesis conditions, an ordered (*P1*) form (François *et al.*, 1998) and a disordered (*P*1̄) form (Renaudin, François & Evrard, 1999), and also for the nitrate 3CaO·Al<sub>2</sub>O<sub>3</sub>·Ca(NO<sub>3</sub>)<sub>2</sub>·10H<sub>2</sub>O (*P*3̄c1) (Renaudin & François, 1999) and the chloride at *T* = 310 K (*R*3̄c) (Renaudin, Kubel *et al.*, 1999).

The structure of the title compound can be compared with the equivalent sulfate compound. Both crystallize in the same space group, *R*3̄, meaning that the relative arrangement of the rigid [Ca<sub>2</sub>Al(OH)<sub>6</sub>]<sup>+</sup> layers is the same. The spherical I<sup>−</sup> monovalent anion takes the place of the tetrahedral divalent SO<sub>4</sub><sup>2−</sup> anion. The structure does not contain any free water molecules, in contrast to the sulfate equivalent, where one third of the water in the interlayer of composition [1/2 SO<sub>4</sub><sup>2−</sup>·3H<sub>2</sub>O] can be considered as simply space filling. Substitution of the

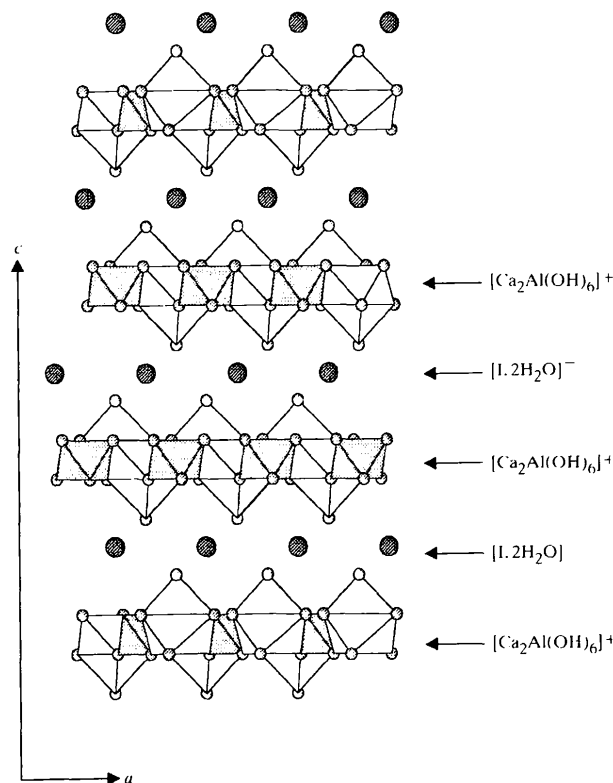


Fig. 1. The projection of the layered structure of the title compound along [110]. The polyhedral [AlO<sub>6</sub>] (shaded) and [CaO<sub>7</sub>] (unshaded) representation is produced using ATOMS (Dowty, 1995).

SO<sub>4</sub><sup>2-</sup> anion by monovalent I<sup>-</sup> leads to a more ordered structure in the title compound. All non-H atoms are situated in special positions, except for the hydroxyl O atoms, which are on general positions. While in sulfate AFm, the sulfate groups are replaced by water molecules in every other cell, here, the I sites are fully occupied.

A general view of the structure of the title compound projected on [110] is shown in Fig. 1. The oxygen-coordination numbers are six and seven for the Al<sup>3+</sup> and Ca<sup>2+</sup> cations, respectively. The seventh coordination of Ca<sup>2+</sup> is adopted, as is usual in the AFm phases, by water molecules considered as linked water in the structure and situated in the interlayer part [I<sup>-</sup>, 2H<sub>2</sub>O].

A possible ordered environment of the I<sup>-</sup> anion is represented in Fig. 2. Each I<sup>-</sup> anion is surrounded by ten H atoms, forming a hydrogen-bond network connecting the layers. Six H atoms come from hydroxyl groups, with I—H distances of 3.10 Å, and four on average come from water molecules, with I—HW distances of 2.78 Å. As HW atoms from water molecules are on general sites with an occupancy factor of  $\frac{2}{3}$ , only four water molecules among the six surrounding any I<sup>-</sup> ion are connected to it. The two remaining water molecules are connected to other I<sup>-</sup> anions.

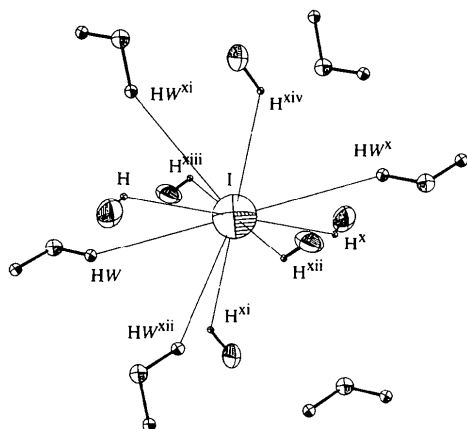


Fig. 2. View (ATOMS; Dowty, 1995) of the hydrogen environment of the I<sup>-</sup> ion. HW atoms from the water molecules are represented in an ordered way. The displacement ellipsoids of I and H atoms are drawn at the 70% probability level; symmetry codes are as in Table 2.

The interlayer spacing of 8.84 Å between two main [Ca<sub>2</sub>Al(OH)<sub>6</sub>]<sup>+</sup> layers in iodide AFm is larger than the values measured in the Cl<sup>-</sup> equivalent (7.78 Å), in agreement with the anionic radii tabulated by Shannon (1976) (Cl<sup>-</sup> = 1.81 and I<sup>-</sup> = 2.20 Å).

## Experimental

Single crystals of the title compound were prepared by hydrothermal synthesis. The starting powders Ca(OH)<sub>2</sub>, Al(OH)<sub>3</sub> and KI (molar proportion 2/1/1) were mixed with water (ratio

solid/water = 0.5) and loaded into a silver capsule (length 100 mm, diameter 5 mm, thickness 0.1 mm) sealed under normal atmosphere. The capsule was then maintained at 393 K and 2 kbar (1 bar = 10<sup>5</sup> Pa) for 45 d.

## Crystal data

Ca<sub>2</sub>Al(OH)<sub>6</sub>I·2H<sub>2</sub>O

*M<sub>r</sub>* = 372.12

Trigonal

*R*<sup>3</sup>

*a* = 5.772 (1) Å

*c* = 26.538 (1) Å

*V* = 765.69 (19) Å<sup>3</sup>

*Z* = 3

*D<sub>x</sub>* = 2.421 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Cu Kα radiation

λ = 1.54058 Å

Cell parameters from 25 reflections

θ = 25–50°

μ = 34.46 mm<sup>-1</sup>

*T* = 293 (2) K

Plate

0.08 × 0.07 × 0.02 mm

Colourless

## Data collection

Enraf–Nonius CAD-4

diffractometer

ω/2θ scans

Absorption correction:

ψ scan fitted by spherical harmonic functions

(SORTAV; Blessing, 1995)

*T<sub>min</sub>* = 0.13, *T<sub>max</sub>* = 0.60

1250 measured reflections

322 independent reflections

310 reflections with

*I* > 2σ(*I*)

*R<sub>int</sub>* = 0.055

θ<sub>max</sub> = 69.68°

*h* = -6 → 6

*k* = 0 → 7

*l* = 0 → 31

3 standard reflections

frequency: 90 min

intensity decay: 3.7%

## Refinement

Refinement on *F*<sup>2</sup>

*R*[*F*<sup>2</sup> > 2σ(*F*<sup>2</sup>)] = 0.039

*wR*(*F*<sup>2</sup>) = 0.112

*S* = 1.100

322 reflections

27 parameters

H atoms: see below

*w* = 1/[σ<sup>2</sup>(*F<sub>o</sub>*<sup>2</sup>) + (0.0408*P*)<sup>2</sup> + 4.3362*P*]

where *P* = (*F<sub>o</sub>*<sup>2</sup> + 2*F<sub>c</sub>*<sup>2</sup>)/3

(Δ/σ)<sub>max</sub> < 0.001

Δρ<sub>max</sub> = 0.873 e Å<sup>-3</sup>

Δρ<sub>min</sub> = -0.962 e Å<sup>-3</sup>

Extinction correction:

SHELXL97 (Sheldrick, 1997)

Extinction coefficient:

0.0017 (4)

Scattering factors from

International Tables for Crystallography (Vol. C)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Al	0	0	0	0.0197 (7)
I	1/3	1/3	1/6	0.0579 (6)
Ca	2/3	1/3	0.02137 (6)	0.0222 (5)
O	0.2500 (5)	0.3057 (5)	0.03762 (12)	0.0217 (7)
OW	2/3	1/3	0.1133 (3)	0.0583 (19)

Table 2. Selected bond lengths (Å)

Al—O	1.909 (3)	OW—HW	0.95 (2)
Al—O <sup>i</sup>	1.909 (3)	I—HW <sup>a</sup>	2.78 (8)
Al—O <sup>ii</sup>	1.909 (3)	I—HW <sup>xi</sup>	2.78 (8)
Al—O <sup>iii</sup>	1.909 (3)	I—HW <sup>xii</sup>	2.78 (8)
Al—O <sup>iv</sup>	1.909 (3)	I—HW <sup>xiii</sup>	2.78 (8)
Al—O <sup>v</sup>	1.909 (3)	I—HW <sup>xiv</sup>	2.78 (8)
Ca—O <sup>i</sup>	2.369 (3)	I—HW	2.78 (8)
Ca—O <sup>ii</sup>	2.369 (3)	I—H <sup>x</sup>	3.10 (4)
Ca—O	2.369 (3)	I—H <sup>xi</sup>	3.10 (4)

Ca—OW	2.441 (9)	I—H <sup>xi</sup>	3.10 (4)
Ca—O <sup>iiii</sup>	2.454 (3)	I—H <sup>xiii</sup>	3.10 (4)
Ca—O <sup>i</sup>	2.454 (3)	I—H	3.10 (4)
Ca—O <sup>ix</sup>	2.454 (3)	I—H <sup>xiii</sup>	3.10 (4)
O—H	0.92 (2)		

Symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $-x+y, -x, z$ ; (iii)  $-y, x-y, z$ ; (iv)  $x-y, x, -z$ ; (v)  $y, -x+y, -z$ ; (vi)  $1-y, x-y, z$ ; (vii)  $1-x+y, 1-x, z$ ; (viii)  $1+x-y, x, -z$ ; (ix)  $1-x, 1-y, -z$ ; (x)  $\frac{2}{3}-x, \frac{4}{3}-y, \frac{1}{3}-z$ ; (xi)  $\frac{2}{3}+x-y, \frac{1}{3}+x, \frac{1}{3}-z$ ; (xii)  $y-\frac{1}{3}, \frac{1}{3}-x+y, \frac{1}{3}-z$ ; (xiii)  $1-y, 1+x-y, z$ ; (xiv)  $-x+y, 1-x, z$ .

Table 3. Hydrogen-bonding geometry (Å, °)

D—H...A	D—H	H...A	D...A	D—H...A
O—H...I	0.92 (2)	3.10 (4)	3.911 (3)	148 (5)
OW—HW...I	0.95 (2)	2.78 (8)	3.620 (3)	148 (11)

The structure was refined in the  $R\bar{3}$  space group. Attempts to refine the model in the non-centrosymmetric  $R3$  space group did not lead to a better fit. The H atoms of the hydroxy group and water molecule were located from a difference Fourier map and allowed to refine subject to an O—H *DFIX* restraint of 0.95 Å, with a fixed individual isotropic displacement parameter  $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{O})$ . The O atom (OW) of the water molecule was located on a special site, 6(c), whereas its H atoms occupy the general site, 18(f), with an occupancy factor of  $\frac{2}{3}$ .

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DREAM* (Blessing, 1987). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ATOMS* (Dowty, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BR1245). Services for accessing these data are described at the back of the journal.

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## KCu<sub>2</sub>VSe<sub>4</sub>

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## Abstract

The reaction of Cu and V in a  $\text{K}_2\text{Se}_5$  melt yields black crystals of potassium dicopper vanadium tetraselenide,  $\text{KCu}_2\text{VSe}_4$ . The structure is comprised of  $[\text{Cu}_2\text{VSe}_4]^-$  layers within the (010) plane separated by  $\text{K}^+$  cations. The layers consist of a network of edge- and corner-sharing  $[\text{VSe}_4]$  and  $[\text{CuSe}_4]$  tetrahedra parallel to (010).

## Comment

The structure determination of the title compound was undertaken as part of a project on the systematic investigation of the  $A/\text{Cu}/\text{V}/Q$  system ( $A = \text{K}, \text{Rb}, \text{Cs}$ ;  $Q = \text{S}, \text{Se}$ ). Recently, a number of one- and two-dimensional compounds were synthesized and characterized within this system, *e.g.*  $\text{K}_2\text{CuVS}_4$  (Dürichen & Bensch, 1996),  $\text{K}_2\text{CuVSe}_4$  (Rumpf, Tillinski *et al.*, 1997) and  $\text{KCu}_2\text{VS}_4$  (Bensch *et al.*, 1996).

$\text{KCu}_2\text{VSe}_4$  is isostructural with  $\text{KCu}_2\text{VS}_4$ ,  $\text{NaCu}_2\text{-NbS}_4$  (Rumpf, Näther *et al.*, 1997) and  $\text{KCu}_2\text{NbS}_4$  (Lu & Ibers, 1991). The structure is built up by chains of corner-sharing  $[\text{VSe}_4]$  and  $[\text{CuSe}_4]$  tetrahedra. These  $[\text{CuVSe}_4]_n^-$  chains are linked into layers by  $[\text{CuSe}_4]$  tetrahedra which share edges between  $[\text{VSe}_4]$  tetrahedra on neighbouring chains. The  $[\text{Cu}_2\text{VSe}_4]^-$  layers are within the (010) plane and are separated by  $\text{K}^+$  cations.

The shortest interlayer  $\text{Se}\cdots\text{Se}$  distance is 3.783 (2) Å. There are three crystallographically distinct metal atoms, *i.e.* Cu1, Cu2 and V. All have a distorted tetrahedral coordination of four Se atoms. The average  $M\text{—Se}$  distances are 2.399 (2) Å for  $M = \text{Cu}$  and 2.324 (2) Å for  $M = \text{V}$ , and lie within the normal range. The  $\text{Se—Cu—Se}$  angles about the two independent Cu atoms indicate stronger distorted tetrahedral environments [105.09 (4)–112.22 (3)° for Cu1 and 104.32 (4)–119.17 (4)° for Cu2] than for the  $\text{VSe}_4$  tetrahedron, with  $\text{Se—V—Se}$  angles deviating less from ideal values [108.09 (3)–110.36 (5)°]. Because the  $[\text{MSe}_4]$  tetrahedra are connected *via* common edges, the large differences in the  $\text{Cu—Se}$  and  $\text{V—Se}$  bond lengths must lead to severe distortions which primarily affect the  $[\text{CuSe}_4]$  tetrahedra. The  $\text{V}\cdots\text{Cu}$  distances are 2.777 (1), 2.788 (1) and 2.775 (1) Å [average 2.779 (2) Å], which are far too long for bonding interactions. As expected, the distances are