INORGANIC COMPOUNDS

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Nonasodium Bis(hexahydroxoaluminate) Trihydroxide Hexahydrate

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Abstract

The Al atoms are six-coordinate and exist as monomeric $[Al(OH)_6]^{3-}$ anions in the title compound, $Na_9[Al(OH)_6]_2(OH)_3.6H_2O$. The Na^+ cations also show octahedral coordination geometry and are coordinated by OH^- ions and water molecules; six Na^+ cations are coordinated by five hydroxyl groups and one water molecule, while the other three are coordinated by four hydroxyl groups and two water molecules. These NaO_6 octahedra are linked through common edges, incorporating the AlO_6 octahedra, to yield a three-dimensional network.

Comment

The title structure displays a marked translational pseudosymmetry; most atoms are related in pairs by a translation of 1/2 in the z direction. These are Al1 and Al2, Na1–Na4 and Na5–Na8, O1–O6 and O7–O12, O16–O17 and O19–O20. In the pairs O13, O14 and O18, O21, this translational relationship is poor and is broken by Na9. For O15, the symmetry operator $2 - x$, $1 - y$, $1 - z$ generates a position close to the one which would have been generated by $z + 1/2$. However, there is a hole at $z + 1/2$ corresponding to Na9.

The Al atoms have octahedral coordination geometry and exist as monomeric $[Al(OH)_6]^{3-}$ anions. With the exception of the title compound and a thermal dehydration product (Geßner, Weinberger, Müller, Ni & Khaljapina, 1987), no other hydroxoaluminate in the system Na_2O–Al_2O_3–H_2O has this octahedral coordination geometry. The Na^+ cations are six-coordinate by OH^- ions and water molecules, forming distorted octahedra. Six Na^+ cations are coordinated by five hydroxyl groups and one water molecule, while three are coordinated by four hydroxyl groups and two water molecules. They are linked through common edges, incorporating the AlO_6 octahedra, to yield a three-dimensional network.

The Na—O distances lie in a wide range [2.290 (1)–2.644 (1) Å], as do the O—Na—O angles [67.19 (4)–113.78 (5)° and 159.23 (5)–178.48 (6)°]. (The latter are available as supplementary material.) The Al—O distances range from 1.887 (1) to 2.004 (1) Å and can be compared with those in barium aluminate hydrate (Cruickshank, Dent Glasser & Howie, 1985) of 1.887 (3)–1.919 (6) Å and those in $Ca_2[Al(OH)_6]Cl.2H_2O$ (Terzis, Filippakis, Kuzel & Burzlaff, 1987) of 1.903 (2)–1.918 (2) Å. Barium aluminate hydrate contains AlO_6 octahedra and AlO_4 tetrahedra, and is thus difficult to compare otherwise with the title structure. In $Ca_2[Al(OH)_6]Cl.2H_2O$, structural motifs similar to those in the title structure are found. Both structures display cationic and anionic layers. The cationic layers are composed of Ca^{2+} and Al^{3+} or Na^+ and Al^{3+}, while the anionic layers are composed of OH^- or OH^- and water molecules for the calcium aluminate and the title structure, respectively. In the Ca compound, there is an interlayer of $(Cl.2H_2O)^-$ between the anionic OH^- layers. In $Na_9[Al(OH)_6]_2(OH)_3.6H_2O$, the cationic and anionic layers alternate parallel to the *ab* plane. The cationic layers have approximate positions $z = 0.13$, 0.38, 0.62 and 0.87 while the anionic layers are positioned in between, at approximately $z = 0.0$, 0.25, 0.50 and 0.75. The water molecules are incorporated into the anionic OH^- layers through water–hydroxyl and water–water hydrogen bonding.

All H atoms were located and the hydrogen-bond parameters are shown in Table 3. Only eight of the 15 hydroxyl ions (atoms O1–O15) are involved in hydrogen bonds, three of them as donors. Two of these donors represent intramolecular hydrogen bonds. However, these three bonds are weak with relatively long H···O distances. The hydroxyl ions O13 and O14 are not involved in any primary cationic coordination;

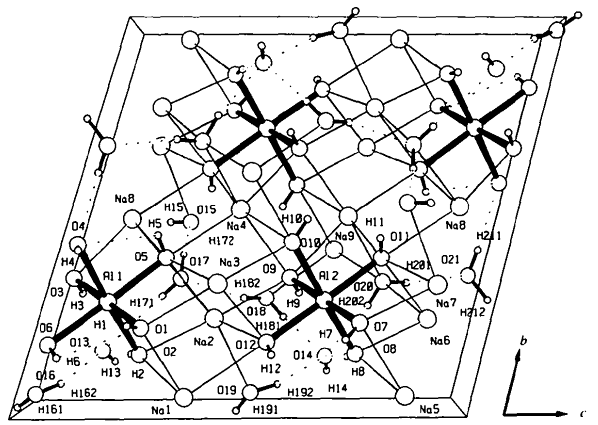

Fig. 1. An *ORTEP* plot (Johnson, 1976) of the two symmetry-related moieties in the unit cell, approximately along [100]. Depicted are the monomeric AlO_6 octahedra connected by NaO_6 octahedra. The thin lines show the Na—O contacts, while the dotted lines indicate the hydrogen bonds.

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they are lone hydroxyls involved in hydrogen bonding only. All six water molecules (atoms O16–O21) are involved in hydrogen bonding through both H atoms. Only those involving H161 and H171 are weak, and the hydrogen bond involving H191 is very weak. The hydrogen-bond parameters involving H172 and H212, with the shortest H···O distances, have to be regarded with caution. These atoms have the highest displacement parameters of the H atoms and, therefore, their positions are not very reliable.

Experimental

Single crystals of $Na_9[Al(OH)_6]_2(OH)_3.6H_2O$ were obtained by slow crystallization at 318 K from a concentrated sodium aluminate solution (42% NaO, 1.4% Al_2O_3). After filtration, the hygroscopic crystals were squeezed between filter paper and immediately transferred into dried hexane and mounted in glass capillaries.

Crystal data

$Na_9[Al(OH)_6]_2(OH)_3.6H_2O$	Mo $K\alpha$ radiation
$M_r = 624.07$	$\lambda = 0.71073$ Å
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	$\theta = 9–15°$
$a = 8.694\ (1)$ Å	$\mu = 0.423$ mm^{-1}
$b = 11.344\ (2)$ Å	$T = 293\ (2)$ K
$c = 11.636\ (3)$ Å	Slightly opaque block
$\alpha = 74.29\ (2)°$	$0.35 \times 0.15 \times 0.15$ mm
$\beta = 87.43\ (2)°$	Colourless
$\gamma = 70.66\ (2)°$	
$V = 1041.1\ (4)$ Å^3	
$Z = 2$	
$D_x = 1.991$ Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius Turbo-CAD-4 diffractometer	$R_{int} = 0.0158$
ω–2θ scans	$\theta_{max} = 34.92°$
Absorption correction: none	$h = 0 \rightarrow 12$
6434 measured reflections	$k = -17 \rightarrow 15$
6068 independent reflections	$l = -16 \rightarrow 16$
4202 observed reflections $[F > 2\sigma(F)]$	2 standard reflections frequency: 60 min intensity decay: none

Refinement

Refinement on F^2	$\Delta\rho_{max} = 0.567$ e Å^{-3}
$R[F^2 > 2\sigma(F^2)] = 0.0320$	$\Delta\rho_{min} = -0.350$ e Å^{-3}
$wR(F^2) = 0.0823$	Extinction correction: *SHELXL93* (Sheldrick, 1993)
$S = 1.052$	Extinction coefficient: 0.0052 (5)
6068 reflections	Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
398 parameters	
All H-atom parameters refined	
$w = 1/[\sigma^2(F_o^2) + (0.0346P)^2 + 0.2034P]$ where $P = (F_o^2 + 2F_c^2)/3$	
$(\Delta/\sigma)_{max} = 0.016$	

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)*

U_{iso} for H atoms, $U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	U_{iso}/U_{eq}
Al1	0.40896 (5)	0.27366 (4)	0.12585 (3)	0.01062 (9)
Al2	0.40252 (5)	0.27516 (4)	0.62321 (3)	0.01006 (9)
Na1	0.41589 (8)	0.03214 (6)	0.36236 (5)	0.02004 (14)
Na2	0.60844 (8)	0.22505 (6)	0.37913 (5)	0.02021 (14)
Na3	0.20520 (8)	0.32243 (6)	0.36867 (5)	0.01869 (14)
Na4	0.42535 (8)	0.50918 (6)	0.37142 (5)	0.01839 (14)
Na5	0.40470 (8)	0.03347 (6)	0.86685 (5)	0.01942 (14)
Na6	0.59262 (8)	0.22235 (6)	0.88010 (5)	0.01904 (13)
Na7	0.20119 (8)	0.31748 (6)	0.86914 (5)	0.01913 (14)
Na8	0.40161 (8)	0.51492 (6)	0.88042 (5)	0.01850 (14)
Na9	1.00374 (8)	0.39908 (6)	0.62102 (5)	0.02063 (15)
O1	0.25708 (14)	0.21133 (11)	0.22234 (9)	0.0159 (2)
O2	0.57637 (14)	0.13393 (10)	0.22825 (9)	0.0143 (2)
O3	0.56192 (13)	0.33185 (10)	0.02530 (9)	0.0140 (2)
O4	0.24111 (14)	0.42138 (11)	0.02545 (9)	0.0164 (2)
O5	0.40846 (13)	0.38586 (10)	0.23016 (9)	0.0139 (2)
O6	0.39831 (13)	0.16507 (10)	0.01816 (9)	0.0140 (2)
O7	0.23550 (13)	0.22215 (11)	0.71534 (9)	0.0141 (2)
O8	0.56018 (14)	0.13442 (10)	0.73046 (9)	0.0142 (2)
O9	0.56511 (13)	0.33086 (10)	0.53080 (9)	0.0139 (2)
O10	0.23736 (13)	0.42556 (10)	0.51320 (9)	0.0140 (2)
O11	0.39583 (14)	0.38360 (11)	0.72978 (9)	0.0137 (2)
O12	0.39822 (13)	0.16973 (10)	0.51613 (9)	0.0141 (2)
O13	0.9360 (2)	0.1325 (2)	0.12919 (15)	0.0418 (4)
O14	0.9081 (2)	0.1158 (2)	0.66693 (14)	0.0445 (4)
O15	0.9728 (2)	0.47591 (12)	0.25194 (11)	0.0247 (3)
O16	0.8007 (2)	0.0253 (2)	0.00535 (14)	0.0331 (3)
O17	0.8092 (2)	0.3258 (2)	0.27004 (13)	0.0317 (3)
O18	0.9864 (2)	0.2692 (2)	0.48690 (15)	0.0461 (4)
O19	0.7970 (2)	0.02625 (15)	0.51161 (14)	0.0329 (3)
O20	0.8057 (2)	0.31625 (15)	0.75703 (13)	0.0290 (3)
O21	0.9520 (2)	0.32893 (14)	0.96482 (12)	0.0279 (3)
H1	0.186 (3)	0.218 (3)	0.192 (2)	0.051 (8)
H2	0.662 (3)	0.132 (2)	0.207 (2)	0.040 (7)
H3	0.648 (3)	0.292 (2)	0.052 (2)	0.036 (6)
H4	0.165 (3)	0.408 (2)	0.033 (2)	0.028 (6)
H5	0.347 (3)	0.444 (2)	0.199 (2)	0.023 (6)
H6	0.340 (3)	0.134 (2)	0.050 (2)	0.033 (6)
H7	0.202 (3)	0.182 (2)	0.693 (2)	0.023 (6)
H8	0.645 (3)	0.125 (2)	0.716 (2)	0.044 (7)
H9	0.649 (3)	0.291 (2)	0.561 (2)	0.032 (6)
H10	0.238 (3)	0.484 (2)	0.533 (2)	0.027 (6)
H11	0.324 (3)	0.434 (2)	0.714 (2)	0.031 (6)
H12	0.333 (3)	0.140 (2)	0.535 (2)	0.037 (7)
H13	1.002 (3)	0.102 (3)	0.164 (2)	0.045 (9)
H14	0.993 (3)	0.075 (2)	0.681 (2)	0.029 (7)
H15	1.018 (3)	0.475 (2)	0.201 (2)	0.037 (7)
H161	0.864 (3)	−0.013 (3)	−0.032 (2)	0.057 (9)
H162	0.850 (3)	0.050 (3)	0.055 (2)	0.053 (8)
H171	0.841 (3)	0.280 (3)	0.237 (2)	0.050 (9)
H172	0.885 (4)	0.389 (3)	0.258 (3)	0.097 (11)
H181	0.973 (3)	0.218 (3)	0.543 (2)	0.056 (8)
H182	0.934 (3)	0.271 (3)	0.433 (3)	0.066 (9)
H191	0.861 (3)	−0.023 (3)	0.489 (2)	0.061 (9)
H192	0.841 (3)	0.047 (3)	0.570 (2)	0.061 (8)
H201	0.851 (3)	0.312 (2)	0.816 (2)	0.044 (7)
H202	0.844 (3)	0.251 (2)	0.737 (2)	0.042 (7)
H211	0.887 (3)	0.398 (2)	0.970 (2)	0.041 (7)
H212	0.947 (4)	0.262 (3)	1.028 (3)	0.082 (10)

Table 2. *Selected geometric parameters (Å)*

Al1—O1	1.8867 (12)	Na4—O5	2.4664 (13)
Al1—O3	1.8966 (12)	Na4—O20^{iii}	2.494 (2)
Al1—O2	1.9119 (13)	Na4—O10	2.4961 (13)
Al1—O4	1.9430 (13)	Na5—O8	2.3466 (14)
Al1—O5	1.9814 (12)	Na5—O2^{i}	2.4025 (13)
Al1—O6	2.0044 (12)	Na5—O6^{i}	2.4114 (14)
Al2—O8	1.9000 (13)	Na5—O16^{i}	2.421 (2)
Al2—O9	1.9082 (12)	Na5—O7	2.4407 (15)
Al2—O7	1.9259 (12)	Na5—O6^{iv}	2.5867 (13)
Al2—O12	1.9558 (12)	Na6—O8	2.2973 (13)

Al2—O11	1.9562 (12)	Na6—O3^{iv}	2.3119 (13)
Al2—O10	1.9927 (13)	Na6—O6^{iv}	2.4031 (14)
Na1—O1	2.2896 (15)	Na6—O11	2.4074 (15)
Na1—O8^{i}	2.3673 (13)	Na6—O16^{iv}	2.488 (2)
Na1—O2	2.3687 (14)	Na6—O20	2.619 (2)
Na1—O12^{i}	2.4197 (14)	Na7—O7	2.2909 (13)
Na1—O19^{i}	2.461 (2)	Na7—O6^{iv}	2.3692 (14)
Na1—O12	2.6438 (13)	Na7—O21^{ii}	2.3715 (15)
Na2—O2	2.3337 (13)	Na7—O15^{iii}	2.413 (2)
Na2—O9	2.3421 (13)	Na7—O11	2.4479 (13)
Na2—O5	2.4110 (15)	Na7—O4^{iv}	2.5113 (14)
Na2—O19	2.459 (2)	Na8—O3^{iv}	2.3442 (14)
Na2—O12	2.4964 (14)	Na8—O4^{iv}	2.3918 (14)
Na2—O17	2.510 (2)	Na8—O3^{iii}	2.3988 (13)
Na3—O1	2.3255 (13)	Na8—O5^{iii}	2.4301 (13)
Na3—O12	2.3418 (14)	Na8—O17^{iii}	2.464 (2)
Na3—O15^{ii}	2.365 (2)	Na8—O11	2.6012 (13)
Na3—O10	2.3663 (13)	Na9—O15^{v}	2.3648 (15)
Na3—O18^{ii}	2.440 (2)	Na9—O7^{vi}	2.3705 (14)
Na3—O5	2.4894 (13)	Na9—O10^{vi}	2.4002 (13)
Na4—O9	2.3559 (14)	Na9—O18	2.458 (2)
Na4—O11^{iii}	2.3656 (14)	Na9—O20	2.525 (2)
Na4—O9^{iii}	2.4126 (13)	Na9—O10^{iii}	2.5767 (15)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5—H5···O4	0.71 (2)	2.37 (2)	2.712 (2)	112 (2)
O6—H6···O1	0.74 (2)	2.39 (2)	2.723 (2)	109 (2)
O8—H8···O14	0.72 (2)	2.31 (2)	3.033 (2)	174 (3)
O16—H161···O13^{i}	0.77 (3)	2.29 (3)	3.062 (2)	176 (3)
O16—H162···O13	0.89 (3)	1.77 (3)	2.643 (2)	167 (2)
O17—H171···O13	0.71 (3)	2.27 (3)	2.982 (3)	179 (3)
O17—H172···O15	1.10 (4)	1.42 (4)	2.520 (2)	174 (3)
O18—H181···O14	0.78 (3)	1.79 (3)	2.562 (2)	171 (3)
O18—H182···O17	0.78 (3)	2.07 (3)	2.823 (2)	163 (3)
O19—H191···O18^{ii}	0.74 (3)	2.61 (3)	3.251 (3)	146 (3)
O19—H192···O14	0.91 (3)	1.75 (3)	2.652 (2)	170 (3)
O20—H201···O21	0.79 (2)	2.06 (3)	2.841 (2)	172 (2)
O20—H202···O14	0.80 (2)	1.84 (3)	2.632 (2)	170 (2)
O21—H211···O4^{iii}	0.82 (2)	2.00 (2)	2.804 (2)	170 (2)
O21—H212···O13^{iv}	0.92 (3)	1.64 (3)	2.553 (2)	173 (3)

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

Several attempts at data collection were undertaken, as the intensities of the standard reflections showed that the crystals decayed rapidly. One crystal, however, showed no decay. The solution of the structure was not straightforward; many reflections with odd *l* showed a marked weakness. It was difficult to recognize structural moieties within the proposed solutions. All but one of the proposed solutions failed to refine to a reasonable *R* value by least-squares procedures and consecutive difference Fourier syntheses. After the true solution was established, several data sets collected on decaying crystals were refined to *R* values of between 4.4 and 9.6%, after proper correction for the decay. These refinements were performed independently of each other to check the functionality of the O atoms (*i.e.* hydroxyl ion or water molecule). All gave the same indications and all H atoms were found in all structures, some with less reliability. This serves as confirmation of the functionality of the O atoms and that this phase is the main product of the synthesis. More chemical details will be published elsewhere (Weinberger, Schneider, Zabel, Müller & Geßner, 1996).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993); *Xtal*3.2 (Hall & Stewart, 1992). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: JZ1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A New Synthetic Fluoride Phosphate of Mixed-Valence Iron: $Cs_8Fe_8^{3+}Fe_7^{2+}F_{10}(PO_4)_{12}$

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Abstract

The title compound, octacaesium pentadecairon decafluoride dodecaphosphate, was prepared by hydrothermal methods. The structure contains three types of Fe

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