Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Synthesis and crystal structures of $[Al(H_2O)_6](SO_4)NO_3\cdot 2H_2O$ and $[Al(H_2O)_6](SO_4)Cl\cdot H_2O$

Fredric G. Svensson*

Department of Molecular Sciences, Swedish University of Agricultural Sciences, Box 7015, 750 07 Uppsala, Sweden. *Correspondence e-mail: fredric.svensson@slu.se

Received 14 September 2020
Accepted 1 December 2020

Edited by M. Weil, Vienna University of Technology, Austria

Keywords: crystal structure; aluminium; double salt; hydrogen bonding.

CCDC references: 2030818; 2028868

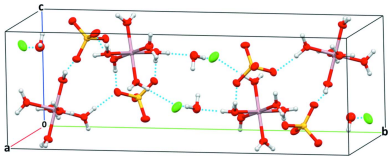
Supporting information: this article has supporting information at journals.iucr.org/e

Two novel aluminium double salts, $[Al(H_2O)_6](SO_4)NO_3\cdot 2H_2O$, hexaquaaluminium sulfate nitrate dihydrate, (**1**), and $[Al(H_2O)_6](SO_4)Cl\cdot H_2O$, hexaquaaluminium sulfate chloride hydrate, (**2**), were obtained in the form of single crystals. Their crystal structures are each based on an octahedral $[Al(H_2O)_6]^{3+}$ unit and both structures have in common one charge-balancing SO_4^{2-} anion. The final positive charge from the aluminium(III) cation is balanced by an NO_3^- or a Cl^- anion for (**1**) and (**2**), respectively. Compound (**1**) further contains two unligated water molecules while compound (**2**) only contains one unligated water molecule. In the crystal structures, all components are spatially separated and interactions are mediated *via* medium–strong hydrogen bonding, compared to many other reported aluminium sulfates where corner-sharing of the building units is common. The two compounds represent rare cases where one aluminium(III) cation is charge-balanced by two different anions.

1. Chemical context

Aluminium is one of the most common elements in Earth's crust and is predominantly found in oxides and silicates. The far most common oxidation state for inorganic compounds is +III. Aluminium is found in many double salts with numerous other cations and sulfate, such as the industrially important alums $MAl(SO_4)_2\cdot 12H_2O$ (M = monovalent cation; Greenwood & Earnshaw, 1997). At low pH, aluminium mainly exists in solution as the $[Al(H_2O)_6]^{3+}$ cation (Hay & Myneni, 2008).

One of the title compounds, $[Al(H_2O)_6](SO_4)NO_3\cdot 2H_2O$, (**1**), was obtained as an unintentional side product when attempting to synthesize an aluminium-modified bismuth-titanium oxo-complex. Efforts to obtain (**1**) by other routes resulted in the formation of $[Al(H_2O)_6]SO_4Cl\cdot H_2O$ (**2**).



2. Structural commentary

The crystal structure of (**1**) comprises an $[Al(H_2O)_6]^{3+}$ cation charge-balanced by one sulfate and one nitrate anion as well as two unligated water molecules; all building units are separated from each other (Fig. 1). Bond lengths in the components are summarized in Table 1. The aqua ligands (O1–O6) of the complex cations serve as hydrogen-bonding donor groups. They connect through O—H···O hydrogen bonds to the two types of anions and to the two unbound water molecules, forming a three-dimensional network (Fig. 2, Table 2). Hydrogen bonds involving H8 and H12 are bifurcated. The water molecules O*W*1 and O*W*2 likewise serve as donor groups, whereby O*W*1 hydrogen-bonds to the nitrate anion

Table 1
Selected bond lengths (Å) for (**1**).

Al1—O6	1.869 (2)	S1—O10	1.466 (2)
Al1—O5	1.872 (2)	S1—O7	1.470 (2)
Al1—O2	1.876 (2)	S1—O9	1.479 (2)
Al1—O3	1.880 (2)	N1—O12	1.209 (4)
Al1—O1	1.880 (2)	N1—O11	1.225 (4)
Al1—O4	1.887 (2)	N1—O13	1.232 (4)
S1—O8	1.464 (2)		

(O12, O13) and to the second water molecule O*W*2. The latter hydrogen bond involving H14 is also bifurcated. Interestingly, O*W*2 shows only one hydrogen bond to a nitrate anion (H16···O12); the second H atom (H15) is not engaged in hydrogen-bonding. The H···O distances involving the $[Al(H_2O)_6]^{3+}$ group are between 1.76 (3) and 2.35 (3) Å and thus can be considered as medium–strong whereas the H···O distances [2.05 (2) to 2.55 (3) Å] involving the unbound water molecules as donor groups indicate much weaker hydrogen bonds.

In the crystal structure of compound (**2**), the charge-balancing nitrate anion of (**1**) is exchanged for a chloride anion, and the formula unit only contains one additional water molecule (Fig. 3). Table 3 collates bond lengths of the individual building units. The $[Al(H_2O)_6]^{3+}$ cation donates hydrogen bonds through the aqua ligands (O1– O6) to the sulfate group, the unligated water molecule and to the chloride anion, resulting in a three-dimensional network (Fig. 4, Table 4). Each sulfate group is hydrogen-bonded to four different $[Al(H_2O)_6]^{3+}$ cations, and the unbound water molecule exclusively hydrogen-bonds to the chloride anions, partly with a bifurcated bond. The O···H distances vary between 1.726 (11) and 1.917 (11) Å and thus are slightly stronger than in (**1**).

According to the Pearson concept, sulfate, nitrate, and chloride are all considered intermediate hard bases while Al^{3+} is a hard acid. The higher charge (2+) of the sulfate group compared to the nitrate group and chloride is a likely reason that the sulfate group is present in both structures while the two latter ones can be interchanged, possibly related to their relative abundance. The chloride ions in the reaction mixture of (**1**) might also have been bonded to the titanium(IV) and bismuth(III) cations, preventing the formation of (**2**). In

Table 2
Hydrogen-bond geometry (Å, °) for (**1**).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O10	0.85 (1)	1.78 (1)	2.627 (3)	173 (4)
O1—H2···O7^{i}	0.85 (1)	1.85 (1)	2.689 (3)	171 (4)
O2—H3···O8^{ii}	0.85 (1)	1.84 (1)	2.684 (3)	176 (4)
O2—H4···O*W*1	0.85 (1)	1.76 (1)	2.600 (3)	171 (4)
O3—H5···O7^{iii}	0.85 (1)	1.83 (1)	2.675 (3)	178 (4)
O3—H6···O9^{i}	0.85 (1)	1.83 (1)	2.670 (3)	169 (4)
O4—H7···O8^{iv}	0.85 (1)	1.91 (1)	2.745 (3)	168 (4)
O4—H8···O11^{v}	0.85 (1)	2.12 (2)	2.884 (4)	150 (4)
O4—H8···O13^{v}	0.85 (1)	2.13 (3)	2.870 (4)	147 (4)
O5—H9···O9^{vi}	0.85 (1)	1.80 (1)	2.650 (3)	179 (4)
O5—H10···O10^{iv}	0.85 (1)	1.79 (1)	2.640 (3)	175 (4)
O6—H11···O*W*2	0.85 (1)	1.79 (2)	2.596 (4)	160 (4)
O6—H12···O11^{vii}	0.85 (1)	2.35 (3)	3.044 (4)	139 (3)
O6—H12···O12^{vii}	0.85 (1)	2.06 (2)	2.876 (4)	162 (4)
O*W*1—H13···O13	0.86 (1)	2.05 (2)	2.850 (5)	155 (3)
O*W*1—H14···O12^{vii}	0.86 (1)	2.52 (4)	3.109 (5)	127 (4)
O*W*1—H14···O*W*2^{viii}	0.86 (1)	2.55 (4)	3.073 (6)	120 (3)
O*W*2—H16···O12^{viii}	0.86 (1)	2.20 (3)	2.908 (5)	139 (3)

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

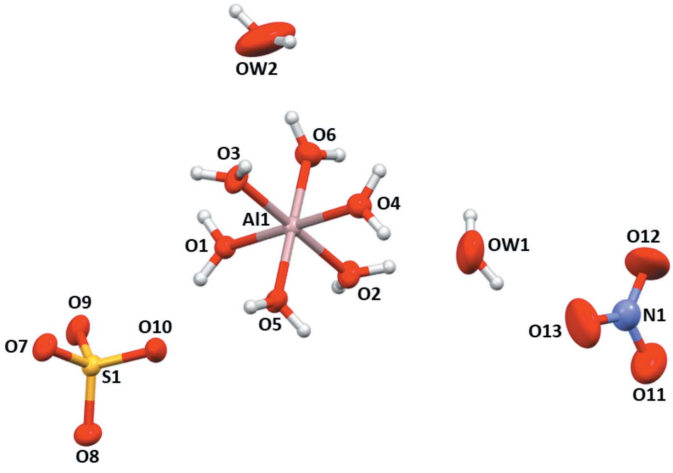


Figure 1
The asymmetric unit of (**1**), representing the building units. Displacement ellipsoids are drawn at the 50% probability level.

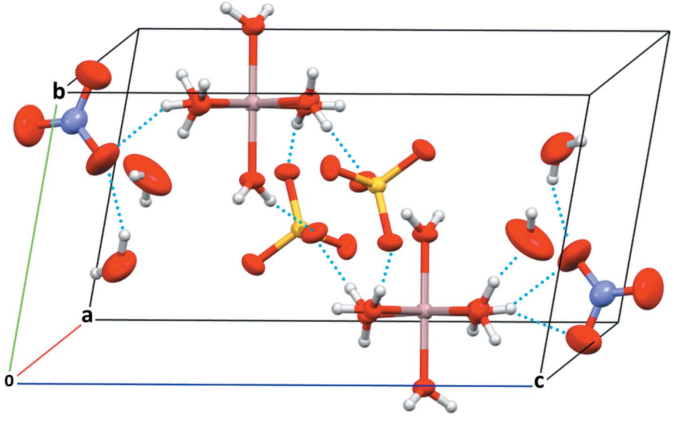


Figure 2
Packing in the crystal structure of compound (**1**). Hydrogen bonding is indicated by dotted lines.

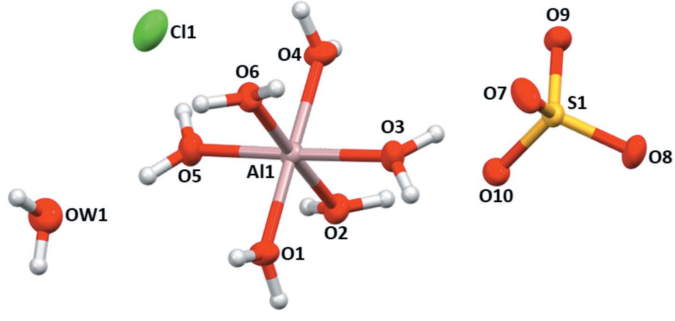


Figure 3
The asymmetric unit of (**2**), representing the building units. Displacement ellipsoids are drawn at the 50% probability level.

Table 3
Selected bond lengths (Å) for (**2**).

Al1—O3	1.8624 (17)	Al1—O2	1.8940 (17)
Al1—O5	1.8718 (18)	S1—O10	1.4670 (16)
Al1—O6	1.8752 (17)	S1—O9	1.4672 (16)
Al1—O1	1.8798 (17)	S1—O8	1.4753 (16)
Al1—O4	1.8855 (17)	S1—O7	1.4767 (16)

particular Bi^{3+} tends to form insoluble BiOCl. Furthermore, (**1**) contains two extra water molecules while (**2**) only contains one of them. The average Al—O bond lengths are 1.880 and 1.884 Å for (**1**) and (**2**), respectively, which is slightly shorter than the literature average distance of 1.90 Å (Hay & Myneni, 2008; Veillard, 1977).

Structures of aluminium sulfate, $Al_2(SO_4)_3$, and derivatives thereof have been reported with different amounts of additional structural water and varying connectivities. Sabelli & Ferroni (1978) reported an aluminium sulfate structure ($Al_2(OH)_4SO_4{\cdot}7H_2O$) where six hydrated aluminum(III) ions are connected *via* edge- and face sharing. These aluminum 'hexamers' are linked *via* hydrogen bonding with unligated water and sulfate ions. In the crystal structure of $Al_2(SO_4)_3{\cdot}8H_2O$, hydrated aluminum(III) ions are connected *via* corner sharing with sulfate groups and a rather extensive hydrogen-bond network between sulfate, aqua ligands, and unligated, structural water molecules (Fischer *et al.*, 1996). In the Al(SO$_4$)OH structure reported by Anderson *et al.* (2015), each sulfate group connects three different aluminium(III) ions *via* corner sharing. The structures of the two reported compounds herein are more open and the principal building units are only connected *via* hydrogen bonding, which may be due to the presence of another anion (NO_3^-/Cl^-).

3. Database survey

According to a database survey using the Inorganic Crystal Structure Database (ICSD), aluminium compounds with an additional cation charge-balanced by sulfate anions appear to be common [*e.g.* KAl(SO$_4$)$_2$, FeAl(SO$_4$)$_3$ (Demartin *et al.*, 2010), or CsAl(SO$_4$)$_2$ (Beattie *et al.*, 1981)]. However, compounds with aluminium as the single cation but with two different anions were found to be much less common although examples include Al(H$_2$PO$_4$)$_2$F (Parnham & Morris, 2006) or Al(SO$_4$)OH (Anderson *et al.*, 2015).

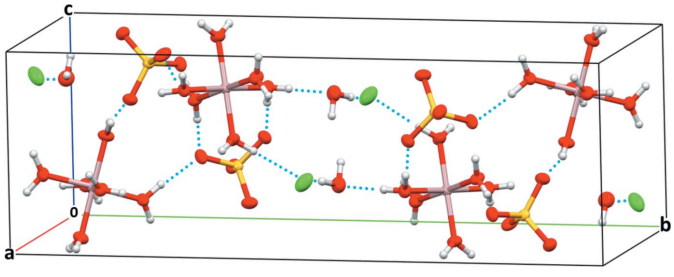


Figure 4
Packing in the crystal structure of compound (**2**). Hydrogen bonding is indicated by dotted lines.

Table 4
Hydrogen-bond geometry (Å, °) for (**2**).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O9^{i}	0.85 (1)	1.88 (1)	2.714 (2)	165 (3)
O1—H2···O8^{ii}	0.85 (1)	1.85 (1)	2.690 (2)	170 (3)
O2—H3···O*W*1^{iii}	0.85 (1)	1.85 (1)	2.692 (2)	178 (3)
O2—H4···O10	0.85 (1)	1.92 (1)	2.767 (2)	177 (3)
O3—H5···O7^{iv}	0.85 (1)	1.78 (1)	2.629 (2)	174 (3)
O3—H6···O7	0.85 (1)	1.73 (1)	2.578 (2)	176 (3)
O4—H7···Cl1^{v}	0.85 (1)	2.18 (1)	3.0311 (18)	177 (3)
O4—H8···O10^{vi}	0.85 (1)	1.83 (1)	2.669 (2)	176 (3)
O5—H9···O*W*1	0.85 (1)	1.82 (1)	2.650 (2)	166 (3)
O5—H10···Cl1	0.85 (1)	2.17 (1)	3.0120 (18)	171 (3)
O6—H11···O8^{vii}	0.85 (1)	1.83 (1)	2.672 (2)	172 (3)
O6—H12···O9^{ii}	0.85 (1)	1.83 (1)	2.671 (2)	171 (3)
O*W*1—H13···Cl1^{viii}	0.85 (1)	2.33 (2)	3.083 (2)	149 (3)
O*W*1—H14···Cl1^{i}	0.84 (1)	2.68 (2)	3.390 (2)	143 (3)
O*W*1—H14···Cl1^{iii}	0.84 (1)	2.74 (3)	3.280 (2)	123 (3)

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

4. Synthesis and crystallization

Compound (**1**) was obtained by mixing equimolar solutions of $TiOSO_4$ (Aldrich) and $Bi(NO_3)_3{\cdot}5H_2O$ (Aldrich), both dissolved in 1 *M* nitric acid (Sigma–Aldrich), and two equivalents of $AlCl_3{\cdot}6H_2O$ (Mallinckrodt Chemical Works) dissolved in 1 *M* hydrochloric acid (Sigma–Aldrich). Colorless needle-shaped crystals formed on a glass substrate after about a week of slow evaporation of the solvent at room temperature. Elemental analysis by energy-dispersive X-ray spectroscopy using a Hitachi TM-1000 scanning electron microscope with an Oxford Instruments EDS system revealed a molar Al:S ratio of 1.37 (expected 1:1). In an attempt to synthesize compound (**1**) by a direct route, aluminium(III) chloride was changed to aluminium(III) lactate to avoid chloride ions. This resulted in formation of crystals with very poor quality that were not suitable for X-ray diffraction.

Compound (**2**) was obtained by dissolving 1 *M* $AlCl_3{\cdot}6H_2O$ in 1 ml of 1 *M* hydrochloric acid and adding one equivalent of 1 *M* sulfuric acid (Sigma–Aldrich), or making a 1 *M* $AlCl_3{\cdot}6H_2O$ solution in 0.5 ml of 1 *M* H_2SO_2 plus 0.5 ml of 1 *M* HNO_3. The solution was poured into a Petri dish and left for slow evaporation. After a few days of evaporation of the solvent, colorless block-shaped crystals suitable for single X-ray crystal diffraction were obtained. The crystals were somewhat fragile. EDS analysis of (**2**) revealed an S:Al:Cl molar composition of 0.9:0.9:1.17 (expected 1:1:1).

For the data collection, both types of crystals were mounted on a glass needle and protected by a layer of paraffin oil.

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 5. In each of the two structures, all hydrogen atoms were discernible in difference-Fourier maps. They were refined with O—H distance restraints of 0.85 (1) Å and a common U_{iso}(H) parameter. Reasonable geometries for

Table 5
Experimental details.

	(**1**)	(**2**)
Crystal data		
Chemical formula	$[Al(H_2O)_6](NO_3)(SO_4)\cdot 2H_2O$	$[Al(H_2O)_6]Cl(SO_4)\cdot H_2O$
M_r	329.18	284.60
Crystal system, space group	Triclinic, $P\overline{1}$	Monoclinic, $P2_1/c$
Temperature (K)	296	296
a, b, c (Å)	6.088 (4), 7.377 (5), 13.721 (9)	6.1640 (14), 22.933 (5), 7.2876 (14)
α, β, γ (°)	77.340 (6), 89.561 (7), 82.712 (7)	90, 97.328 (2), 90
V (Å^3)	596.3 (7)	1021.8 (4)
Z	2	4
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.43	0.71
Crystal size (mm)	0.20 × 0.02 × 0.02	0.20 × 0.10 × 0.10
Data collection		
Diffractometer	Bruker APEXII CCD	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2015)	Multi-scan (*SADABS*; Bruker, 2015)
T_{min}, T_{max}	0.919, 0.992	0.872, 0.933
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4506, 1642, 1519	8454, 1457, 1304
R_{int}	0.026	0.044
θ_{max} (°)	23.4	23.3
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.559	0.556
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.034, 0.090, 1.10	0.024, 0.064, 1.03
No. of reflections	1642	1457
No. of parameters	213	170
No. of restraints	97	14
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.50, −0.38	0.20, −0.29

Computer programs: *APEX2* and *SAINT* (Bruker, 2015), *SHELXS* (Sheldrick, 2008), *SHELXL* (Sheldrick, 2015), *Mercury* (Macrae *et al.*, 2020) and *publCIF* (Westrip, 2010).

the unligated water water molecules were ensured by using restrained H···H distances of 1.55 (1) Å.

Acknowledgements

Professor Vadim Kessler is acknowledged for valuable discussions.

Funding information

The support from the Swedish Research Council (Vetenskapsrådet) (grant 2014–3938) is gratefully acknowledged.

References

Anderson, A. J., Yang, H. X. & Downs, R. T. (2015). *Am. Mineral.* **100**, 330–333.
Beattie, J. K., Best, S. P., Skelton, B. W. & White, A. H. (1981). *J. Chem. Soc. Dalton Trans.* pp. 2105–2111.
Bruker (2015). *APEX2, SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Demartin, F., Castellano, C., Gramaccioli, C. M. & Campostrini, I. (2010). *Can. Mineral.* **48**, 323–333.
Fischer, T., Eisenmann, B. & Kniep, R. Z. (1996). *Z. Kristallogr.* **211**, 473–474.
Greenwood, N. N. & Earnshaw, A. (1997). *Chemistry of the Elements*. London: Butterworth–Heinemann.
Hay, M. B. & Myneni, S. C. B. (2008). *J. Phys. Chem. A*, **112**, 10595–10603.
Macrae, C. F., Sovago, I., Cottrell, S. J., Galek, P. T. A., McCabe, P., Pidcock, E., Platings, M., Shields, G. P., Stevens, J. S., Towler, M. & Wood, P. A. (2020). *J. Appl. Cryst.* **53**, 226–235.
Parnham, E. R. & Morris, R. E. (2006). *J. Mater. Chem.* **16**, 3682–3684.
Sabelli, C. & Ferroni, R. T. (1978). *Acta Cryst.* B**34**, 2407–2412.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.
Veillard, M. (1977). *J. Am. Chem. Soc.* **99**, 7194–7199.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

supporting information

Acta Cryst. (2021). E**77**, 58-61 [https://doi.org/10.1107/S2056989020015741]

Synthesis and crystal structures of $[Al(H_2O)_6](SO_4)NO_3{\cdot}2H_2O$ and $[Al(H_2O)_6](SO_4)Cl{\cdot}H_2O$

Fredric G. Svensson

Computing details

For both structures, data collection: *APEX2* (Bruker, 2015); cell refinement: *SAINT* (Bruker, 2015); data reduction: *SAINT* (Bruker, 2015); program(s) used to solve structure: *SHELXS* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015); molecular graphics: *Mercury* (Macrae *et al.*, 2020); software used to prepare material for publication: *publCIF* (Westrip, 2010).

Hexaquaaluminium sulfate nitrate dihydrate (1)

Crystal data

$[Al(H_2O)_6](NO_3)(SO_4){\cdot}2H_2O$
M_r = 329.18
triclinic, $P\overline{1}$
a = 6.088 (4) Å
b = 7.377 (5) Å
c = 13.721 (9) Å
α = 77.340 (6)°
β = 89.561 (7)°
γ = 82.712 (7)°
V = 596.3 (7) Å^3
Z = 2
$F(000)$ = 344
D_x = 1.833 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3914 reflections
θ = 2.9–23.4°
μ = 0.43 mm^{-1}
T = 296 K
Needle, colorless
0.20 × 0.02 × 0.02 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2015)
T_{min} = 0.919, T_{max} = 0.992
4506 measured reflections
1642 independent reflections
1519 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 23.4°, θ_{min} = 2.9°
h = −6→6
k = −8→8
l = −15→15

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.090
S = 1.10
1642 reflections
213 parameters
97 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0404P)^2 + 0.6205P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.50$ e Å^{-3}
$\Delta\rho_{min} = -0.38$ e Å^{-3}
Extinction correction: SHELXL, $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.021 (4)

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Al1	0.49771 (11)	−0.14486 (9)	0.30419 (5)	0.0196 (2)
S1	1.01766 (9)	−0.31760 (8)	0.62701 (4)	0.0206 (2)
O1	0.7790 (3)	−0.2120 (2)	0.36672 (13)	0.0244 (4)
O2	0.5436 (3)	0.1080 (2)	0.27387 (14)	0.0283 (4)
O3	0.4467 (3)	−0.3969 (2)	0.33515 (14)	0.0290 (5)
O4	0.2144 (3)	−0.0792 (3)	0.24229 (14)	0.0286 (4)
O5	0.3748 (3)	−0.1058 (2)	0.42456 (13)	0.0270 (4)
O6	0.6292 (3)	−0.1776 (3)	0.18465 (14)	0.0316 (5)
O7	0.9553 (3)	−0.4996 (2)	0.67900 (14)	0.0288 (4)
O8	1.0542 (3)	−0.2042 (3)	0.69915 (14)	0.0315 (5)
O9	1.2243 (3)	−0.3510 (2)	0.57270 (14)	0.0322 (5)
O10	0.8384 (3)	−0.2193 (3)	0.55706 (14)	0.0353 (5)
N1	0.2189 (5)	0.8543 (4)	0.0100 (2)	0.0446 (7)
O11	0.2452 (5)	1.0059 (4)	0.0276 (2)	0.0725 (8)
O12	0.2331 (6)	0.8332 (5)	−0.0748 (2)	0.0901 (10)
O13	0.1767 (6)	0.7326 (4)	0.0821 (2)	0.0823 (9)
OW1	0.3034 (5)	0.3374 (4)	0.1321 (2)	0.0754 (8)
OW2	0.7579 (7)	−0.4488 (6)	0.0962 (4)	0.1134 (14)
H1	0.809 (7)	−0.220 (6)	0.4280 (11)	0.069 (3)*
H2	0.867 (6)	−0.294 (4)	0.347 (3)	0.069 (3)*
H3	0.672 (3)	0.139 (6)	0.279 (3)	0.069 (3)*
H4	0.478 (6)	0.187 (4)	0.225 (2)	0.069 (3)*
H5	0.320 (3)	−0.432 (6)	0.332 (3)	0.069 (3)*
H6	0.540 (5)	−0.487 (4)	0.364 (3)	0.069 (3)*
H7	0.117 (5)	0.004 (4)	0.256 (3)	0.069 (3)*
H8	0.193 (7)	−0.087 (6)	0.1826 (13)	0.069 (3)*
H9	0.327 (7)	−0.183 (5)	0.473 (2)	0.069 (3)*
H10	0.313 (6)	0.001 (3)	0.431 (3)	0.069 (3)*
H11	0.648 (7)	−0.279 (3)	0.164 (3)	0.069 (3)*
H12	0.657 (7)	−0.083 (4)	0.141 (2)	0.069 (3)*
H13	0.265 (7)	0.451 (2)	0.137 (3)	0.069 (3)*
H14	0.367 (7)	0.298 (4)	0.083 (2)	0.069 (3)*
H15	0.616 (2)	−0.421 (5)	0.091 (3)	0.069 (3)*
H16	0.831 (5)	−0.555 (3)	0.092 (3)	0.069 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Al1	0.0169 (4)	0.0196 (4)	0.0222 (4)	−0.0027 (3)	−0.0003 (3)	−0.0041 (3)
S1	0.0178 (4)	0.0187 (4)	0.0248 (4)	−0.0008 (2)	−0.0005 (2)	−0.0046 (2)

O1	0.0199 (9)	0.0249 (9)	0.0279 (10)	0.0008 (7)	−0.0036 (7)	−0.0068 (8)
O2	0.0250 (10)	0.0236 (10)	0.0349 (11)	−0.0063 (8)	−0.0027 (8)	−0.0011 (8)
O3	0.0202 (9)	0.0205 (10)	0.0453 (12)	−0.0043 (7)	−0.0014 (8)	−0.0040 (8)
O4	0.0209 (9)	0.0333 (11)	0.0323 (10)	0.0002 (8)	−0.0040 (8)	−0.0106 (8)
O5	0.0313 (10)	0.0220 (10)	0.0255 (10)	0.0014 (8)	0.0054 (8)	−0.0032 (7)
O6	0.0321 (10)	0.0358 (11)	0.0268 (10)	−0.0035 (9)	0.0052 (8)	−0.0075 (8)
O7	0.0229 (9)	0.0220 (9)	0.0406 (11)	−0.0050 (7)	0.0033 (8)	−0.0039 (8)
O8	0.0263 (9)	0.0310 (10)	0.0411 (11)	−0.0042 (8)	−0.0033 (8)	−0.0158 (8)
O9	0.0282 (10)	0.0257 (10)	0.0373 (11)	0.0021 (8)	0.0103 (8)	0.0012 (8)
O10	0.0368 (11)	0.0348 (11)	0.0313 (10)	0.0134 (8)	−0.0101 (8)	−0.0107 (8)
N1	0.0476 (15)	0.0430 (16)	0.0396 (16)	0.0011 (12)	0.0073 (12)	−0.0053 (12)
O11	0.0610 (16)	0.0542 (16)	0.103 (2)	−0.0068 (13)	−0.0250 (15)	−0.0186 (15)
O12	0.126 (3)	0.100 (2)	0.0455 (16)	0.008 (2)	0.0206 (16)	−0.0325 (16)
O13	0.098 (2)	0.0772 (19)	0.0586 (17)	−0.0316 (17)	−0.0027 (15)	0.0257 (15)
OW1	0.085 (2)	0.0536 (16)	0.0713 (19)	0.0160 (15)	−0.0088 (16)	0.0071 (14)
OW2	0.092 (3)	0.107 (3)	0.171 (4)	−0.005 (2)	0.016 (3)	−0.101 (3)

Geometric parameters (Å, º)

Al1—O6	1.869 (2)	S1—O10	1.466 (2)
Al1—O5	1.872 (2)	S1—O7	1.470 (2)
Al1—O2	1.876 (2)	S1—O9	1.479 (2)
Al1—O3	1.880 (2)	N1—O12	1.209 (4)
Al1—O1	1.880 (2)	N1—O11	1.225 (4)
Al1—O4	1.887 (2)	N1—O13	1.232 (4)
S1—O8	1.464 (2)		
O6—Al1—O5	177.66 (9)	O2—Al1—O4	90.05 (8)
O6—Al1—O2	90.30 (9)	O3—Al1—O4	89.21 (8)
O5—Al1—O2	87.90 (8)	O1—Al1—O4	179.48 (9)
O6—Al1—O3	90.38 (9)	O8—S1—O10	109.31 (11)
O5—Al1—O3	91.45 (9)	O8—S1—O7	110.17 (12)
O2—Al1—O3	179.02 (8)	O10—S1—O7	108.97 (12)
O6—Al1—O1	88.42 (9)	O8—S1—O9	109.41 (12)
O5—Al1—O1	90.10 (9)	O10—S1—O9	110.42 (12)
O2—Al1—O1	90.37 (8)	O7—S1—O9	108.55 (11)
O3—Al1—O1	90.36 (8)	O12—N1—O11	119.5 (3)
O6—Al1—O4	91.88 (9)	O12—N1—O13	124.4 (3)
O5—Al1—O4	89.61 (9)	O11—N1—O13	116.2 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O10	0.85 (1)	1.78 (1)	2.627 (3)	173 (4)
O1—H2···O7^{i}	0.85 (1)	1.85 (1)	2.689 (3)	171 (4)
O2—H3···O8^{ii}	0.85 (1)	1.84 (1)	2.684 (3)	176 (4)
O2—H4···O*W*1	0.85 (1)	1.76 (1)	2.600 (3)	171 (4)
O3—H5···O7^{iii}	0.85 (1)	1.83 (1)	2.675 (3)	178 (4)

O3—H6···O9^{i}	0.85 (1)	1.83 (1)	2.670 (3)	169 (4)
O4—H7···O8^{iv}	0.85 (1)	1.91 (1)	2.745 (3)	168 (4)
O4—H8···O11^{v}	0.85 (1)	2.12 (2)	2.884 (4)	150 (4)
O4—H8···O13^{v}	0.85 (1)	2.13 (3)	2.870 (4)	147 (4)
O5—H9···O9^{vi}	0.85 (1)	1.80 (1)	2.650 (3)	179 (4)
O5—H10···O10^{iv}	0.85 (1)	1.79 (1)	2.640 (3)	175 (4)
O6—H11···O*W*2	0.85 (1)	1.79 (2)	2.596 (4)	160 (4)
O6—H12···O11^{vii}	0.85 (1)	2.35 (3)	3.044 (4)	139 (3)
O6—H12···O12^{vii}	0.85 (1)	2.06 (2)	2.876 (4)	162 (4)
O*W*1—H13···O13	0.86 (1)	2.05 (2)	2.850 (5)	155 (3)
O*W*1—H14···O12^{vii}	0.86 (1)	2.52 (4)	3.109 (5)	127 (4)
O*W*1—H14···O*W*2^{viii}	0.86 (1)	2.55 (4)	3.073 (6)	120 (3)
O*W*2—H16···O12^{viii}	0.86 (1)	2.20 (3)	2.908 (5)	139 (3)

Symmetry codes: (i) −*x*+2, −*y*−1, −*z*+1; (ii) −*x*+2, −*y*, −*z*+1; (iii) −*x*+1, −*y*−1, −*z*+1; (iv) −*x*+1, −*y*, −*z*+1; (v) *x*, *y*−1, *z*; (vi) *x*−1, *y*, *z*; (vii) −*x*+1, −*y*+1, −*z*; (viii) −*x*+1, −*y*, −*z*.

Hexaquaaluminium sulfate chloride monohydrate (2)

Crystal data

$[Al(H_2O)_6]Cl(SO_4)\cdot H_2O$
M_r = 284.60
monoclinic, $P2_1/c$
a = 6.1640 (14) Å
b = 22.933 (5) Å
c = 7.2876 (14) Å
β = 97.328 (2)°
V = 1021.8 (4) Å^3
Z = 4
$F(000)$ = 592
D_x = 1.850 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 3645 reflections
θ = 3.0–23.3°
μ = 0.71 mm^{-1}
T = 296 K
Block, coloress
0.20 × 0.10 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2015)
T_{min} = 0.872, T_{max} = 0.933
8454 measured reflections
1457 independent reflections
1304 reflections with $I > 2\sigma(I)$
R_{int} = 0.044
θ_{max} = 23.3°, θ_{min} = 3.0°
h = −6→6
k = −25→25
l = −8→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.064
S = 1.03
1457 reflections
170 parameters
14 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0256P)^2 + 0.8819P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.20 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Al1	0.94442 (10)	0.36368 (3)	0.83030 (9)	0.01735 (19)
S1	0.41721 (9)	0.32296 (2)	0.34162 (7)	0.01806 (17)
O1	0.8883 (3)	0.34621 (7)	1.0718 (2)	0.0242 (4)
O2	0.6779 (3)	0.40544 (7)	0.7845 (2)	0.0236 (4)
O3	0.7994 (3)	0.29620 (7)	0.7410 (2)	0.0236 (4)
O4	1.0001 (3)	0.38033 (7)	0.5873 (2)	0.0243 (4)
O5	1.0925 (3)	0.43174 (7)	0.9146 (2)	0.0262 (4)
O6	1.2075 (3)	0.32177 (7)	0.8685 (2)	0.0218 (4)
O7	0.5853 (3)	0.28049 (7)	0.4172 (2)	0.0288 (4)
O8	0.2061 (2)	0.29253 (7)	0.2976 (2)	0.0251 (4)
O9	0.4791 (3)	0.34900 (7)	0.1719 (2)	0.0257 (4)
O10	0.3963 (2)	0.36795 (7)	0.4814 (2)	0.0237 (4)
Cl1	1.22318 (11)	0.52579 (3)	0.66184 (10)	0.0399 (2)
OW1	1.2769 (3)	0.47795 (8)	1.2298 (3)	0.0329 (4)
H1	0.768 (3)	0.3524 (14)	1.115 (4)	0.054 (3)*
H2	0.977 (4)	0.3286 (12)	1.152 (3)	0.054 (3)*
H3	0.691 (5)	0.4422 (5)	0.783 (5)	0.054 (3)*
H4	0.588 (4)	0.3942 (14)	0.693 (3)	0.054 (3)*
H5	0.734 (5)	0.2727 (11)	0.805 (4)	0.054 (3)*
H6	0.734 (5)	0.2915 (14)	0.632 (2)	0.054 (3)*
H7	0.933 (4)	0.4067 (10)	0.520 (4)	0.054 (3)*
H8	1.126 (3)	0.3750 (14)	0.557 (4)	0.054 (3)*
H9	1.143 (5)	0.4415 (13)	1.025 (2)	0.054 (3)*
H10	1.130 (5)	0.4554 (11)	0.834 (3)	0.054 (3)*
H11	1.215 (5)	0.2853 (5)	0.855 (4)	0.054 (3)*
H12	1.304 (4)	0.3305 (14)	0.957 (3)	0.054 (3)*
H13	1.400 (3)	0.4634 (13)	1.270 (4)	0.054 (3)*
H14	1.220 (5)	0.4762 (14)	1.329 (3)	0.054 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Al1	0.0135 (4)	0.0205 (4)	0.0175 (4)	−0.0001 (3)	0.0002 (3)	0.0011 (3)
S1	0.0136 (3)	0.0220 (3)	0.0178 (3)	0.0011 (2)	−0.0007 (2)	−0.0008 (2)
O1	0.0173 (9)	0.0370 (10)	0.0184 (9)	0.0042 (8)	0.0026 (7)	0.0054 (7)
O2	0.0171 (9)	0.0264 (9)	0.0260 (9)	0.0017 (7)	−0.0017 (7)	0.0001 (8)
O3	0.0230 (9)	0.0267 (10)	0.0194 (9)	−0.0064 (7)	−0.0034 (7)	0.0031 (7)
O4	0.0193 (9)	0.0306 (10)	0.0236 (9)	0.0051 (7)	0.0052 (7)	0.0074 (7)
O5	0.0265 (9)	0.0250 (10)	0.0256 (10)	−0.0063 (7)	−0.0028 (8)	0.0010 (8)
O6	0.0176 (9)	0.0234 (9)	0.0233 (9)	0.0033 (7)	−0.0022 (7)	−0.0020 (8)
O7	0.0267 (9)	0.0316 (10)	0.0253 (9)	0.0133 (8)	−0.0071 (7)	−0.0062 (8)
O8	0.0188 (9)	0.0258 (9)	0.0286 (9)	−0.0053 (7)	−0.0042 (7)	0.0044 (7)
O9	0.0210 (9)	0.0364 (10)	0.0197 (9)	−0.0048 (7)	0.0030 (7)	0.0009 (7)
O10	0.0202 (9)	0.0260 (9)	0.0249 (9)	0.0015 (7)	0.0027 (7)	−0.0049 (7)
Cl1	0.0288 (4)	0.0426 (4)	0.0458 (4)	−0.0069 (3)	−0.0045 (3)	0.0166 (3)

OW1	0.0298 (10)	0.0329 (11)	0.0349 (11)	0.0066 (8)	0.0000 (8)	0.0006 (9)

Geometric parameters (Å, º)

Al1—O3	1.8624 (17)	Al1—O2	1.8940 (17)
Al1—O5	1.8718 (18)	S1—O10	1.4670 (16)
Al1—O6	1.8752 (17)	S1—O9	1.4672 (16)
Al1—O1	1.8798 (17)	S1—O8	1.4753 (16)
Al1—O4	1.8855 (17)	S1—O7	1.4767 (16)
O3—Al1—O5	178.65 (8)	O5—Al1—O2	90.67 (8)
O3—Al1—O6	89.63 (8)	O6—Al1—O2	178.38 (8)
O5—Al1—O6	90.14 (8)	O1—Al1—O2	90.78 (8)
O3—Al1—O1	90.72 (8)	O4—Al1—O2	89.41 (7)
O5—Al1—O1	90.61 (8)	O10—S1—O9	110.75 (10)
O6—Al1—O1	90.61 (7)	O10—S1—O8	109.30 (10)
O3—Al1—O4	88.68 (8)	O9—S1—O8	109.04 (9)
O5—Al1—O4	89.99 (8)	O10—S1—O7	108.95 (9)
O6—Al1—O4	89.19 (7)	O9—S1—O7	109.71 (10)
O1—Al1—O4	179.37 (8)	O8—S1—O7	109.07 (10)
O3—Al1—O2	89.53 (8)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O9^{i}	0.85 (1)	1.88 (1)	2.714 (2)	165 (3)
O1—H2···O8^{ii}	0.85 (1)	1.85 (1)	2.690 (2)	170 (3)
O2—H3···O*W*1^{iii}	0.85 (1)	1.85 (1)	2.692 (2)	178 (3)
O2—H4···O10	0.85 (1)	1.92 (1)	2.767 (2)	177 (3)
O3—H5···O7^{iv}	0.85 (1)	1.78 (1)	2.629 (2)	174 (3)
O3—H6···O7	0.85 (1)	1.73 (1)	2.578 (2)	176 (3)
O4—H7···Cl1^{v}	0.85 (1)	2.18 (1)	3.0311 (18)	177 (3)
O4—H8···O10^{vi}	0.85 (1)	1.83 (1)	2.669 (2)	176 (3)
O5—H9···O*W*1	0.85 (1)	1.82 (1)	2.650 (2)	166 (3)
O5—H10···Cl1	0.85 (1)	2.17 (1)	3.0120 (18)	171 (3)
O6—H11···O8^{vii}	0.85 (1)	1.83 (1)	2.672 (2)	172 (3)
O6—H12···O9^{ii}	0.85 (1)	1.83 (1)	2.671 (2)	171 (3)
O*W*1—H13···Cl1^{viii}	0.85 (1)	2.33 (2)	3.083 (2)	149 (3)
O*W*1—H14···Cl1^{i}	0.84 (1)	2.68 (2)	3.390 (2)	143 (3)
O*W*1—H14···Cl1^{iii}	0.84 (1)	2.74 (3)	3.280 (2)	123 (3)

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*+1, *y*, *z*+1; (iii) −*x*+2, −*y*+1, −*z*+2; (iv) *x*, −*y*+1/2, *z*+1/2; (v) −*x*+2, −*y*+1, −*z*+1; (vi) *x*+1, *y*, *z*; (vii) *x*+1, −*y*+1/2, *z*+1/2; (viii) −*x*+3, −*y*+1, −*z*+2.