

Synthesis and Structure of Aluminium Selenite Trihydrate, $\text{Al}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$

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Abstract. Aluminium selenite trihydrate, synthetic, $M_r = 488.88$, trigonal, $R3c$, $a = 8.3806(4) \text{ \AA}$, $\alpha = 65.527(3)^\circ$, $V = 466.2 \text{ \AA}^3$, $Z = 2$, $D_x = 3.48 \text{ g cm}^{-3}$, $\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$, $\mu = 119.7 \text{ cm}^{-1}$, $F(000) = 460$, $T = 298(2) \text{ K}$, $R = 4.48\%$, $wR = 5.10\%$ for 556 observed reflections with $I > 3\sigma(I)$. Synthesized hydrothermally, $\text{Al}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$ consists of a three-dimensional network of vertex-sharing octahedral AlO_6 and pyramidal SeO_3 groups, connected via Al—O—Se links. The three water molecules are coordinated by one of the aluminium atoms. The title compound is isostructural with $\text{Ga}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$ and $\text{Cr}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$, and is closely related to aluminium selenite hexahydrate, $\text{Al}_2(\text{SeO}_3)_3 \cdot 6\text{H}_2\text{O}$.

Introduction. In the solid state, the selenium(IV)-containing selenite ion, SeO_3^{2-} , shows a characteristic pyramidal coordination. As yet, there are few well defined structural families of selenites, but a number of phases containing a trivalent octahedral metal ion, M^{3+} , selenite, SeO_3^{2-} , and/or hydrogenselenite, HSeO_3^- , and possibly water have been studied by single-crystal X-ray diffraction methods. These include: $\text{Mn}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$ (Koskenlinna & Valkonen, 1977); $\text{FeH}(\text{SeO}_3)_2$ (Valkonen & Koskenlinna, 1978); $\text{Sc}(\text{HSeO}_3)_3$ (Valkonen & Leskelä, 1978); $\text{Ga}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$ (Rastsvetaeva, Andrianov & Volodnia, 1986); $\text{Fe}(\text{Se}_2\text{O}_5)(\text{HSeO}_3)$ and $\text{Fe}(\text{HSeO}_3)_3$ (Muilu & Valkonen, 1987); $\text{Al}_2(\text{SeO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Al}(\text{SeO}_3)(\text{HSeO}_3) \cdot 2\text{H}_2\text{O}$ (Morris, Harrison, Stucky & Cheetham, 1991); and $\text{Cr}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$ and $\text{InH}(\text{SeO}_3)_2$ (Harrison, McManus, Stucky & Cheetham, 1992). Here we report the preparation and crystal structure of $\text{Al}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$.

Experimental. The title compound was synthesized hydrothermally from the starting materials $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fisher, 2 g) and excess SeO_2 (Aldrich, 5 g) in 15 cm^3 of water. The Teflon-lined steel bomb was heated to $473(5) \text{ K}$ for 48 h and cooled to room temperature overnight. An estimated maximum pressure of 3 MPa was achieved. Transparent rhombic crystals with linear dimensions of up

to 0.5 mm were recovered from the reaction mixture.

An irregular crystal, dimensions ca $0.12 \times 0.12 \times 0.12 \text{ mm}$, was mounted on a Huber automated diffractometer. The unit-cell constants were determined and refined from 14 centred reflections ($18 < 2\theta < 24^\circ$). Data were collected at room temperature [$298(2) \text{ K}$] in the θ - 2θ scan mode (scan speed = 6° min^{-1}) using graphite-monochromated $\text{Mo } K\alpha$ radiation over the range $0 < 2\theta < 65^\circ$ for $-6 \leq h \leq 9$, $-5 \leq k \leq 10$, $1 \leq l \leq 12$, $[(\sin\theta)/\lambda]_{\text{max}} = 0.76 \text{ \AA}^{-1}$, with regular checks on reflection intensity (every 100 reflections; no variation observed), absorption correction based on ψ scans of reflections with $\chi \sim 90^\circ$ (min. 1.0, max. 1.2) applied during data reduction. 2293 reflections were measured, of which 556 were used in the structure solution and refinement [merging $R = 6.6\%$; reflections with $I < 3\sigma(I)$ considered unobserved].

The initial model, in the rhombohedral setting of space group $R3c$ (No. 161), was taken from our study of the isostructural chromium selenite trihydrate (Harrison, McManus, Stucky & Cheetham, 1992), and the usual atomic positional and anisotropic thermal parameters were refined to convergence. For the final cycle of full-matrix anisotropic refinement against F : 53 parameters, origin defined as centroid of structure (Waser, 1974), $\Sigma(\text{shift/e.s.d.}) = 0.01$, $R = 4.48$, $wR = 5.10\%$ [three-term Chebyshev weighting scheme (Carruthers & Watkin, 1979) with coefficients 24(6), $-11(7)$ and $11(5)$ where the digit in parentheses is the e.s.d.], maximum residual electron density = 2 e \AA^{-3} near O(4) which could not be refined as an atomic position, no proton positions located. Structure refinement and analysis were carried out using the Oxford *CRYSTALS* system (Watkin, Carruthers & Betteridge, 1985) on a MicroVAX II computer. Complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). An isotropic secondary-extinction correction [Larson (1970): refined value = $46(4)$] was also applied: the reflection most affected was 002.

Discussion. Table 1 gives final atomic positional and thermal parameters for $\text{Al}_2(\text{SeO}_3)_3 \cdot 3\text{H}_2\text{O}$ and Table 2 gives selected bond distance/angle data for this

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Table 1. Atomic positional parameters

$$U_{eq} = (U_1 U_2 U_3)^{1/3}.$$

	<i>W</i> *	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i> (Å ²)
Al(1)	2(<i>a</i>)	0.2048 (3)	0.2048	0.2048	0.0052
Al(2)	2(<i>a</i>)	0.4398 (3)	0.4398	0.4398	0.0088
Se(1)	6(<i>b</i>)	0.9188 (2)	0.5458 (2)	0.0086 (2)	0.0067
O(1)	6(<i>b</i>)	0.848 (1)	0.594 (1)	0.504 (1)	0.0109
O(2)	6(<i>b</i>)	0.204 (1)	0.542 (1)	0.423 (1)	0.0136
O(3)	6(<i>b</i>)	0.405 (1)	0.310 (1)	0.056 (1)	0.0125
O(4)†	6(<i>b</i>)	0.458 (1)	0.690 (1)	0.357 (1)	0.0144

* Wyckoff position.

† O atom of water molecule.

Table 2. Bond distances (Å) and angles (°)

Al(1)—O(1)	1.958 (8)	Se(1)—O(1)	1.699 (7)
Al(1)—O(3)	1.932 (8)	Se(1)—O(2)	1.754 (8)
Al(2)—O(2)	1.836 (8)	Se(1)—O(3)	1.679 (7)
Al(2)—O(4)	1.967 (8)		
O(1)—Al(1)—O(1)	91.5 (4)	O(2)—Al(2)—O(2)	94.1 (4)
O(3)—Al(1)—O(1)	86.6 (3)	O(4)—Al(2)—O(2)	173.8 (5)
O(3)—Al(1)—O(3)	87.6 (3)	O(4)—Al(2)—O(2)	88.1 (3)
O(3)—Al(1)—O(1)	177.9 (4)	O(4)—Al(2)—O(2)	91.5 (4)
O(3)—Al(1)—O(3)	94.3 (4)	O(4)—Al(2)—O(4)	86.0 (4)
O(2)—Se(1)—O(1)	100.5 (4)	Se(1)—O(1)—Al(1)	122.7 (4)
O(3)—Se(1)—O(1)	89.8 (4)	Se(1)—O(2)—Al(2)	124.4 (4)
O(3)—Se(1)—O(2)	98.8 (4)	Se(1)—O(3)—Al(1)	127.1 (5)

phase.* The structure of aluminium selenite trihydrate (Fig. 1) consists of a three-dimensional network of vertex-sharing AlO_6 and SeO_3 groups linked *via* $Al-O-Se$ bonds: there are two crystallographically distinct Al atoms, one Se atom and four O atoms, one of which [O(4)] is from a water molecule. Both Al atoms form typical octahedral coordination with O atoms [$d_{av}[Al(1)-O] = 1.945$ (6), $d_{av}[Al(2)-O] = 1.902$ (6) Å]; the Se atom [$d_{av}(Se-O) = 1.711$ (5) Å, $\theta_{av}(O-Se-O) = 96.4$ (3)°] is pyramidal, and three of the four O atoms form $Al-O-Se$ bridges [$\theta_{av} = 124.7$ (3)°]. The selenite-ion geometry compared well with the average values [$\langle d(Se-O) \rangle = 1.709$ (10) Å, $\langle \theta(O-Se-O) \rangle = 100.2$ (13)°; values in parentheses = r.m.s. deviations] derived by Hawthorne, Groat & Ercit (1987) for a large number of (H)SeO₃ species.

The structure of $Al_2(SeO_3)_3 \cdot 3H_2O$ consists of stacks of alternating Al(1) and Al(2) octahedra in the rhombohedral [111] direction. Each Al(1) octahedron is linked to its nearest Al(2) neighbour by three different $Al(1)-O(3)-Se(1)-O(2)-Al(2)$ links, thus forming an empty 'cage', centred at approximately $(\frac{1}{3}, \frac{1}{3}, \frac{1}{3})$. The three O(1) atoms around Al(1) are also bonded to Se(1), thus adjacent octahedra of Al(1) are cross-linked by $Al(1)-O(1)-Se(1)-O(3)-Al(1)$ and $Al(1)-O(1)-Se(1)-O(2)-Al(2)$

* Lists of observed and calculated structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54996 (5 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CR0386]

links, building up an infinite network of octahedra and pyramids. $Al_2(SeO_3)_3 \cdot 3H_2O$ is isostructural with $Ga_2(SeO_3)_3 \cdot 3H_2O$ (Rastsvetaeva, Andrianov & Volodnia, 1986) and $Cr_2(SeO_3)_3 \cdot 3H_2O$ (Harrison, McManus, Stucky & Cheetham, 1992).

Two other aluminium selenite hydrate phases have been characterized by X-ray single-crystal methods: $Al_2(SeO_3)_3 \cdot 6H_2O$ (AlSeO-I) and $Al(SeO_3)(HSeO_3) \cdot 2H_2O$ (AlSeO-II), which were also prepared under mild hydrothermal conditions (Morris, Harrison, Stucky & Cheetham, 1992), indicating the wealth of new systems accessible by these methods by subtle variation of reactant concentrations, pH and temperature. Both AlSeO-I and AlSeO-II contain three-dimensional networks of octahedral aluminium cations and pyramidal selenium species, and both also contain $Al-OH_2$ links as part of the Al-atom coordination. AlSeO-II has a quite different structure to $Al_2(SeO_3)_3 \cdot 3H_2O$, but AlSeO-I is closely related to the phase described here, and contains octahedral AlO_6 stacks joined by a similar triad of $Al-O-Se-O'-Al'$ bonds surrounding an empty cavity. However, in AlSeO-I, compared to $Al_2(SeO_3)_3 \cdot 3H_2O$, each terminal Al atom is coordinated to three water molecules and has three oxo-selenium bridges to its neighbour. As opposed to $Al_2(SeO_3)_3 \cdot 3H_2O$, the third $Se-O$ vertex in AlSeO-I only partakes in H bonds (and not an $Se-O-Al$ link), and is not associated with another Al cation. Thus, 'molecular' units of $Al_2(SeO_3)_3 \cdot 6H_2O$ make up the repeating motif in AlSeO-I; in $Al_2(SeO_3)_3 \cdot 3H_2O$, three water molecules are eliminated, adjacent octahedral stacks shift relative to each other to form the $Al-O-Se-O-Al$ cross-linking bonds described above, and a three-dimensional, as opposed to molecular, structure results. Investigation into related selenite phases is ongoing.

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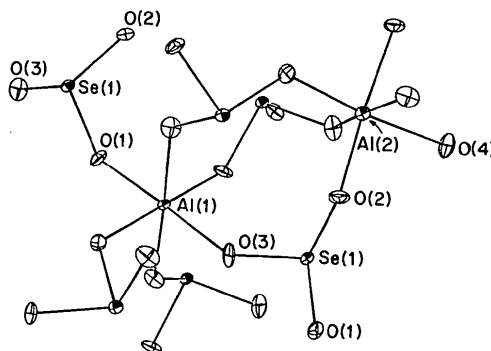


Fig. 1. Linkages along the threefold axis in $Al_2(SeO_3)_3 \cdot 3H_2O$ showing the atomic labelling scheme and the linkage of Al(1) and Al(2) octahedra *via* selenite bridges. O(4) is the O atom of the water molecule.

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Structure of Strontium Thiocyanate Trihydrate, Sr(SCN)₂·3H₂O, at 295 and 125 K

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Abstract. Sr(SCN)₂·3H₂O, $M_r = 257.82$, monoclinic, $P2_1/n$. At $T = 295$ K: $a = 9.501$ (1), $b = 7.140$ (1), $c = 13.470$ (2) Å, $\beta = 94.27$ (1)°, $V = 911.3$ (2) Å³, $Z = 4$, $D_x = 1.879$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 61.4$ cm⁻¹, $F(000) = 504$, final $R = 0.029$ for 1458 independent reflections; at $T = 125$ K: $a = 9.452$ (2), $b = 7.103$ (2), $c = 13.373$ (3) Å, $\beta = 94.51$ (2)°, $V = 895.1$ (4) Å³, $Z = 4$, $D_x = 1.913$ g cm⁻³, $\mu = 62.9$ cm⁻¹, final $R = 0.031$ for 1511 independent reflections. The structure contains SrSN₄(H₂O)₃ polyhedra which are linked by the SCN groups into chains of composition Sr(SCN)₂·3H₂O. The water molecules form exclusively O—H···S type hydrogen bonds which are all oriented approximately perpendicular to the acceptor SCN groups.

Introduction. Combined structural and vibrational spectroscopic studies have shown that hydrogen bonds between H₂O molecules as donors and S atoms as acceptors depend in strength not only on the donor–acceptor distance (O···S) but also on the chemical nature of the acceptor S atom (Mikenda, Mereiter & Preisinger, 1989). This means that O—H···S bonds of comparable bond distances may differ considerably in strength for different kinds of S acceptor atoms. Thiocyanates were found to form rather weak O—H···S bonds, but further experimental data were desirable. The present work was carried out in order to find compounds suitable for corre-

lations between structure and spectroscopy. Low-temperature data were required to that end.

Experimental. The title compound was obtained by the reaction Sr(ClO₄)₂ + 2KSCN → Sr(SCN)₂ + 2KClO₄ in aqueous solution, removal of the KClO₄ precipitate, and evaporation crystallization at room temperature. A prismatic crystal of size 0.11 × 0.20 × 0.50 mm was selected. A Philips PW 1100 diffractometer with graphite-monochromated Mo $K\alpha$ radiation was used. Lattice parameters were determined from least-squares fit of 33 reflections with $10 < \theta < 28^\circ$. Data collection at $T = 295$ K was carried out with $\omega/2\theta$ scans, scan width $(1 + 0.33\tan\theta)^\circ$, scan speed 4° min^{-1} . Three standard reflections (400, 040, 008) were monitored every 60 min and showed a continuous intensity loss of up to 6%. 4124 reflections with $2 \leq \theta \leq 27^\circ$, $-17 \leq h \leq 17$, $0 \leq k \leq 9$, $-17 \leq l \leq 17$ were measured, corrected for Lorentz–polarization, decay and absorption effects (Gaussian integration, minimum and maximum transmission factors 0.29 and 0.54), and averaged ($R_{\text{int}} = 0.045$ based on F) to 1991 unique reflections, 1458 of which with $F_o > 6\sigma(F_o)$ were subsequently used. Data collection at 125 K was performed with a Leybold Heraeus NCD2 nitrogen-gas-stream cooler. Crystal, measurement conditions and data processing methods were the same as at 295 K. The standard reflections remained