

Triammonium Scandium Selenate

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Abstract. $(\text{NH}_4)_3\text{Sc}(\text{SeO}_4)_3$, hexagonal, $R3$ (No. 146), $a = 15.567$ (5), $c = 9.871$ (3) Å, $Z = 6$, $V = 2071.6$ Å³ [rhombohedral cell: $a = 9.570$ (3) Å, $\alpha = 108.83$ (2)°], $D_x = 2.54$, $D_m = 2.55$ (2) g cm⁻³, $\mu(\text{Mo } K\alpha) = 88.2$ cm⁻¹. $R = 0.063$ for 1028 reflections. The structure consists of octahedrally coordinated Sc atoms which are linked together in infinite columns by sharing O atoms with the selenate tetrahedra.

Introduction. The crystal structure of scandium selenate pentahydrate (Valkonen, Niinistö, Eriksson, Larsson & Skoglund, 1975) was determined earlier as part of a systematic investigation into the structures of rare-earth sulfates and selenates. In order to improve the picture obtained of these structures, structural work on $(\text{NH}_4)_3\text{Sc}(\text{SeO}_4)_3$, corresponding to the complex anion $[\text{Sc}(\text{SeO}_4)_3]^{3-}$, was initiated.

Single crystals suitable for X-ray diffraction study were obtained by slow evaporation of an aqueous solution slightly acidified with selenic acid and containing Sc^{3+} , NH_4^+ and SeO_4^{2-} in the approximate molar ratio 1:10:10. The elongated plate-like crystals were found to be rhombohedral and not monoclinic as suggested by Tezu, Ivanov-Ermin, Korotaeva & Zaitzev (1970). Erämetsä & Haukka (1966) had also suggested monoclinic symmetry for the corresponding sulfate. These earlier sets of results were based only on microscopic and X-ray powder diffraction studies, however.

The cell parameters were obtained at 298 K from a least-squares refinement of the angular settings of 25 reflections with a Syntex $P2_1$ single-crystal automatic diffractometer.

Three-dimensional intensity data were collected on the same diffractometer with graphite-monochromatized Mo $K\alpha$ radiation by the θ - 2θ method and at a fixed scan rate of 1° min⁻¹. All 2039 reflections up to 2θ of 70° were measured and, of those, 1028 with $I > 3\sigma(I)$ were considered significant. The net intensities were corrected for Lorentz and polarization effects and for absorption from the φ -scan data.

The structure was solved by direct methods using the symbolic addition procedure (Karle & Karle, 1966). The statistics of normalized structure factors indicated the absence of an inversion center; the rhombohedral space group $R3$ was confirmed by the successful refinement of the positional and thermal parameters.

Refinement by the method of full-matrix least-squares calculations with anisotropic thermal parameters led to the final value for the conventional R index. In the refinement, scattering factors for neutral atoms given in the XRAY 76 program system (Stewart, 1976) were used. A difference Fourier map calculated after the refinement with low-angle intensity data ($2\theta \leq 30^\circ$) did not reveal any distinct H atom positions around the N

Table 1. Positional parameters ($\times 10^4$) for $(\text{NH}_4)_3\text{Sc}(\text{SeO}_4)_3$

The standard deviations of the last two figures are given in parentheses.

	x	y	z
Se(1)	1831 (2)	5025 (2)	3878 (2)
Se(2)	3523 (1)	5120 (1)	8866 (2)
Sc(1)	0	0	4699 (15)
Sc(2)	0	0	9673 (17)
O(1)	7268 (12)	7684 (12)	7194 (19)
O(2)	5479 (9)	2406 (11)	9193 (16)
O(3)	902 (13)	9724 (12)	8532 (16)
O(4)	8660 (16)	1053 (20)	7083 (25)
O(5)	7983 (16)	4376 (16)	6896 (19)
O(6)	2236 (17)	6871 (21)	7453 (24)
O(7)	2736 (16)	2376 (16)	2121 (24)
O(8)	4711 (11)	5757 (13)	8829 (19)
N(1)	5921 (15)	5678 (12)	6876 (21)
N(2)	2317 (18)	3093 (19)	6062 (26)

Table 2. Distances (Å) and angles (°) in the selenate tetrahedra

Se(1)—O(1)	1.660 (17)	O(1)—Se(1)—O(2)	106.2 (8)
Se(1)—O(2)	1.646 (16)	O(1)—Se(1)—O(3)	107.8 (9)
Se(1)—O(3)	1.643 (17)	O(1)—Se(1)—O(4)	108.4 (11)
Se(1)—O(4)	1.642 (22)	O(2)—Se(1)—O(3)	106.6 (8)
Mean	1.648	O(2)—Se(1)—O(4)	109.3 (10)
		O(3)—Se(1)—O(4)	118.0 (11)
		Mean	109.4
Se(2)—O(5)	1.649 (20)	O(5)—Se(2)—O(6)	112.8 (11)
Se(2)—O(6)	1.643 (24)	O(5)—Se(2)—O(7)	104.5 (11)
Se(2)—O(7)	1.607 (22)	O(5)—Se(2)—O(8)	112.3 (10)
Se(2)—O(8)	1.604 (16)	O(6)—Se(2)—O(7)	100.4 (12)
Mean	1.626	O(6)—Se(2)—O(8)	106.7 (12)
		O(7)—Se(2)—O(8)	119.7 (11)
		Mean	109.4

Table 3. Distances (Å) in the coordination octahedra of scandium

Sc(1)—O(2)	2.037 (17) (3×)	Sc(2)—O(3)	2.007 (20) (3×)
Sc(1)—O(5)	2.183 (23) (3×)	Sc(2)—O(6)	2.185 (26) (3×)
Mean	2.110	Mean	2.096

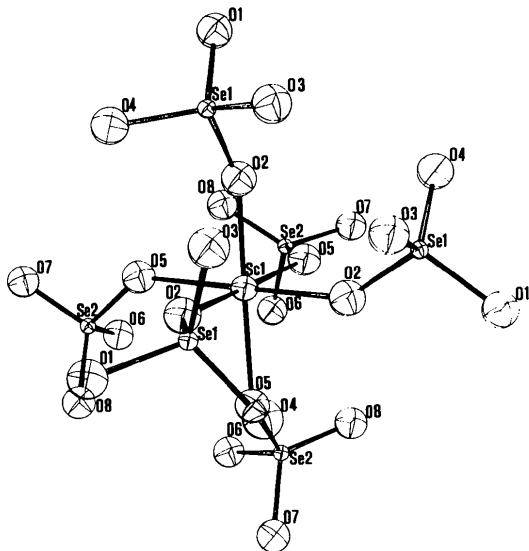


Fig. 1. The coordination around Sc(1).

atoms. Positional parameters are given in Table 1, bonding distances and selected angles in Tables 2 and 3.*

Discussion. In the structure of $(\text{NH}_4)_3\text{Sc}(\text{SeO}_4)_3$ scandium is octahedrally coordinated (Fig. 1) as in most of its compounds (Melson & Stotz, 1971). A rather uncommon feature of the present compound, however, is the linking together of the ScO_6 octahedra. They are joined, in the direction of the c axis of the hexagonal cell, into infinite columns by SeO_4 tetrahedra sharing two O atoms with the Sc atoms (Fig. 2). These columns are joined together in the (001) plane, probably by hydrogen bonding involving ammonium groups. A perspective view showing the unit-cell packing in the rhombohedral setting is shown in Fig. 3.

In its infinite $[\text{Sc}(\text{SeO}_4)_3]^{3n-}$ columns, the present structure closely resembles that of $\text{Na}_3\text{Sc}(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ for which a preliminary report has appeared (Sizova, Voronkov & Belov, 1974).

The mean distances in the coordination polyhedra are quite normal as compared with other structures. Thus, the mean Sc—O distance in $\text{Sc}(1)\text{O}_6$ and $\text{Sc}(2)\text{O}_6$

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32990 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

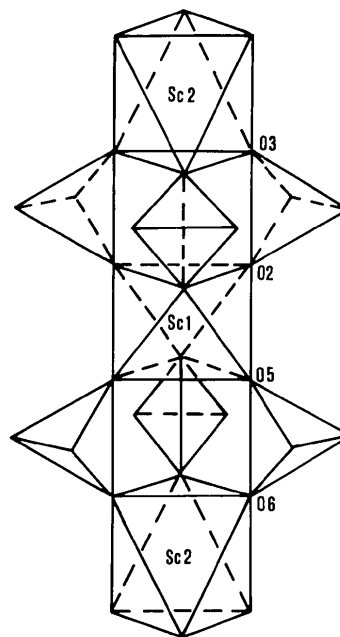
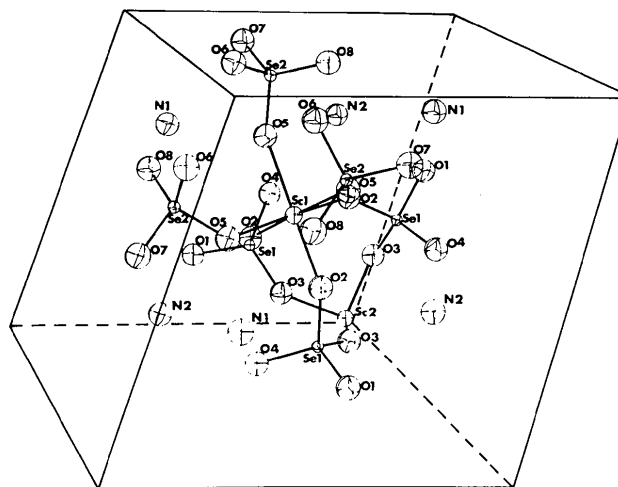

 Fig. 2. The basic building unit of the structure: $[\text{Sc}(\text{SeO}_4)_3]^{3n-}$ column.


Fig. 3. A perspective view showing the unit-cell packing in the rhombohedral setting.

octahedra is 2.11 and 2.10 Å, respectively, or nearly the same as the average of all Sc—O distances (2.09 Å) in the structure of $\text{Sc}_2(\text{SeO}_4)_3 \cdot 5\text{H}_2\text{O}$. Also the mean Se—O distances in the selenate tetrahedra represent values normally encountered in metal selenate structures (Valkonen *et al.*, 1975).

The mean value of all bond angles for both SeO_4 groups is 109.4° , or almost exactly the theoretical value for a tetrahedron. However, there are some significant deviations from the mean among the angle values (*cf.* Table 2). Benelli, Di Vaira, Noccioli & Sacconi

Table 4. Distances less than 3.2 Å in the environment of ammonium ions (Å)

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

N(1)—O(8 ⁱ)	2.740 (27)	N(2)—O(7 ^{iv})	2.793 (34)
N(1)—O(1 ⁱ)	2.778 (24)	N(2)—O(1 ^v)	2.942 (30)
N(1)—O(8 ⁱⁱ)	2.956 (27)	N(2)—O(7 ^{vi})	2.942 (35)
N(1)—O(5 ⁱⁱⁱ)	3.019 (28)	N(2)—O(4 ⁱⁱ)	2.948 (36)
N(1)—O(7 ^{iv})	3.181 (30)	N(2)—O(4 ^v)	2.967 (36)
N(1)—O(1 ⁱⁱ)	3.196 (28)	N(2)—O(2 ^{vi})	3.096 (29)

(1977) have recently reported large distortions in the bidentate SeO_4 group when it is acting as a chelating group. In the present structure the selenate group is a bridging one and the angles involved [O(2)—Se(1)—O(3) and O(5)—Se(2)—O(5)] appear normal. Thus, the distortions observed are probably due to hydrogen bonding and also partly to data inaccuracy.

In the environment of each of the two ammonium ions there are six possible hydrogen-bond contacts to selenate O atoms, ranging from 2.74 to 3.20 Å and from 2.79 to 3.10 Å for N(1) and N(2) respectively (Table 4). After our failure to locate H atoms from Fourier maps, an attempt was made to elucidate a possible hydrogen-bonding scheme from geometrical considerations. It too proved unsuccessful.

According to a survey by Khan & Bauer (1972), the ammonium ions are in static or dynamic disorder or no hydrogen bonding is present when the coordination number of ammonium is higher than four. Recently it

was shown, however, that the ammonium ion, at higher coordination numbers, is capable of acting simultaneously as a hydrogen-bond donor and as a strongly electropositive large cation, thus having a dual character (Catti & Franchini-Angela, 1976). In the case of $(\text{NH}_4)_3\text{Sc}(\text{SeO}_4)_3$ the presence of disordered hydrogen bonds around N atoms, possibly together with some purely electrostatic interactions, seems likely.

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Tetraethylammonium Trichloro(ethyl vinyl ether)platinum(II)

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Abstract. $[(\text{C}_2\text{H}_5)_4\text{N}][\text{PtCl}_3(\text{C}_4\text{H}_8\text{O})]$, $P2_1/n$, $a = 7.728$ (4), $b = 17.763$ (6), $c = 13.418$ (9) Å, $\beta = 103.71$ (1)°, $U = 1789.4$ Å³, $Z = 4$, $D_x = 1.87$ g cm⁻³, $\mu = 86.9$ cm⁻¹ (Mo $K\alpha$). The structure contains undistorted tetraethylammonium cations and complex anions of Pt^{II} ligated by three chloride ions and the double bond of the vinyl ether in a square-planar coordination arrangement. The mid-point of the double bond is 0.19 Å off the plane determined by the Pt and three Cl atoms. The C atom of the double bond which

bears the ether O atom is 0.08 Å further from the Pt atom than the unsubstituted C atom. There appears to be no significant interaction between the ether O atom and the Pt atom in the solid state. The structure was refined to an R of 0.022 for 1602 independent observed reflections.

Introduction. The structure of $[(\text{C}_2\text{H}_5)_4\text{N}][\text{PtCl}_3(\text{C}_4\text{H}_8\text{O})]$ has been determined as part of a study of the catalytic activity of Pt^{II} complexes for alkoxide