$Na_4[Ru(SO_3)_2(HSO_3)_2(NH_3)_2].6H_2O$

Table 1. *Fractional atomic coordinates and thermal parameters*

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as $\frac{4}{3}(a^2B_{11} + b^2B_{22} + c^2B_{33} + acB_{13}\cos\beta)$.

	x	y	z	$B_{eq}/B(\text{Å}^2)$
Ru	0·000	0·000	0·000	0·718 (8)
S(1)	0·1262 (1)	0·1074 (2)	0·12889 (8)	0·93 (2)
S(2)	0·1716 (1)	0·1225 (2)	−0·07373 (8)	1·02 (2)
Na(1)	0·0349 (3)	0·6132 (4)	0·2293 (2)	1·58 (4)
Na(2)	0·6135 (3)	0·3543 (5)	0·2841 (2)	1·91 (5)
O(1)	0·0679 (5)	0·2994 (7)	0·1618 (3)	1·68 (8)
O(2)	0·1308 (5)	−0·0648 (7)	0·1918 (3)	1·52 (8)
O(3)	0·2839 (4)	0·1557 (7)	0·1280 (3)	1·49 (8)
O(4)	0·3230 (4)	0·1357 (9)	−0·0171 (3)	1·90 (9)
O(5)	0·1990 (4)	−0·0183 (8)	−0·1415 (2)	1·77 (8)
O(6)	0·1414 (4)	0·3378 (7)	−0·1075 (3)	1·67 (8)
O(7)	0·3777 (4)	0·4813 (8)	0·2442 (3)	1·91 (8)
O(8)	0·6358 (5)	0·3924 (9)	0·1382 (3)	2·5 (1)
O(9)	0·5686 (5)	0·2118 (9)	0·4140 (3)	2·6 (1)
N(1)	−0·1117 (5)	0·2913 (8)	−0·0149 (3)	1·35 (9)
H(1)	−0·1074	0·3906	0·0371	1·7
H(2)	−0·1973	0·2773	−0·0371	1·7
H(3)	−0·0859	0·3887	−0·0547	1·7
H(4)	0·3242	0·1680	0·0547	2·3
H(5)	0·3496	0·3887	0·2051	2·3
H(6)	0·3047	0·4434	0·2793	2·3
H(7)	0·6973	0·5000	0·1309	3·0
H(8)	0·6289	0·3906	0·2031	3·0
H(9)	0·6094	0·3340	0·3711	3·1
H(10)	0·5957	0·2578	0·4687	3·1

Table 2. *Selected interatomic distances (Å) and angles (°)*

Ru—S(1)	2·337 (1)	S(2)—O(4)	1·577 (4)
Ru—S(2)	2·333 (1)	S(2)—O(5)	1·482 (4)
Ru—N(1)	2·128 (5)	S(2)—O(6)	1·482 (4)
S(1)—O(1)	1·481 (4)	O(4)—H(4)	1·189
S(1)—O(2)	1·497 (4)	O(3)···H(4)	1·324
S(1)—O(3)	1·540 (4)		
S(1)—Ru—S(2)	94·0 (1)	O(2)—S(1)—O(3)	104·0 (2)
S(1)—Ru—N(1)	91·1 (1)	O(4)—S(2)—O(5)	101·9 (2)
S(2)—Ru—N(1)	92·0 (1)	O(4)—S(2)—O(6)	105·5 (3)
O(1)—S(1)—O(2)	108·6 (3)	O(5)—S(2)—O(6)	109·1 (3)
O(1)—S(1)—O(3)	105·8 (3)		

Cation—anion		Cation—water	
Na(1)···O(1)	2·325 (5)	Na(2)···O(7)	2·374 (5)
Na(1)···O(1^i)	2·479 (5)	Na(2)···O(7^{vi})	2·416 (6)
Na(1)···O(2^{ii})	2·364 (5)	Na(2)···O(8)	2·443 (5)
Na(1)···O(2^i)	2·483 (5)	Na(2)···O(9)	2·415 (6)
Na(1)···O(5^{iii})	2·473 (5)		
Na(1)···O(6^{iv})	2·392 (5)		
Na(2)···O(2^v)	2·461 (5)		
Na(2)···O(3^v)	2·488 (5)		

Symmetry code: (i) $-x$, $0.5+y$, $0.5-z$; (ii) x, $1+y$, z; (iii) x, $0.5-y$, $0.5+z$; (iv) $-x$, $1-y$, $-z$; (v) $1-x$, $0.5+y$, $0.5-z$; (vi) $1-x$, $-0.5+y$, $0.5-z$.

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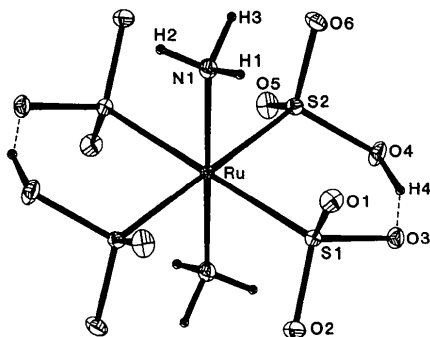VOGT, L. H., KATZ, J. L. & WIBERLY, S. E. (1965). *Inorg. Chem.* **24**, 1157–1163.

Fig. 1. *ORTEP*II diagram (Johnson, 1976) and atom-numbering scheme. Non-H ellipsoids at 30% probability level, H atoms given arbitrary radii.

Structure of PbPSe₃

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Abstract. Lead phosphorus triselenide, $M_r = 475.04$, monoclinic, $P2_1/n$, $a = 6.897$ (3), $b = 7.642$ (3), $c = 9.696$ (4) Å, $\beta = 91.51$ (1)°, $V = 510.9$ Å³, $Z = 4$, $D_x = 6.174$ g cm⁻³, $\lambda(\text{Mo } K\alpha_1) = 0.7093$ Å, $\mu = 545.7$ cm⁻¹, $F(000) = 780.61$ (including anomalous dispersion), $T = 123$ K, $R(F^2) = 0.070$ for 1301

Table 1. *Positional parameters and equivalent isotropic thermal parameters for* PbPSe₃

$$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}\mathbf{a}_i^*.\mathbf{a}_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å²)
Pb	−0·037294 (65)	0·113027 (63)	0·748730 (42)	1·04 (1)
Se(1)	0·39243 (16)	−0·00357 (16)	−0·23255 (10)	0·79 (2)
Se(2)	0·17639 (16)	0·20244 (16)	0·45673 (11)	0·76 (2)
Se(3)	0·16575 (15)	0·19184 (16)	0·05467 (11)	0·76 (2)
P	0·44118 (40)	0·10744 (41)	−0·43641 (27)	0·73 (6)

Table 2. *Selected bond distances* (Å) *and angles* (°) *for* PbPSe₃

Pb—Se(1)	3·096 (2)	Pb—Se(2)	3·298 (2)
Pb—Se(1)	3·101 (2)	Pb—Se(3)	3·302 (2)
Pb—Se(3)	3·124 (1)	P—P	2·220 (6)
Pb—Se(3)	3·152 (2)	P—Se(3)	2·183 (3)
Pb—Se(2)	3·188 (2)	P—Se(1)	2·185 (3)
Pb—Se(2)	3·256 (2)	P—Se(2)	2·199 (3)

Se(2)—P—Se(3)	109·30 (14)	P—P—Se(1)	106·41 (19)
Se(1)—P—Se(2)	114·12 (13)	P—P—Se(2)	107·08 (16)
Se(1)—P—Se(3)	115·78 (12)	P—P—Se(3)	103·16 (18)

averaged reflections (including those having $F_o^2 < 0$), $R(F) = 0.034$ for 1062 reflections having $F_o^2 > 3\sigma(F_o^2)$. The compound can be formulated as $Pb_2(P_2Se_6)$ and the crystal structure consists of the packing of Pb^{2+} and $P_2Se_6^{4-}$ ions. The Pb^{2+} ions are coordinated by eight Se atoms at the corners of a distorted bicapped trigonal prism. The $P_2Se_6^{4-}$ ion has crystallographically imposed $\bar{1}$ symmetry and approximate $\bar{3}m$ molecular symmetry. An earlier structure determination of PbPSe₃ [Becker, Brockner & Schäfer (1984). *Z. Naturforsch. Teil A*, **39**, 357–361] in space group *Pn* appears to be in error.

Experimental. A stoichiometric combination of the elements, Pb powder, P powder, and Se pellets, was loaded into a silica tube with a small amount of I_2. The tube was evacuated to $\sim 10^{-4}$ Torr $(\sim 10^{-2}$ Pa) and sealed. The vessel was placed for 7 d in a furnace having a temperature gradient of 973/1023 K. Red, irregularly shaped polyhedral crystals formed at the cool end of the tube. The crystal used for data collection was a thin plate bounded by {101}, (011), and (0$\bar{1}$0); crystal volume 1·04 × 10⁻⁴ mm³. Unit-cell parameters were derived from a least-squares refinement of 14 reflections in the range of $8 < \theta < 13°$, automatically centered on a Picker FACS-1 diffractometer. Intensity data were collected with the $\theta–2\theta$ scan technique; intensities of six standards monitored throughout data collection were constant within intensity statistics. A total of 5064 X-ray diffraction intensities, measured to $[(\sin\theta)/\lambda]_{max} = 0.6727$ Å⁻¹, in the index range $-9 \leq h \leq 9$, $-10 \leq k \leq 10$, $-13 \leq l \leq 13$, were corrected for absorption with use of the analytical method (de Meulenaer & Tompa, 1965);

min. and max. transmission factors were 0·08 and 0·31. The F_o^2 values were averaged to yield 1301 unique data $[R_{int}(F^2) = 0.061$ for $F_o^2 > 3\sigma(F_o^2)]$.

The initial position for the Pb atom was determined from a Patterson synthesis. Positions for the Se and P atoms were obtained from a subsequent electron density synthesis. Scattering factors and anomalous-dispersion terms were taken from the usual sources (Cromer & Waber, 1974; Cromer, 1974). All calculations were performed on a Harris 1000 computer with methods and programs standard for this laboratory (Waters & Ibers, 1977). The final anisotropic refinement on F_o^2, based on 47 variables and 1301 observations, resulted in an R index on F^2 of 0·070 and an isotropic-extinction parameter (Zachariasen, 1968) of 1.97×10^{-6}, with Δ/σ not exceeding 0·005. Other residuals are $wR(F^2) = 0.086$, where the weights were derived from counting statistics and a value of p of 0·04, and $R(F)$ $[F_o^2 > 3\sigma(F_o^2)]$ $= 0.034$. The error in an observation of unit weight is 1·27. A final difference electron density map exhibited no features with heights greater than about 8% that of the P atom.

Table 1 lists fractional coordinates and equivalent isotropic thermal parameters.* A list of selected bond distances and angles may be found in Table 2. A perspective view down [100] of the structure is given in Fig. 1.
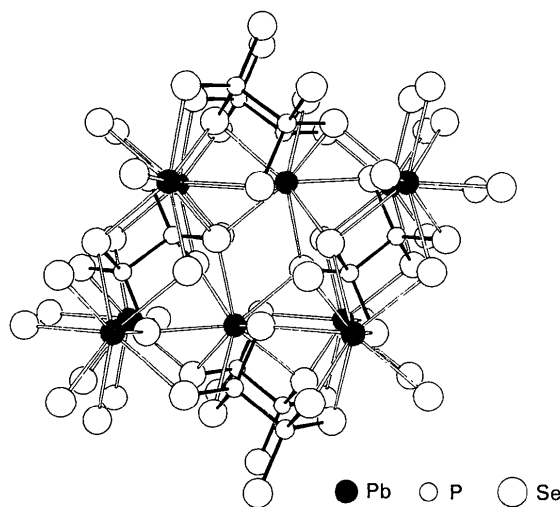

Fig. 1. Perspective view of PbPSe₃ along [100]. The $P_2Se_6^{4-}$ ions are shown with darkened bonds connecting the P and Se atoms.

Related literature. The distorted bicapped trigonal-prismatic arrangement of Se atoms about the Pb atom is similar to that of the S atoms in $Pb_3(PS_4)_2$ (Post & Kramer, 1984). The $P_2Se_6^{4-}$ geometry found here is typical of other $P_2Q_6^{4-}$ units ($Q = S$ or Se) such as those found in ZrP_2S_6 and ThP_2S_6 (Simon, Peters, Peters & Hahn, 1982).

After the completion of this determination we discovered the report by Becker, Brockner & Schäfer (1984) on the same structure. For reasons that are not clear from that report, they chose to refine the structure of PbPSe₃ in space group Pn, even though they note that $0k0$ reflections with k odd were not observed. Their structural refinement [$R(F) = 0.085$, 79 variables, 1388 observations] is inferior to the present one even though it involves the extra variables that result from placement of two independent formula units in the asymmetric unit. Their final results give a calculated Patterson function that is indistinguishable from that calculated from the present parameters. We conclude that their choice of space group is incorrect. As would be expected in such circumstances, the distances and angles found by Becker et al. (1984) are much less regular than those found here. For example, their P—Se distances range from 2·127 (22) to 2·245 (22) Å compared with 2·183 (3) to 2·199 (3) Å here. It is probable that the structures of $PbPS_3$ (Becker, Brockner & Schäfer, 1983) and $SnPS_3$ (Dittmar & Schäfer, 1974) suffer from the same error in space-group choice.

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Structure du Germanate d'Indium et de Lithium

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Abstract. LiInGeO₄, $M_r = 258·3$, orthorhombic, Pnma, $a = 10·754$ (5), $b = 6·088$ (2), $c = 5·007$ (2) Å, $V = 328$ (1) Å³, $Z = 4$, $D_x = 5·237$ Mg m⁻³, $\lambda(Mo\ K\bar{\alpha}) = 0·71069$ Å, $\mu = 16·53$ mm⁻¹, $F(000) = 464$, $T = 293$ K, final $R = 0·027$ for 1033 unique observed reflections. Monocrystals have been obtained by cooling a $2Li_2CO_3–In_2O_3–4GeO_2$ melt from 1473 K. This compound has an olivine-type structure with four LiInGeO₄ motifs per cell. It is built from LiO_6 and InO_6 octahedra and GeO_4 tetrahedra joined by their apices.

Li occupies all 4(a) positions and In one 4(c) position. Analyses have been performed to disclose a possible sharing of the sites between Li and In; the refinement of the ratios of distribution showed a clear separation of the two elements in their respective positions. Likewise an attempt to reveal a partial occupation of site 4(a) by Ge showed the total absence of six-coordination for Ge.

Partie expérimentale. Les composés Li_2CO_3, In_2O_3 et GeO_2, en proportion 2:1:4, sont portés à 1473 K en 12 h puis maintenus à cette température pendant 1 h; un refroidissement lent (10 K h⁻¹) conduit à des

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