$C_6H_4(PPh_2)_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$, was reported (Levason, McAuliffe & McCullough, 1977). Only in 1986 was the first crystallographic structural study of an oxotungsten(IV) compound, namely $WOCl_2(PMePh_2)_2(CH_2{=}CH_2)$, (3), reported (Su, Cooper, Geib, Rheingold & Mayer, 1986).

The structures of the two compounds are fundamentally similar and also share several key characteristics with the structure of (3) (Su, Cooper, Geib, Rheingold & Mayer, 1986). The W=O bond lengths are the same to within $\pm 3\sigma$, *viz* 1·68 (1), 1·711 (5) and 1·714 (6) Å for (1), (2) and (3) respectively. Also, in each case the *trans* influence of the W=O bond is seen in the relatively long W—Cl bonds *trans* to it, namely, 2·539 (5), 2·554 (2) and 2·495 (3) Å for (1), (2) and (3). In (3) one has an internal comparison of W—Cl bond lengths since there is a *cis* W—Cl bond that has a length of only 2·444 (3) Å. In all three cases, the W=O unit tends to demand a larger solid angle in the coordination sphere and the O—W—P or O—W—S angles are larger than 90°.

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References

Butcher, A. V., Chatt, J., Leigh, G. J. & Richards, P. L. (1972). *J. Chem. Soc. Dalton Trans.* pp. 1064–1069.
Carmona, E., Sanchez, L., Poveda, M. L. Jones, R. A. & Hefner, J. G. (1983). *Polyhedron*, **2**, 797–801.
Enraf–Nonius (1979). *Structure Determination Package.* Enraf–Nonius, Delft, The Netherlands.
Levason, W., McAuliffe, C. A. & McCullough, F. P. Jr (1977). *Inorg. Chem.* **16**, 2911–2916.
Sheldrick, G. M. (1986). *SHELX*86. Program for crystal structure determination. Univ. of Göttingen, Federal Republic of Germany.
Su, F.-M., Cooper, C., Geib, S. J., Rheingold, A. L. & Mayer, J. M. (1986). *J. Am. Chem. Soc.* **108**, 3545–3547.

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Structure of $Sr_8PtSi_2O_{14}$

By Lars Stenberg

Inorganic Chemistry 2, *Chemical Centre, PO Box* 124, 221 00 *Lund, Sweden*

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Abstract. $Sr_8(PtO_6)(SiO_4)_2$, $M_r = 1176{\cdot}21$, monoclinic, $C2$, $a = 18{\cdot}830\,(2)$, $b = 5{\cdot}744\,(1)$, $c = 7{\cdot}172\,(1)$ Å, $\beta = 110{\cdot}72\,(1)°$, $V = 725{\cdot}547$ Å^3, $Z = 2$, $D_x = 5{\cdot}383$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7093$ Å, $\mu = 383{\cdot}38$ cm^{-1}, $F(000) = 1044$, $T = 292$ K, $R = 0{\cdot}026$ for 1495 independent reflexions. This is a new structure type, with isolated SiO_4 tetrahedra and PtO_6 octahedra. Three of the four nonequivalent Sr atoms are coordinated by O in distorted trigonal prisms. The fourth is located in a square antiprism, which has one small and one large square face, *i.e.* half a cuboctahedron. Two such small faces are shared, which gives a short Sr—Sr distance of 3·28 Å.

Introduction. A great deal of interest has been spent on the structure and chemistry of platinum oxides over the years. The main interest has been focused on properties like catalysis, inertness or metallic conduction in the 'bronzes'. The chemistry of platinum is not trivial, depending on the inertness of the metal itself and the ease with which PtO_2 decomposes. Sometimes highly sophisticated methods have to be used (Gallagher, Johnson, Vogel, Wertheim & Schnettler, 1977; Muller & Roy, 1969) and sometimes again good crystals grow by mistake (Boivin, Conflant & Thomas, 1976; Czaya, 1970). In the present case, during synthesis of a strontium silicate, light brown crystals of $Sr_8PtSi_2O_{14}$ were found growing on the wall of the platinum crucible used. To the best of our knowledge, this compound is the first platinum silicate reported.

Experimental. An irregular crystal of approximate size 0·07 × 0·06 × 0·05 mm was studied with a CAD-4 diffractometer using graphite-monochromatized Mo $K\alpha$ radiation. The data set was collected in a hemisphere for $6 \le 2\theta \le 60°$ with $-27 \le h \le 27$, $-10 \le k \le 10$ and $0 \le l \le 8$. Three standard reflexions measured every 2 h showed no systematic variations. Unit-cell dimensions were determined from least-squares refinements of 44 2θ values from powder data. The data set was corrected for polarization and the Lorentz effect and for absorption. Systematic absences of reflexions for hkl when $h + k \neq 2n$, $h0l$ when $h \neq 2n$ and $0k0$ when $k \neq 2n$ suggested space groups $C2/m$, Cm or $C2$. After averaging of equivalent reflexions 2090 unique data remained. 1495 reflexions with $I > 2\sigma(I)$ were used in the structure determination. The structure was solved by the heavy-atom method, which gave the Pt and Sr

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atomic positions. Difference electron density maps gave the rest of the atomic positions. The parameters were first refined in space group $C2/m$, but this attempt gave high isotropic temperature factors in two oxygen positions belonging to the SiO_4 tetrahedron. Full-matrix least-squares refinement on F, based on 1495 reflexions, was then used in space group $C2$ to refine 114 parameters: one scale factor, one secondary-extinction parameter, 36 atomic and 76 anisotropic thermal parameters. $R = 0{\cdot}026$, $w = [\sigma^2(F_o) + (0{\cdot}033F_o)^2]^{-1}$, $S = 0{\cdot}9993$, final max. shift/e.s.d. $< 0{\cdot}005$, final residual electron density $R_{\max} = 1{\cdot}8$ e Å^{-3}, secondary extinction of type I, with a Gaussian distribution (Becker & Coppens, 1974) of $1{\cdot}65\,(3) \times 10^{-5}$. Computer programs used from Lundgren (1982). Atomic scattering factors and anomalous corrections from *International Tables for X-ray Crystallography* (1974).

During refinement the two anisotropic temperature factors for O(1) and O(3), belonging to the PtO_6 octahedron, became slightly negative. U_{eq} is, however, positive for these atoms. We believe this is due to an imperfect absorption correction of the crystal used for data collection.

An attempt to refine the parameters with changed absolute configuration gave no significant change in the R value and gave negative anisotropic temperature factors for O(1) and O(2), which also belong to the PtO_6 octahedron.

Discussion. The final parameters are given in Table 1 and the selected interatomic distances and angles in Table 2.*

Description of the structure. A projection of the structure along the b axis is given in Fig. 1, where the PtO_6 octahedra and SiO_4 tetrahedra are outlined. The SiO_4 tetrahedron has a regular shape with O—O distances ranging from 2·626 (11) to 2·686 (10) Å. The Si atom is off centre, which gives an O(5)—Si—O(7) angle of 105·5 (6)° and O(4)—Si—O(5) angle of 113·5 (5)°. The Si—O distances vary from 1·582 (11) to 1·697 (14) Å. The PtO_6 octahedron shows three different Pt—O distances, but considering their e.s.d.'s (Table 2) there is possibly a 4+2 coordination for Pt.

A limit of 3·75 Å was set for the Sr—O interactions, which gives the following coordinations: Sr(1) monocapped square antiprism. Sr(2) four-, Sr(3) three- and Sr(4) two-capped trigonal prisms.

The structure type is new and is most easily described with the help of the distorted trigonal prisms surrounding Sr(2), Sr(3) and Sr(4). The Sr(2) and Sr(4) prisms form infinite layers by means of edge-sharing. These layers run parallel to the c axis, with the threefold axis of the prisms along the b axis. The arrangement of the SrO_6 trigonal prisms is the same as we find for $AsNi_6$ trigonal prisms in the NiAs structure. The infinite layers are connected by two edge-sharing Sr(3) prisms lying down (see Fig. 2). Two such bridges create the octahedral oxygen environment between two adjacent prisms for the Pt atoms. A similar arrangement can be found for Ge in the δ-Mn_2GeO_4 structure (Sr_2PbO_4)

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters*

$U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}(Å^2)
Pt	0·0000	0·0000	0·0000	0·0051 (1)
Sr(1)	0·4778 (1)	−0·0004 (11)	0·2014 (1)	0·0098 (2)
Sr(2)	0·1671 (1)	−0·0002 (10)	−0·0021 (1)	0·0085 (2)
Sr(3)	0·0941 (1)	−0·0009 (11)	0·4615 (1)	0·0149 (3)
Sr(4)	0·3148 (1)	0·0003 (9)	0·7132 (1)	0·0089 (2)
Si	0·3279 (1)	0·0058 (20)	0·2939 (4)	0·0110 (45)
O(1)	0·0808 (9)	−0·2325 (31)	0·1398 (29)	0·0110 (45)
O(2)	0·0786 (10)	0·2438 (27)	0·1413 (27)	0·0112 (48)
O(3)	−0·0376 (3)	0·0051 (37)	0·2410 (9)	0·0115 (19)
O(4)	0·4117 (4)	−0·0053 (50)	0·4608 (9)	0·0157 (21)
O(5)	0·3258 (4)	−0·0536 (14)	0·0738 (11)	0·0146 (29)
O(6)	0·2701 (6)	−0·1490 (17)	0·3554 (13)	0·0225 (31)
O(7)	0·2992 (5)	0·2872 (15)	0·2844 (13)	0·0152 (26)

Table 2. *Selected interatomic distances* (Å) *up to* 3·75 Å *and angles* (°)

Pt—2O(1)	2·006 (17)	Sr(3)—O(3)	2·424 (6)
2O(2)	2·029 (17)	O(7)	2·500 (9)
2O(3)	2·087 (6)	O(1)	2·598 (19)
		O(2)	2·619 (18)
Sr(1)—O(2)	2·554 (18)	O(3)	2·700 (6)
O(4)	2·575 (6)	O(4)	2·908 (29)
O(4)	2·579 (6)	O(4)	2·958 (29)
O(1)	2·632 (17)	O(6)	3·157 (11)
O(5)	2·696 (8)	O(6)	3·752 (10)
O(2)	2·734 (18)		
O(1)	2·767 (19)	Sr(4)—O(2)	2·409 (17)
O(3)	2·878 (22)	O(1)	2·421 (17)
O(3)	2·940 (22)	O(7)	2·476 (9)
Sr(1)	3·278 (2)	O(6)	2·510 (11)
		O(5)	2·540 (8)
Sr(2)—O(3)	2·434 (6)	O(6)	2·549 (9)
O(1)	2·573 (17)	O(4)	2·991 (6)
O(5)	2·627 (10)	O(7)	3·408 (9)
O(7)	2·628 (9)		
O(2)	2·647 (18)	Si—O(6)	1·582 (12)
O(6)	2·748 (9)	O(5)	1·602 (8)
O(5)	2·860 (8)	O(4)	1·610 (7)
O(7)	3·085 (9)	O(7)	1·697 (14)
O(5)	3·228 (10)		
O(6)	3·742 (10)		
O(1)—Pt—O(1)	96·6 (9)	O(4)—Si—O(5)	113·5 (5)
O(1)—Pt—O(2)	85·3 (7)	O(4)—Si—O(6)	111·1 (8)
O(1)—Pt—O(2)	177·8 (7)	O(4)—Si—O(7)	106·4 (11)
O(1)—Pt—O(3)	90·9 (7)	O(5)—Si—O(6)	112·1 (6)
O(1)—Pt—O(3)	90·2 (7)	O(5)—Si—O(7)	105·5 (6)
O(2)—Pt—O(2)	92·8 (9)	O(6)—Si—O(7)	107·8 (5)
O(2)—Pt—O(3)	88·7 (7)		
O(2)—Pt—O(3)	90·1 (7)		
O(3)—Pt—O(3)	178·4 (12)		

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44778 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and the isostructural Cd_2PtO_4 (Muller & Roy, 1970). The Sr(1) atom is coordinated by a distorted square antiprism, or rather half a cuboctahedron, with an additional oxygen outside its larger square face. The smaller square face is generated by the empty space between two PtO_6 octahedra. Two of these square antiprisms share such a small face, which yields a short Sr(1)–Sr(1) distance of 3·28 Å. The SiO_4 tetrahedron shares an edge with one Sr(2) and one Sr(4) prism, with one of the other two oxygen atoms [O(4)] capping two lying prisms. The remaining oxygen atom, O(5), caps Sr(2) and Sr(4) prisms outside a square face and also a Sr(2) prism outside its trigonal faces.

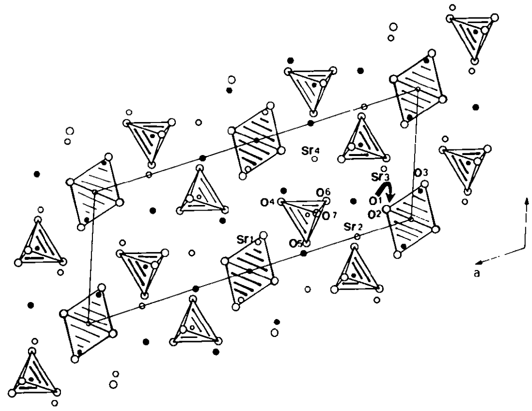

Fig. 1. Projection along [010]. PtO_6 octahedra and SiO_4 tetrahedra outlined. Unfilled and filled circles on approximately 0; 1 and $\frac{1}{2}$. Heights for the O atoms not explicitly indicated.

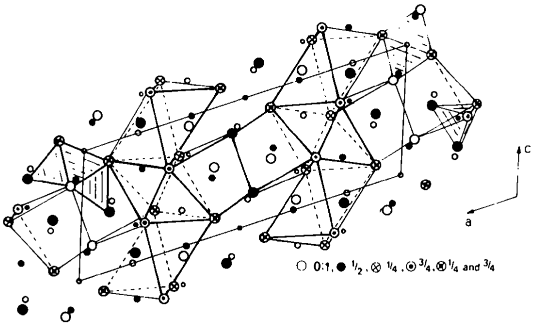

Fig. 2. Projection along [010]. SrO_6 trigonal prisms outlined. Position of PtO_6 octahedron, SiO_4 tetrahedron and square antiprism is indicated. Heights approximate.

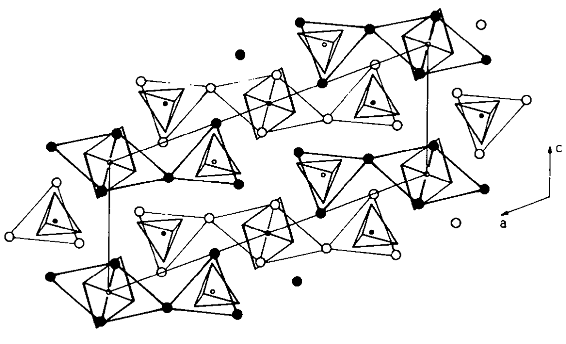

Fig. 3. Projection along [010]. Description according to O'Keeffe & Hyde (1985).

Alternative description. It has recently been shown (O'Keeffe & Hyde, 1985) that the use of cation polyhedra may be extremely useful in the description of some crystal structures. Among these are a number of orthosilicates of alkali or alkaline-earth metals, in which the eutaxy of the cations can be described as well known alloy structures. The β-Ca_2SiO_4 (and β-Sr_2SiO_4) structures can in this manner be seen as built of elongated trigonal Ca_6Si prisms, joined as the $PbCl_6$ prisms in the $PbCl_2$ structure. The oxygen atoms are then stuffed tetrahedrally around the silicon atoms. In the leucophoenicite $\{Mn_7[SiO_4]_2[SiO_4(OH)_2]\}$ family (White & Hyde, 1983) a similar arrangement occurs, but here we also find face-sharing trigonal prisms (here Mn_6Si). The two possible central sites in these prisms are here statistically occupied by one SiO_4 tetrahedron. In the present case for $Sr_8(PtO_6)(SiO_4)_2$, isolated strings of single–double–single trigonal prisms are filled with an SiO_4 tetrahedron, a PtO_6 octahedron and an SiO_4 tetrahedron respectively (see Fig. 3).

This description with cation polyhedra also gives some clues how to make new compounds. Hydrothermal methods may very well give strontium/platinum analogues to the leuchophoenicite group of structures.

It is possible to replace strontium, partially or totally, with barium. These results will be published later.

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References

Becker, P. J. & Coppens, P. (1974). *Acta Cryst.* **A30**, 129–147.
Boivin, J. C., Conflant, P. & Thomas, D. (1976). *Mater. Res. Bull.* **11**, 1503–1510.
Czaya, R. (1970). *Z. Anorg. Allg. Chem.* **375**, 61–65.
Gallagher, P. K., Johnson, D. W. Jr, Vogel, E. M., Wertheim, G. K. & Schnettler, F. J. (1977). *J. Solid State Chem.* **21**, 277–282.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
Lundgren, J.-O. (1982). Report No. UUIC-B13-4-05. Univ. of Uppsala, Sweden.
Muller, O. & Roy, R. (1969). *J. Less-Common Met.* **19**, 209–214.
Muller, O. & Roy, R. (1970). *J. Less-Common Met.* **20**, 161–163.
O'Keeffe, M. & Hyde, B. G. (1985). *Struct. Bonding* (*Berlin*), **61**, 79–144.
White, T. J. & Hyde, B. G. (1983). *Am. Mineral.* **68**, 1009–1021.