

The Crystal Structure of Pt_5P_2

ERIC DAHL

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

The crystal structure of Pt_5P_2 has been determined by single-crystal methods. The symmetry is monoclinic (space group probably $C2/c$) and the cell dimensions are $a = 10.764 \text{ \AA}$; $b = 5.385 \text{ \AA}$; $c = 7.438 \text{ \AA}$; $\beta = 99^\circ.17$. The unit cell contains 20 platinum and 8 phosphorus atoms. One set of 4 platinum atoms is situated in position $4(e)$, while the remaining atoms occupy $8(f)$ positions. The structure can be described as a complex array of interconnected Pt_4P distorted octahedra.

In the system platinum-phosphorus the intermediate phase PtP_2 has been characterized by Thomassen¹ and later confirmed by Biltz *et al.*² and Rundqvist.³ Biltz *et al.* studied the system using metallographic methods, X-ray methods and thermal analysis. They found in addition to the known phase PtP_2 another intermediate phase which they gave the formula Pt_{20}P_7 (25.9 at. % P). The structure of this phase has now been determined and its formula established as Pt_5P_2 .

EXPERIMENTAL

Alloys of varying compositions were prepared by heating mixtures of platinum metal powder (Johnson, Matthey & Co. Ltd., claimed purity 99.9 %) and red phosphorus (99 % or better) at temperatures between 600°C and 800°C for several days in evacuated and sealed silica tubes. After re-annealing at 570°C and quenching in water powder photographs of the samples were recorded in a Guinier-Hägg type focussing camera using $\text{CuK}\alpha$ -radiation. By studying these photographs it could be concluded that the composition of the platinum-rich intermediate phase does not quite correspond to the formula given by Biltz *et al.*² but a slightly higher phosphorus content was indicated. The ideal composition Pt_5P_2 established by the structure determination (see below) corresponds to 28.6 at. % phosphorus. No variations of cell dimensions with composition were observed.

Crystals of Pt_5P_2 were prepared by heating a platinum-phosphorus alloy containing 27 at. % P in an evacuated and sealed silica tube at about 570°C for three weeks. The crystals were rather small and of irregular shape. In spite of much effort, no well-developed crystals could be produced. The crystal fragment selected had the dimensions 0.06 mm \times 0.04 mm \times 0.04 mm. From oscillation and Weissenberg photographs the crystal was found to be monoclinic. Approximate values of the unit-cell parameters were also obtained. These were used to index a powder pattern recorded in a Guinier-Hägg type focussing camera using $\text{CrK}\alpha_1$ -radiation. Silicon was used as the internal calibration

Table 1. All the calculations have been carried out on a CDC 3600 electronic computer using the following programs (all programs are written in Fortran IV).

| Program | Authors |
|--|---|
| Least squares refinement of unit-cell dimensions | J. Tegenfeldt, Uppsala, Sweden |
| Lorentz-polarization corrections | A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden |
| Absorption correction | P. Coppens, L. Leiserowitz and D. Rabino- vich, Rehovoth, Israel; modified by O. Olofsson, Uppsala, Sweden |
| Fourier summations, structure factor calculations | A. Zalkin, Berkeley, U.S.A.; modified by R. Liminga and J.-O. Lundgren, Uppsala, Sweden |
| Least squares refinements of positional parameters and temperature factors | P. K. Gantzel, R. A. Sparks and K. N. Trueblood, Los Angeles, U.S.A.; modified by A. Zalkin, Berkeley, U.S.A. and by C.-I. Brändén, R. Liminga and J.-O. Lundgren, Uppsala, Sweden. |
| Interatomic distances | A. Zalkin, Berkeley, U.S.A. |

standard ($a=5.4305 \text{ \AA}$). The following values for the cell parameters and their standard deviations were obtained after a least-squares refinement (for details of the computer and the programs used, see Table 1):

$$\begin{aligned} a &= 10.7642 \text{ \AA} \pm 0.0009 \text{ \AA} \\ b &= 5.3854 \text{ \AA} \pm 0.0005 \text{ \AA} \\ c &= 7.4378 \text{ \AA} \pm 0.0008 \text{ \AA} \\ \beta &= 99.170^\circ \pm 0.009^\circ \end{aligned}$$

Due to a computing error, incorrect dimensions were unfortunately reported in Ref. 6. Multiple-film equi-inclination Weissenberg photographs were recorded about the b -axis using Zr-filtered MoK-radiation. Thin iron foils were interleaved between the films. Seven reciprocal layers $h0l$ through $h6l$ were recorded.

The only systematic absences found were for hkl -reflexions when $h+k=2n+1$, and for $h0l$ -reflexions when $l=2n+1$. Thus the space group is either Cc or $C2/c$. At this stage it can be concluded that there must be four formula units Pt_2P_2 in the unit-cell, since any other number of formula units in the cell and/or another formula would be either impossible with respect to space group symmetry or would give (in comparison to the densities for elemental Pt and PtP_2) improbably high or low density values. The relative intensities of 759 independent reflexions were measured visually using an intensity scale on which one of the reflexions from the crystal had been recorded during measured time intervals.

DETERMINATION AND REFINEMENT OF THE CRYSTAL STRUCTURE

It was decided to use Patterson methods for solving the structure. The following preliminary considerations were then made. The symmetry in the space groups Cc and $C2/c$ shows that for the general atomic positions (x,y,z) there are Harker vectors giving maxima in the Patterson space on the line $P(0,v,\frac{1}{2})$ where $v=2y$. In addition the Patterson section $P(u,0,w)$ must contain maxima caused by Harker vectors if the structure has the symmetry $C2/c$ and has atoms lying in the general position (x,y,z) . Then $u=2x$, $w=2z+\frac{1}{2}$.

The intensity data obtained from the Weissenberg photographs were corrected for Lorentz and polarization effects and were used for calculating the Patterson function along the line $(0, v, \frac{1}{2})$ and in the section $(u, 0, w)$. The section $P(u, 0, w)$ contained a number of strong maxima, the presence of which strongly indicated $C2/c$ symmetry. This supposition was further supported by the observation that $P(0, v, \frac{1}{2})$ contained only two maxima for $v \leq 0.5$ (at $v \sim 0.24$ and $v \sim 0.5$), the second maximum being about eight times as large as the first one. Further analysis of $P(0, v, \frac{1}{2})$ and $P(u, 0, w)$ and, in addition, the section $P(u, 0.13, w)$ yielded an arrangement of the 20 platinum atoms which was wholly consistent with all strong maxima observed in the calculated parts of the Patterson function. The proposed arrangement of the platinum atoms was based on $C2/c$ symmetry with 16 atoms in two sets of 8 (f) positions and 4 atoms in one 4 (e) position.

The positions of the platinum atoms were further confirmed by three-dimensional electron density calculations. In the structure factor calculations, values for the atomic scattering factors as given in *Intern. Tables*⁵ were used. For spatial reasons, the eight phosphorus atoms in the cell must occupy one eightfold position, and their locations were finally settled by the appearance of appropriate maxima in the difference electron density maps calculated.

The structure was finally refined by the least-squares method. Weights for the reflexions were assigned according to the formula $w = 1/(a + |F_o| + c|F_o|^2)$ following a suggestion by Cruickshank.⁴ After some adjustments the constants were given the values $a = 146$ and $c = 0.0023$. After refinements of the positional parameters for the atoms, temperature factors and scale factors the R -value obtained was 0.136. This rather high value is probably an effect of the very large absorption in the crystal. (The linear absorption coefficient $\mu = 1727$). This is probably also the reason for the low values obtained for the temperature factors. (Positional parameters and temperature factors are listed in Table 2). Since the crystal had a highly irregular shape it was extremely difficult to find a geometrical description suitable for calculations of the absorption correction. An attempt was made but the result was far from satisfactory giving a higher R -value than for the uncorrected data.

While the atomic arrangement closely corresponds to $C2/c$ symmetry, minor deviations from this symmetry may still exist. Refinements by the least-squares method were therefore made on the basis of Cc symmetry using

Table 2. Final structure data for Pt₃P₂.

| Space-group $C2/c$; $Z = 4$ | | | | | | | | | |
|------------------------------|----------|---------------------------|-------------|--------|----------------------------------|--------|-------------|-------------------|-------------|
| | | $a = 10.7642 \text{ \AA}$ | | | $\sigma(a) = 0.0009 \text{ \AA}$ | | | | |
| | | $b = 5.3854 \text{ \AA}$ | | | $\sigma(b) = 0.0005 \text{ \AA}$ | | | | |
| | | $c = 7.4378 \text{ \AA}$ | | | $\sigma(c) = 0.0008 \text{ \AA}$ | | | | |
| | | $\beta = 99.170^\circ$ | | | $\sigma(\beta) = 0.009^\circ$ | | | | |
| Atom | Position | x | $\sigma(x)$ | y | $\sigma(y)$ | z | $\sigma(z)$ | $B \text{ \AA}^2$ | $\sigma(B)$ |
| Pt _I | 4(e) | — | — | 0.1087 | 0.0009 | — | — | 0.000 | 0.033 |
| Pt _{II} | 8(f) | 0.3811 | 0.0003 | 0.2274 | 0.0006 | 0.0352 | 0.0004 | 0.019 | 0.026 |
| Pt _{III} | 8(f) | 0.1437 | 0.0002 | 0.2253 | 0.0006 | 0.5912 | 0.0004 | 0.038 | 0.031 |
| P | 8(f) | 0.8396 | 0.0015 | 0.5898 | 0.0042 | 0.7287 | 0.0024 | -0.178 | 0.153 |

both the uncorrected and the absorption corrected data. However, the results indicated no significant deviations from the $C2/c$ symmetry, and the final structure of Pt_5P_2 is therefore reported with space group $C2/c$ (see Table 2).

Interatomic distances are given in Table 3. A list of observed and calculated structure factors can be obtained from this Institute on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Fig. 1 shows the structure projected along the b -axis. The calculated interatomic distances — see Table 3 — show that the Pt—Pt distances are as large as or larger than twice the Goldschmidt metal-radius and that the shortest Pt—P distances are about 0.15 Å shorter than the sum of the atomic radii. ($r_{Pt} = 1.38$ Å, $r_P = 1.10$ Å.) The fourfold platinum atoms have eight platinum neighbours and two phosphorus neighbours and the two sets of eightfold platinum atoms have seven platinum neighbours and two and three phosphorus neighbours, respectively. The phosphorus atoms have six

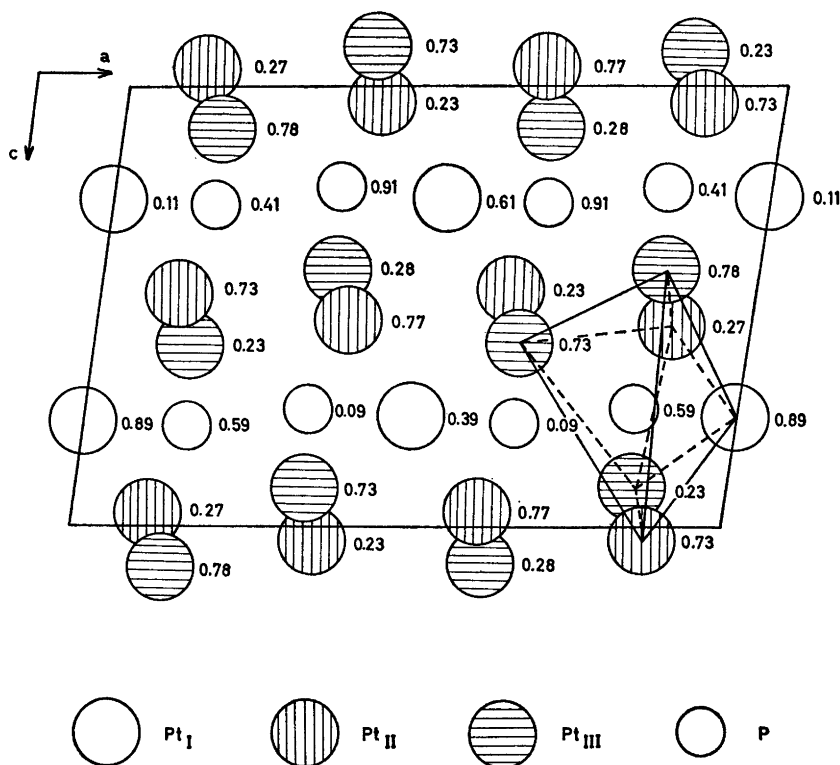


Fig. 1. The Pt_5P_2 structure projected along the b -axis. The figures to the right of the atoms are the y -parameters. The extra lines in the lower right part of the figure are explained in connection with Fig. 2.

Table 3. Interatomic distances and standard deviations (\AA units) in Pt_5P_2 . Distances shorter than 4 \AA listed.

| | Dist. | S.d. | | | | | |
|------------------|-----------------------|-------|--------------------|---------------------|---------------------|-------|-------|
| Pt _I | — 2 P | 2.356 | 0.020 | Pt _{III} | — P | 2.311 | 0.017 |
| | — 2 Pt _{III} | 2.758 | 0.004 | | — P | 2.368 | 0.021 |
| | — 2 Pt _{II} | 2.785 | 0.005 | | — P | 2.611 | 0.018 |
| | — 2 Pt _{II} | 2.789 | 0.003 | | — Pt _I | 2.758 | 0.004 |
| | — 2 Pt _{III} | 2.824 | 0.003 | | — Pt _{II} | 2.802 | 0.004 |
| | — 2 Pt _{II} | 3.826 | 0.005 | | — Pt _I | 2.824 | 0.003 |
| | — 2 P | 3.837 | 0.016 | | — Pt _{II} | 2.839 | 0.005 |
| | — 2 Pt _I | 3.899 | 0.003 | | — Pt _{II} | 2.845 | 0.004 |
| | — 2 Pt _{III} | 3.932 | 0.003 | | — Pt _{III} | 2.853 | 0.005 |
| | | | | | — Pt _{II} | 2.862 | 0.005 |
| Pt _{II} | — P | 2.322 | 0.021 | — Pt _{II} | 3.604 | 0.004 | |
| | — P | 2.371 | 0.018 | — P | 3.669 | 0.022 | |
| | — Pt _I | 2.785 | 0.005 | — Pt _{II} | 3.841 | 0.004 | |
| | — Pt _I | 2.789 | 0.003 | — Pt _I | 3.932 | 0.003 | |
| | — Pt _{II} | 2.799 | 0.006 | — Pt _{II} | 3.967 | 0.004 | |
| | — Pt _{III} | 2.802 | 0.004 | — Pt _{III} | 3.994 | 0.006 | |
| | — Pt _{III} | 2.839 | 0.005 | P | — Pt _{III} | 2.311 | 0.017 |
| | — Pt _{III} | 2.845 | 0.004 | | — Pt _{II} | 2.322 | 0.021 |
| | — Pt _{III} | 2.862 | 0.005 | | — Pt _I | 2.356 | 0.020 |
| | — P | 3.321 | 0.017 | | — Pt _{III} | 2.368 | 0.021 |
| | — P | 3.438 | 0.019 | | — Pt _{II} | 2.371 | 0.018 |
| | — Pt _{III} | 3.604 | 0.004 | | — Pt _{III} | 2.611 | 0.018 |
| | — Pt _{II} | 3.640 | 0.006 | | — Pt _{II} | 3.321 | 0.017 |
| | — P | 3.654 | 0.018 | | — 2 P | 3.357 | 0.019 |
| | — Pt _{II} | 3.762 | 0.006 | | — P | 3.416 | 0.031 |
| | — Pt _I | 3.826 | 0.005 | | — Pt _{II} | 3.438 | 0.019 |
| | — Pt _{III} | 3.841 | 0.004 | — Pt _{II} | 3.654 | 0.018 | |
| | — P | 3.913 | 0.017 | — Pt _{III} | 3.669 | 0.022 | |
| | — Pt _{III} | 3.967 | 0.004 | — Pt _I | 3.837 | 0.016 | |
| | — Pt _{II} | 3.984 | 0.006 | — 2 P | 3.843 | 0.011 | |
| — P | 3.999 | 0.022 | — Pt _{II} | 3.913 | 0.017 | | |
| | | | — Pt _{II} | 3.999 | 0.022 | | |

platinum neighbours one of which is situated at an appreciably larger distance (2.61 \AA) from the phosphorus atom than the other five (2.31–2.37 \AA). A tendency towards five-coordination is apparently indicated. A somewhat similar situation is encountered in the structure of NiP, where six nickel atoms are arranged at the corners of a very distorted triangular prism about the phosphorus atom with one Ni–P distance more than 0.6 \AA larger than the remaining five.⁷ This low coordination around the phosphorus atom in Pt_5P_2 is in agreement with the observation that phosphorus in conjunction with the platinum metals develops very short Me–P bonds and has few metal neighbours.

It is rather hard to describe the coordination of the platinum atoms around the phosphorus atoms in terms of any regular polyhedron. However, a very distorted octahedron with the phosphorus atom at the center and platinum atoms at the corners might be used. Seen parallel to the a -axis the top and bottom vertices are displaced normal to one of the sides in the central plane. One of the vertices is actually outside the plane. The central plane is not a square but has three edges of about the same length, the fourth edge being 60 % larger. In addition there is a small difference in height of the corners

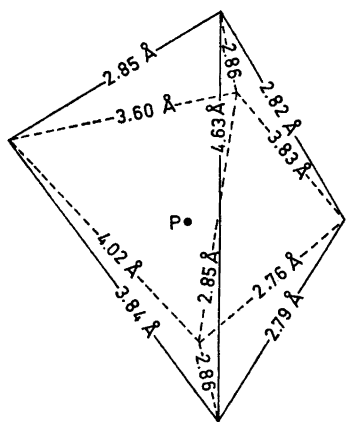


Fig. 2. Coordination octahedron seen parallel to the b -axis.

in the "plane" (0.3 Å). See further Fig. 2. The extra lines in the bottom right region in Fig. 1 show how the octahedra are placed in the structure which might be described as a complex array of such octahedra. Alternatively the structure might be described using puckered double-layers of atoms parallel to the bc -plane. Each double-layer consists of the eightfold platinum atoms and the phosphorus atoms as illustrated in Fig. 3. The fourfold platinum atoms are inserted between the double-layers. Among the six platinum neighbours of the phosphorus atom, five are placed in the double sheet and the sixth is one of the fourfold platinum atoms between the layers.

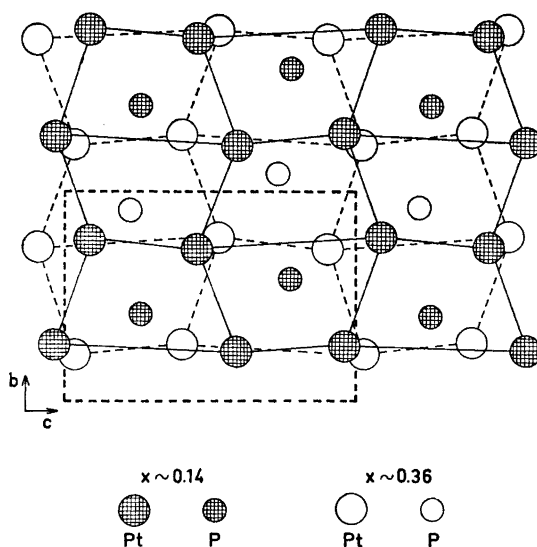


Fig. 3. Puckered double sheet in the Pt_5P_3 structure viewed along the a -axis.

Acknowledgements. I wish to thank Professor G. Hägg for all the facilities placed at my disposal. I also wish to thank Dr. S. Rundqvist for his interest in this work and for much valuable advice. The work has been supported financially by the *Swedish Natural Science Research Council*.

REFERENCES

1. Thomassen, L. *Z. physik. Chem.* **B 4** (1929) 277.
2. Biltz, W., Weibke, F., May, E. and Meisel, K. *Z. anorg. allgem. Chem.* **223** (1935) 129.
3. Rundqvist, S. *Nature* **185** (1960) 31.
4. Cruickshank, D. W. J., Philling, D. E., Bujosa, A., Lovell, F. M. and Truter, M. R. *Computing Methods and the Phase Problem*, Pergamon, Oxford 1961, p. 32.
5. *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham 1962, Vol. III.
6. Aronsson, B., Lundström, T. and Rundqvist, S. *Borides, Silicides and Phosphides*, Methuen, London 1965.
7. Larsson, E. *Arkiv Kemi* **23** (1965) 335.

Received February, 8, 1967.