# Structure of Monoclinic Black Zinc Diphosphide, ZnP₂

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**Abstract.** $M_r = 127.3$, monoclinic, $P2_1/c$, $a = 8.8668$ (4), $b = 7.2913$ (5), $c = 7.5615$ (6) Å, $\beta = 102.308$ (5)°, $V = 477.6$ Å³, $Z = 8$, $D_x = 3.541$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 112.0$ cm⁻¹, $F(000) = 480$, room temperature, final $R = 0.035$ for 2943 unique reflections. The structure of monoclinic black ZnP₂ has been redetermined and shown to be isostructural with monoclinic ZnAs₂. Zn and P are tetrahedrally coordinated and P atoms are arranged in semi-spiral chains parallel to the *c* axis. Average Zn–P and P–P bond lengths are 2.39 (4) and 2.20 (1) Å, respectively.

**Introduction.** Monoclinic black ZnP₂ and ZnAs₂ appear to be isostructural on the basis of similarity in unit-cell dimensions, space group ($P2_1/c$) and electrical and optical properties (Fleet, 1974). However, the crystal structure of black ZnP₂ is reported to contain metallic Zn–Zn bonds (Hegyi, Loebner, Poor & White, 1963) which are not observed in the ZnAs₂ structure. The Hegyi *et al.* (1963) structure for black ZnP₂ and the Fleet (1974) structure for monoclinic ZnAs₂ are related through different ordering of Zn(2) and P(1), As(1) atoms in the **b** direction. Fleet (1974) suggested that the Hegyi *et al.* (1963) structure was suspect because it was based on two-dimensional intensity data. The Zn(2) and P(1) atoms overlap in projection down the *b* and *c* axes and in *a*-axis-projection electron-density peaks associated with these atoms would tend to coalesce. With the recent synthesis of single crystals of black ZnP₂ (Mowles, 1981) and modern methods of structural analysis, this longstanding structural ambiguity is resolved in the present study.

**Experimental.** Black ZnP₂ crystals were synthesized by vapor transport at about 1223 K and $5 \times 10^5$ Pa from high-purity (99.999%) Zn and red P in a sealed silica-glass tube with excess P. The crystals are tabloid, several mm in longest dimension, and twinned, with (100) twin plane, to give a pseudo-orthorhombic unit cell with $a = c_m$, $b = 4(a_m \sin\beta)$, $c = b_m$, where $a_m$, $b_m$ and $c_m$ are the monoclinic unit-cell parameters. Crystal rhombic prismatic in shape, approximately equidimensional with calculated volume $1.9 \times 10^{-3}$ mm³, selected for data collection. It was obtained by size reduction of a larger, twinned crystal by trimming with a scalpel blade until reflections of the twin orientation were not observed by long-exposure X-ray precession photography, and final grinding with 600 abrasive paper lubricated with a light oil. Enraf–Nonius CAD-4F diffractometer, graphite-monochromatized Mo $K\alpha$ radiation. 21 reflections in $2\theta$ range 47.9–68.2° for cell parameters. Data collected by $\theta$–$2\theta$ scan. 3108 $hkl$, $h\bar{k}l$ reflections permitted by space group $P2_1/c$ out to $2\theta = 80°$ measured. Variation of standard reflections ($\bar{1}04$, $402$ and $140$) insignificant. Background, Lorentz, polarization and absorption corrections applied; transmission factors (by Gaussian integration with a $12 \times 12 \times 12$ grid) varied from 0.258 for $0\bar{2}0$ to 0.390 for $\bar{1}3,0,10$. 2943 unique reflections. 724 reflections considered unobserved $[I < 3\sigma(I)]$. Crystal structure analysis proceeded by refinement of the two proposed structures (Fleet, 1974; Hegyi *et al.*, 1963) in space group $P2_1/c$; $\sum w(\Delta F)^2$ minimized, $w = 1/\sigma^2$. Initial structural parameters for the ZnAs₂-type structure from Fleet (1974; Table 1). Refinement of the ZnAs₂-type structure using reflection data out to $2\theta = 45°$ and anisotropic thermal parameters converged to $R = 0.028$, $R_w = 0.041$, $S = 0.37$. In contrast, refinement of the Hegyi *et al.* (1963) structure with Zn(2)–Zn(2) bonds was abandoned through lack of convergence with $R = 0.27$, $R_w = 0.38$, $S = 3.0$. Refinement of the ZnAs₂-type structure using all reflection data out to $2\theta = 80°$ converged to $R = 0.035$, $R_w = 0.048$, $S = 0.45$, $(\Delta/\sigma)_{max} = 3 \times 10^{-5}$, $\Delta\rho = -1.8$ to $3.3$ e Å⁻³. Anisotropic extinction parameters for type I extinction (Coppens & Hamilton, 1970) are $G_{11} = 1.0$ (2), $G_{22} = 0.9$ (4), $G_{33} = 0.43$ (6), $G_{12} = 0.9$ (2), $G_{13} = -0.02$ (8), $G_{23} = -0.2$ (2). Scattering factors for neutral atomic species and $f'$, $f''$ taken, respectively, from Tables 2.2B and 2.3.1 of *International Tables for X-ray Crystallography* (1974). Computations carried out with *DATAP77* and *LINEX77* (State University of New York at Buffalo).

Table 1. *Positional and thermal parameters for refined structure of black* $ZnP_2$

$$B_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j B_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

| | Equi-point | $x$ | $y$ | $z$ | $B_{eq}(\text{Å}^2)$ |
|---|---|---|---|---|---|
| Zn(1) | 4(e) | 0·08054 (6) | 0·74695 (8) | 0·39391 (8) | 0·71 (2) |
| Zn(2) | 4(e) | 0·39312 (7) | 0·09647 (8) | 0·22491 (8) | 0·79 (2) |
| P(1) | 4(e) | 0·37453 (13) | 0·42724 (18) | 0·21599 (16) | 0·65 (4) |
| P(2) | 4(e) | 0·23501 (14) | 0·01970 (17) | 0·44080 (17) | 0·62 (4) |
| P(3) | 4(e) | 0·24275 (14) | 0·48480 (17) | 0·42781 (17) | 0·63 (4) |
| P(4) | 4(e) | 0·07871 (13) | 0·25654 (13) | 0·39571 (17) | 0·64 (4) |
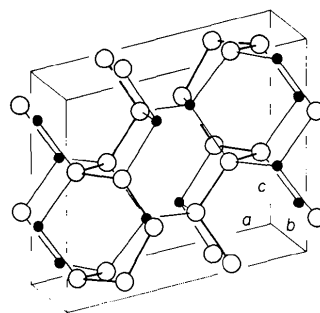


Fig. 1. Crystal structure of monoclinic black $ZnP_2$: Zn small full circles; P large circles.

Table 2. *Selected interatomic distances* (Å) *and bond angles* (°) *in black* $ZnP_2$
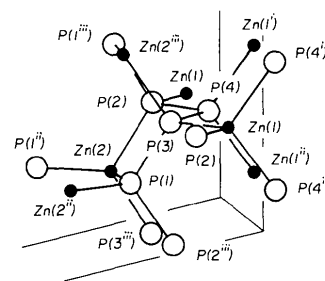
| | | | |
|---|---|---|---|
| Zn(1)–P(2)* | 2·398 (1) | Zn(2)–P(2) | 2·433 (1) |
| Zn(1)–P(3) | 2·373 (1) | Zn(2)–P(3ⁱⁱⁱ)* | 2·429 (1) |
| Zn(1)–P(4ⁱ)* | 2·342 (1) | P(1)–P(2ⁱⁱⁱ)* | 2·216 (2) |
| Zn(1)–P(4ⁱⁱ)* | 2·340 (1) | P(1)–P(3) | 2·215 (2) |
| Zn(2)–P(1) | 2·417 (1) | P(2)–P(4) | 2·195 (2) |
| Zn(2)–P(1ⁱⁱ)* | 2·361 (1) | P(3)–P(4) | 2·190 (2) |

| | | | |
|---|---|---|---|
| P(2)*–Zn(1)–P(3) | 109·76 (5) | Zn(1)*–P(2)–Zn(2) | 118·97 (5) |
| P(2)–Zn(1)–P(4ⁱ)* | 108·47 (5) | Zn(1)*–P(2)–P(1ⁱⁱⁱ) | 118·07 (6) |
| P(2)–Zn(1)–P(4ⁱⁱ)* | 108·98 (5) | Zn(1)*–P(2)–P(4) | 107·92 (6) |
| P(3)–Zn(1)–P(4ⁱ)* | 110·93 (5) | Zn(2)–P(2)–P(1ⁱⁱⁱ) | 107·68 (6) |
| P(3)–Zn(1)–P(4ⁱⁱ)* | 110·86 (5) | Zn(2)–P(2)–P(4) | 98·62 (6) |
| P(4ⁱ)*–Zn(1)–P(4ⁱⁱ)* | 107·77 (5) | P(1ⁱⁱⁱ)–P(2)–P(4) | 102·48 (7) |
| P(1)–Zn(2)–P(1ⁱⁱ)* | 125·33 (4) | Zn(1)–P(3)–Zn(2ⁱⁱⁱ) | 119·80 (6) |
| P(1)–Zn(2)–P(2) | 101·69 (4) | Zn(1)–P(3)–P(1) | 118·40 (6) |
| P(1)–Zn(2)–P(3ⁱⁱⁱ)* | 101·35 (5) | Zn(1)–P(3)–P(4) | 103·14 (6) |
| P(1ⁱⁱ)*–Zn(2)–P(2) | 110·92 (5) | Zn(2ⁱⁱⁱ)–P(3)–P(1) | 110·64 (6) |
| P(1ⁱⁱ)*–Zn(2)–P(3ⁱⁱⁱ)* | 109·41 (5) | Zn(2ⁱⁱⁱ)–P(3)–P(4) | 97·92 (6) |
| P(2)–Zn(2)–P(3ⁱⁱⁱ)* | 106·46 (5) | P(1)–P(3)–P(4) | 102·49 (7) |
| Zn(2)–P(1)–Zn(2ⁱⁱ) | 117·68 (5) | Zn(1ⁱ)*–P(4)–Zn(1ⁱⁱ)* | 107·73 (5) |
| Zn(2)–P(1)–P(2ⁱⁱⁱ)* | 102·79 (6) | Zn(1ⁱ)*–P(4)–P(2) | 109·76 (6) |
| Zn(2)–P(1)–P(3) | 102·25 (6) | Zn(1ⁱ)*–P(4)–P(3) | 114·55 (6) |
| Zn(2ⁱⁱ)–P(1)–P(2ⁱⁱⁱ)* | 112·11 (6) | Zn(1ⁱⁱ)*–P(4)–P(2) | 110·91 (6) |
| Zn(2ⁱⁱ)–P(1)–P(3) | 109·74 (6) | Zn(1ⁱⁱ)*–P(4)–P(3) | 112·37 (6) |
| P(2ⁱⁱⁱ)*–P(1)–P(3) | 111·77 (7) | P(2)–P(4)–P(3) | 101·44 (7) |

Symmetry code: (i) $-x,\ -y,\ -z$; (ii) $-x,\ \tfrac{1}{2} + y,\ \tfrac{1}{2} - z$; (iii) $x,\ \tfrac{1}{2} - y,\ \tfrac{1}{2} + z$; (*) in adjacent unit cell; see Fig. 2.



Fig. 2. Zn and P environments in black $ZnP_2$.

**Discussion.** Positional parameters are given in Table 1 and selected interatomic distances and bond angles are given in Table 2.*

The present study confirms the suggestion of Fleet (1974) that monoclinic black $ZnP_2$ has the monoclinic $ZnAs_2$-type structure, and also reaffirms the monoclinic $ZnAs_2$ structure itself. Although the assignment of the structure without Zn–Zn bonds to monoclinic $ZnAs_2$ was statistically significant, the similar X-ray scattering efficiencies of Zn and As resulted in similar $R$ values for refinements of the two alternative structures. There is good scattering contrast between Zn and P and the present structural assignment for black $ZnP_2$ is quite unambiguous.

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* Tables of anisotropic thermal parameters and structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39606 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

In the black $ZnP_2$ structure, each Zn position is tetrahedrally coordinated to four P and each P is tetrahedrally coordinated to two Zn and two P (Figs. 1 and 2). The P atoms are arranged in semi-spiral chains oriented parallel to the $c$ axis and interconnected by Zn atoms. Tetragonal red $ZnP_2$ has a similar crystal structure (Hegyi et al., 1963), with the same Zn and P nearest-neighbor coordinations and P atoms arranged in chains normal to the $c$ axis. The average Zn–P and P–P bond lengths in black $ZnP_2$ [2·39 (4) and 2·20 (1) Å, respectively] are very similar to the equivalent data for tetragonal red $ZnP_2$ (2·40 and 2·19 Å, respectively) and are in reasonably good agreement with theoretical values for covalent bonding (2·36 and 2·26 Å, respectively; Van Vechten & Phillips, 1970).

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