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Structure of the Occupationally Disordered Crystal of Diphosphorus Diarsenic Trisulfide

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Abstract. $P_2As_2S_3$, $M_r = 308{\cdot}0$, orthorhombic, *Pnma*, $a = 10{\cdot}976\ (2)$, $b = 9{\cdot}930\ (3)$, $c = 6{\cdot}582\ (2)$ Å, $V = 717{\cdot}4$ Å^3, $Z = 4$, $D_x = 2{\cdot}85$ g cm^{-3}, $\lambda(\text{Mo } K\bar{\alpha}) = 0{\cdot}71069$ Å, $\mu = 110$ cm^{-1}, $F(000) = 576$, $T = 298$ K, $R = 0{\cdot}028$ for 565 observed reflections. The structure is isomorphous with that of β-As_4S_3 (β-dimorphite) and contains cage-like $P_2As_2S_3$ molecules with crystallographic mirror symmetry and P and As atoms disordered at both the apical and the basal positions. P shows a preference for the apical site which is 81% P. The basal positions contain 43% and 35% (× 2) P.

Introduction. The compound As_4S_4 and 1:1 As:Se fused mixtures on oxidation with the Lewis acids AsF_5 and SbF_5 give the novel cations $As_3S_4^+$ and $As_3Se_4^+$ (Christian, Gillespie & Sawyer, 1981). In extending this work to the oxidation of the sulfides and selenides of P some investigations were carried out on the preparation of the starting materials. In particular, the preparation of a compound formulated as $P_2As_2S_3$ from a P_4S_3/As_2S_3 melt has been previously reported (Levia, Fluck, Müller & Wallenwein, 1974). In the present work crystals of this compound obtained by vacuum sublimation of P:As:S melts of composition 1:3:3, 2:2:3 or 1:3:4 had the same Raman spectra as those previously reported.

Experimental. The pale-yellow crystals used in the X-ray analysis were grown by vacuum sublimation of the 2:2:3 melt at ~673 K. Many crystals not single. Single crystal eventually found which approximated to a pentagonal plate bound by the form $\{100\}$ and the faces $(00\bar{1})$, $(\bar{1}01)$, (101), $(0\bar{1}0)$ and $(05\bar{1})$ which were 0·1125, 0·1125, 0·1125, 0·1125, 0·0875 and 0·0875 mm from an origin within the crystal. Unit-cell dimensions by least-squares refinement of 2θ, ω and χ for 15 reflections ($27 < 2\theta < 33°$) on a Syntex $P2_1$ diffractometer using graphite-monochromatized Mo $K\bar{\alpha}$ radiation. Intensity data collected in the θ:2θ mode with reflection scan ranges of ($K\alpha_1$ −0·9°) to ($K\alpha_2$ +0·9°) and variable scan rates of 3·0–29·3° min^{-1} (dependent on the intensity of a prescan). Intensities of three standard reflections monitored every 67 reflections collected showed only statistical variations. All 3102 reflections in quadrants (h, $\pm k$, $\pm l$) with $2\theta < 55°$ were measured and corrected for Lorentz and polarization effects. Reflections with negative intensities rejected. Absorption corrections using the program *ABSORB* (*XRAY*76, Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976). Symmetry-related intensities, expected to be identical, averaged.

Comparison of the measured unit-cell parameters with those of other Group V*b* chalconides suggested that the structure was isomorphous with that of β-As_4S_3 (β-dimorphite) (Whitfield, 1970). Thus in the assumed centrosymmetric space group *Pnma* the $P_2As_2S_3$ molecule has crystallographic mirror symmetry. Initially coordinates and atomic assignments from β-dimorphite used in the least-squares refinements. Resulting isotropic temperature factors did not enable the P atoms to be located. When the P scattering curve was used instead of that for As the resulting temperature factors were too low and it was concluded that there was As/P disorder at the apical and basal positions of the As_4S_3 structure of the present molecule. Further refinement of the anisotropic thermal parameters of all atoms and of the population parameters of the apical and basal positions in the structure improved the crystallographic residual and showed the extent of the disorder in the structure. The resulting population parameters were consistent with an overall formula for the molecule of $P_{2.0}As_{2.0}S_3$ (Table 1). Single-crystal Raman spectra and ^{31}P NMR investigations recorded at this point indicated that other members of the series $P_xAs_{4-x}S_3$ ($x = 0$–4) were present in the initial melts (Christian, Gillespie & Schrobilgen, unpublished data). Above population parameters used to compile composite scattering curves for the apical and basal sites $A(1,2,3)$ of the form $f_A = af_{As} + (1-a)f_P$ where a = percentage As at each site $A(1,2,3)$. The structural and population parameters of these pseudo-atoms as well as those of the S atoms then simultaneously refined using the least-squares routines in *XRAY*76. Refinement minimizing $\sum w\|F_o| - |F_c\|^2$ then converged (max. $\Delta/\sigma < 10\%$) to the final residuals $R = 0{\cdot}028$ and $wR = 0{\cdot}035$ for 565 observed [$I > 3\sigma(I)$] reflections. A structure-factor calculation using all 864 non-zero data gave $R = 0{\cdot}056$ ($wR = 0{\cdot}051$). Weights: $w^{-1} = 4\sigma^2(F) + 0{\cdot}0035F^2$. The final distribution of $\langle w\Delta F^2\rangle$ as a function of F_o and $\sin\theta$ after the use of this scheme showed no systematic trends and a final difference Fourier map was featureless with no

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residual peaks $> \pm 0{\cdot}8$ e Å^{-3}. Computer programs: *XRAY76* and *SHELX76* (Sheldrick, 1976) on a CDC 6400 computer. The final atomic positional and population parameters are included in Table 1 and bond lengths and bond angles in P_4S_3, $P_2As_2S_3$ and As_4S_3 are given in Table 2.* Atom numbering is shown in Fig. 1.

Discussion. Crystals of '$P_2As_2S_3$' are isomorphous with those of *β*-dimorphite, As_4S_3 (Whitfield, 1970), although the averaged molecule of $P_2As_2S_3$, which has crystallographic mirror symmetry, is not ordered in the lattice and all the As sites in As_4S_3 are partially occupied by P atoms giving an overall composition of $P_{2.02(4)}As_{1.98(4)}S_3$ (Table 1). P shows a preference for the apical position which is consistent with the observation that the ^{31}P NMR spectra of P/As/S melt extracts show a greater proportion of molecules $P_xAs_{4-x}S_3$ ($x = 0$–4) with P in the apical position (Christian, Gillespie & Schrobilgen, unpublished data). Average bond lengths and bond angles in $P_2As_2S_3$ are compared to those in P_4S_3 (Leung, Waser, van Houten, Vos, Wiegers & Wiebenga, 1957) and in α- and *β*-As_4S_3 (Whitfield, 1970, 1973) in Table 2. Table 3 shows that the agreement between the observed bond lengths in $P_2As_2S_3$ and bond lengths predicted using the compositions of the *A*(1,2,3) sites and comparable averaged As–S, P–S, As–As and P–P distances in As_4S_3 and P_4S_3 is reasonably good (to within 0·02 Å). The agreement for the basal bond lengths (which does not consider any As–P distances) is slightly better using the basal bond lengths in the isostructural anions As_7^{3-} and P_7^{3-} [2·498 and 2·25 Å, respectively, e.s.d.'s not given (Dahlmann & von Schnering, 1972; Schmettow & von Schnering, 1977)]. For comparison, the As–As and As–S bond lengths in the isostructural $As_3S_4^+$ cation are 2·461 (2) (As–As), 2·223 (2) and 2·249 (4)

Table 1. *Final atomic positional* (× 10⁴), *site population and equivalent isotropic thermal parameters* (× 10³) *for* $P_2As_2S_3$ *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	A(1)	*A*(2)	*A*(3)	S(1)	S(2)
x	6796 (1)	4145 (1)	5689 (1)	6994 (1)	4880 (2)
y	2500	2500	1279 (1)	865 (1)	2500
z	1699 (2)	−1026 (2)	−2802 (1)	−355 (2)	2072 (3)
%As(*a*)*	19 [13 (1)]	57 [59 (1)]	65 [67 (1)]	–	–
%P(1−*a*)	81 [87 (1)]	43 [41 (1)]	35 [33 (1)]	–	–
PP†	0·940 (8)	1·020 (7)	1·013 (6)	–	–
U_{eq}(Å²)	43·8 (11)	41·0 (6)	43·6 (4)	49·1 (9)	44·2 (11)

* Values in square brackets represent the final compositions of sites *A*(1), *A*(2) and *A*(3). Overall composition of the average molecule is $P_{2.02(4)}As_{1.98(4)}S_3$.

† Population parameters are for pseudo-atoms *A*(1), *A*(2) and *A*(3) with scattering curves given by $f_{A(n)} = af_{As} + (1-a)f_P$ where f_{As} and f_P are the scattering curves for neutral As and P.

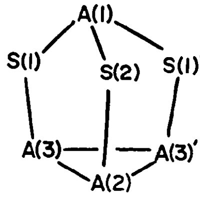

Fig. 1. The numbering of the atoms.

Table 2. *Bond lengths* (Å) *and bond angles* (°) *in* $P_2As_2S_3$ *and some related molecules*

	α-$As_4S_3^a$	*β*-$As_4S_3^b$	$P_2As_2S_3^c$	P_4S_3 (2 independent molecules)^d	
Bond lengths					
A(1)–S(1)	2·220 (9)	2·230 (8)	2·124 (2)	2·096	2·087
A(1)–S(2)	2·216 (11)	2·234 (16)	2·117 (2)	2·091	2·070
A(2)–S(2)	2·213 (12)	2·221 (12)	2·193 (2)	2·097	2·092
A(2)–*A*(3)	2·445 (6)	2·460 (7)	2·390 (1)	2·246	2·223
A(3)–*A*(3)	2·450 (10)	2·480 (7)	2·426 (1)	2·240	2·232
A(3)–S(1)	2·200 (8)	2·218 (10)	2·194 (2)	2·089	2·095
					σ ~ 0·01
Bond angles					
S(2)–*A*(1)–S(1)	97·8 (3)	98·8 (4)	100·11 (7)	99·6	99·7
S(1)–*A*(1)–S(1′)	98·0 (5)	98·3 (5)	99·73 (9)	98·8	99·5
A(1)–S(1)–*A*(3)	105·7 (3)	105·0 (4)	104·90 (7)	103·3	102·7
A(1)–S(2)–*A*(2)	106·1 (4)	105·4 (5)	104·92 (9)	103·0	102·7
S(2)–*A*(2)–*A*(3)	101·1 (3)	102·8 (3)	101·19 (6)	103·2	103·3
A(3)–*A*(2)–*A*(3′)	60·2 (2)	60·5 (2)	61·01 (4)	59·8	60·3
S(1)–*A*(3)–*A*(2)	102·4 (3)	101·4 (4)	101·48 (5)	103·0	103·1
S(1)–*A*(3)–*A*(3′)	101·8 (3)	101·6 (2)	100·80 (5)	103·0	103·2
A(2)–*A*(3)–*A*(3′)	59·9 (1)	59·7 (1)	59·50 (3)	60·1	59·9
					σ ~ 0·5

References: (*a*) α-As_4S_3 (α-dimorphite), space group *Pnma*, $a = 9{\cdot}12$, $b = 7{\cdot}99$, $c = 10{\cdot}10$ Å (Whitfield, 1970). (*b*) *β*-As_4S_3 (*β*-dimorphite), space group *Pnma*, $a = 11{\cdot}21$ (2), $b = 9{\cdot}90$ (2), $c = 6{\cdot}58$ (1) Å (Whitfield, 1973). (*c*) This work, space group *Pnma*, $a = 10{\cdot}976$ (2), $b = 9{\cdot}930$ (3), $c = 6{\cdot}582$ (2) Å. (*d*) P_4S_3, space group *Pmnb*, $a = 9{\cdot}660$, $b = 10{\cdot}597$, $c = 13{\cdot}671$ Å (Leung *et al.*, 1957).

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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 43266 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Observed and predicted bond lengths* (Å) *in* $P_2As_2S_3$

Averaged As—S, P—S, As—As and P—P distances for α- and β-As_4S_3 and P_4S_3 in Table 2 and relative compositions for the sites *A*(1,2,3) from Table 1 are used.

Bond	Predicted bond length (e.s.d.'s *ca* 0·01 Å)	Observed
A(1)—S(1)	0·19 (2·225) + 0·81 (2·086)	
A(1)—S(2)	= 2·112	2·120
A(2)—S(2)	0·57 (2·217) + 0·43 (2·095)	
	= 2·165	2·193
A(3)—S(1)	0·65 (2·209) + 0·35 (2·092)	
	= 2·168	2·194
A(2)—*A*(3)	0·61 (As—As) + 0·39 (P—P)	
	0·61 (2·452) + 0·39 (2·235)	
	= 2·367	
	[0·61 (2·498) + 0·39 (2·25)	
	= 2·401]*	2·390
A(3)—*A*(3′)	0·65 (As—As) + 0·35 (P—P)	
	0·65 (2·465) + 0·35 (2·236)	
	= 2·385	
	[0·65 (2·498) + 0·35 (2·25)	
	= 2·411]*	2·426

* Using As—As and P—P distances in As_7^{3-} and P_7^{3-}.

(As_{apex}—S_{bridge}) and 2·173 (3) Å (As_{base}—S_{bridge}) (Christian *et al.*, 1981). No similar trends in the average bond angles in $P_2As_2S_3$ are observed and it is notable that bond angles in the apex of $P_2As_2S_3$ are slightly larger [99·7 (1)°] than those in either P_4S_3 or As_4S_3, while the angles in the base are generally smaller than expected. The crystal packing is the same as that of β-dimorphite.

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Electron-Density Distribution in Crystals of Ammonium Tetrachlorozincate(II) Chloride at 120 K

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Abstract. $[NH_4]_3[ZnCl_4]Cl$, $M_r = 296·76$, orthorhombic, *Pnma*, $a = 8·6597\ (9)$, $b = 9·8307\ (6)$, $c = 12·4588\ (7)$ Å, $V = 1060·6\ (1)$ Å^3, $Z = 4$, $D_x = 1·86$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha_1) = 0·70930$ Å, $\mu = 3·59$ mm^{-1}, $F(000) = 592$, $T = 120\ (1)$ K, $R = 0·042$ for 2456 observed unique reflections up to $\sin\theta/\lambda = 0·91$ Å^{-1}. The Zn^{2+} ion is surrounded tetrahedrally by Cl^- ions with mean Zn—Cl bond distance 2·2613 (7) Å. The charge distribution around the Zn^{2+} ion is slightly aspherical. In the deformation density there is a trough of −0·42 (7) e Å^{-3} on the Zn—Cl bond axis at 0·4 Å from the Zn nucleus and a peak of 0·29 (10) e Å^{-3} on the bisector of the Cl—Zn—Cl angle and at 0·7 Å from the Zn atom. This asphericity suggests that the 3*d* shell of the Zn^{2+} ion is not closed and the electronic configuration can be expressed as $(3d\text{: } e^4t_2^{6-x})(4s)^x$, $0 < x < 2$.

Introduction. Simple crystal field theory tells us that the charge distribution around the Zn^{2+} ion will be spherical because of fully occupied 3*d* orbitals. Recently Sakabe, Sasaki & Sakabe (1984) detected a charge asphericity around the Zn atom in 2Zn insulin. To reveal the origin of the asphericity, several examinations should be performed for small molecules with high symmetry. The title complex was selected first, because the tetrahedral environment is suitable to distinguish the aspherical charge distribution of the non-bonding *d*

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