

$wR = 0.027$
 $S = 1.004$
 1175 reflections
 71 parameters
 $w = F \sin(\theta/\lambda)$
 $(\Delta/\sigma)_{\max} = 0.004$

$\Delta\rho_{\min} = -1.1 \text{ e } \text{\AA}^{-3}$
 Extinction correction: none
 Atomic scattering factors
 from *International Tables*
 for X-ray Crystallography
 (1974, Vol. IV)

Symmetry codes: (i) $x, y, \frac{1}{2} - z$; (ii) $y, y - x, -\frac{1}{2} + z$; (iii) $x - y, x, -\frac{1}{2} + z$; (iv) $-x + y, -x, \frac{1}{2} - z$; (v) $y, x, \frac{1}{2} - z$; (vi) $-x + y, -x, z$; (vii) y, x, z ; (viii) $1 - y, 1 - y + x, \frac{1}{2} - z$; (ix) $-x + y, 1 - x, \frac{1}{2} - z$; (x) $1 - y, 1 - x, -\frac{1}{2} + z$; (xi) $x, 1 + x - y, -\frac{1}{2} + z$; (xii) $-x + y, y, -\frac{1}{2} + z$; (xiii) $1 - y, 1 + x - y, z$; (xiv) $-x + y, 1 - x, z$; (xv) $1 - y, x - y, z$; (xvi) $1 - x + y, -x, z$; (xvii) $1 - x, -y, \frac{1}{2} + z$; (xviii) $1 - x, -x + y, z$; (xix) $1 - y, -y + x, \frac{1}{2} - z$; (xx) $1 - x, -x + y, \frac{1}{2} - z$; (xxi) $1 - x, -y, 1 - z$.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$B_{\text{eq}} = (4/3) \sum_i \sum_j \beta_{ij} a_i \cdot a_j$$

	x	y	z	B_{eq}
Nb(1)	0.24520 (7)	0.0	0.04437 (2)	0.579 (9)
Nb(2)	0.23777 (6)	0.0	0.18222 (2)	0.715 (8)
Nb(3)	1/3	2/3	0.0	0.79 (1)
Si	1/3	2/3	0.19176 (7)	0.37 (2)
K(1)	0.5924 (2)	0.0	0.10739 (6)	1.29 (3)
K/Ca	0.6018 (6)	0.0	0.25	1.15 (9)
O(1)	0.2172 (5)	0.0	0.1106 (2)	0.89 (9)
O(2)	0.2752 (8)	0.0	0.25	0.9 (1)
O(3)	0.1973 (5)	0.0	0.5328 (2)	0.69 (9)
O(4)	0.1744 (5)	0.0	0.6862 (2)	0.55 (8)
O(5)	1/3	2/3	0.25	1.4 (1)
O(6)	0.1817 (4)	0.4856 (4)	0.1731 (1)	0.74 (6)
O(7)	0.1684 (4)	0.4815 (4)	0.4584 (1)	0.88 (6)

Table 2. Distances (\AA) angles ($^\circ$) in the NbO_6SiO_4 and BiO_4 polyhedra and main K—O and K/Ca—O distances (\AA)

The Nb—O(*i*) or Si—O(*i*) are on the diagonal, above it are the O(*i*)—O(*j*) distances and under it are O(*i*)—Nb—O(*j*) or O(*i*)—P—O(*j*) angles.

Nb(1)	O(1)	O(3 ⁱ)	O(3 ⁱⁱ)	O(3 ⁱⁱⁱ)	O(7 ^{iv})	O(7 ^v)
O(1)	1.863 (5)	4.001 (8)	2.872 (5)	2.872 (5)	2.846 (6)	2.846 (6)
O(3 ⁱ)	160.8 (2)	2.194 (5)	2.554 (8)	2.554 (8)	3.051 (6)	3.051 (6)
O(3 ⁱⁱ)	93.9 (2)	73.7 (2)	2.062 (1)	3.09 (1)	2.723 (5)	3.946 (8)
O(3 ⁱⁱⁱ)	93.9 (2)	73.7 (2)	97.1 (2)	2.062 (2)	3.946 (8)	2.723 (5)
O(7 ^{iv})	98.0 (2)	95.9 (2)	86.5 (2)	167.3 (2)	1.908 (4)	2.638 (7)
O(7 ^v)	98.0 (2)	95.9 (2)	167.3 (2)	86.5 (2)	87.5 (2)	1.908 (4)
Nb(2)	O(1)	O(2)	O(4 ⁱⁱ)	O(4 ⁱⁱⁱ)	O(6 ^{iv})	O(6 ^v)
O(1)	2.006 (5)	3.923 (8)	2.774 (6)	2.774 (6)	2.766 (6)	2.766 (6)
O(2)	175.2 (3)	1.920 (2)	2.815 (6)	2.815 (6)	2.791 (5)	2.791 (5)
O(4 ⁱⁱ)	89.5 (2)	93.9 (2)	1.932 (1)	2.733 (8)	2.807 (5)	3.957 (8)
O(4 ⁱⁱⁱ)	89.5 (2)	93.9 (2)	90.0 (3)	1.932 (1)	3.957 (8)	2.807 (5)
O(6 ^{iv})	86.6 (2)	90.0 (2)	90.3 (2)	176.1 (2)	2.027 (4)	2.847 (8)
O(6 ^v)	86.6 (2)	90.0 (2)	176.1 (2)	90.3 (2)	89.2 (2)	2.027 (4)
Nb(3)	O(7)	O(7 ⁱⁱⁱ)	O(7 ^{iv})	O(7 ^v)	O(7 ^{vi})	O(7 ^{vii})
O(7)	1.969 (4)	2.756 (7)	2.756 (7)	3.925 (8)	2.970 (7)	2.663 (7)
O(7 ⁱⁱⁱ)	88.9 (2)	1.969 (4)	2.756 (7)	2.663 (7)	3.925 (8)	2.970 (7)
O(7 ^{iv})	88.9 (2)	88.9 (2)	1.969 (4)	2.970 (7)	2.663 (7)	3.925 (8)
O(7 ^v)	170.8 (2)	85.1 (2)	97.9 (2)	1.969 (4)	2.756 (7)	2.756 (7)
O(7 ^{vi})	97.9 (2)	170.8 (2)	85.1 (2)	88.9 (2)	1.969 (4)	2.756 (7)
O(7 ^{vii})	85.1 (2)	97.9 (2)	170.8 (2)	88.9 (2)	88.9 (2)	1.969 (4)
Si	O(5)	O(6)	O(6 ⁱⁱⁱⁱ)	O(6 ^{vii})		
O(5)	1.624 (2)	2.629 (3)	2.629 (3)	2.629 (3)		
O(6)	108.8 (1)	1.608 (4)	2.637 (7)	2.637 (7)		
O(6 ⁱⁱⁱⁱ)	108.8 (1)	110.1 (1)	1.608 (4)	2.637 (7)		
O(6 ^{vii})	108.8 (1)	110.1 (1)	110.1 (1)	1.608 (4)		
K(1)—O(1 ⁱⁱ)	3.197 (2)	K/Ca—O(2)	2.956 (1)			
K(1)—O(1 ⁱⁱⁱ)	3.197 (2)	K/Ca—O(2 ⁱⁱ)	3.194 (5)			
K(1)—O(3 ⁱⁱⁱⁱ)	2.819 (6)	K/Ca—O(2 ⁱⁱⁱ)	3.194 (5)			
K(1)—O(4 ^{vii})	3.046 (5)	K/Ca—O(4 ^{vii})	2.695 (7)			
K(1)—O(6 ^{viii})	3.079 (4)	K/Ca—O(4 ^{viii})	2.695 (7)			
K(1)—O(6 ^{ix})	2.930 (4)	K/Ca—O(5 ^{ix})	2.769 (2)			
K(1)—O(6 ^x)	2.930 (4)	K/Ca—O(5 ^x)	2.769 (2)			
K(1)—O(6 ^{xi})	3.079 (4)	K/Ca—O(6 ^{xi})	3.256 (4)			
K(1)—O(7 ^{xii})	3.154 (4)	K/Ca—O(6 ^{xii})	3.182 (5)			
K(1)—O(7 ^{xiii})	2.867 (4)	K/Ca—O(6 ^{xiii})	3.182 (5)			
K(1)—O(7 ^{xiv})	2.867 (4)	K/Ca—O(6 ^{xiv})	3.256 (4)			
K(1)—O(7 ^{xv})	3.154 (4)	K/Ca—O(6 ^{xv})	3.256 (4)			
		K/Ca—O(6 ^{xvi})	3.182 (5)			
		K/Ca—O(6 ^{xvii})	3.182 (5)			
		K/Ca—O(6 ^{xviii})	3.256 (4)			

Calculations were performed on a MicroVAX II computer using the SDP system (B. A. Frenz & Associates, Inc., 1982). The θ -scan width was $(1.00 + 0.35 \tan\theta)^\circ$ with a ω -4/3 θ scan. The figure was drawn using STRUPLO84 (Fischer, 1985).

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55663 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1008]

References

- B. A. Frenz & Associates, Inc. (1982). *SDP Structure Determination Package*. College Station, Texas, USA.
 Birkett, D. P., Wiseman, P. J. & Goodenough, J. B. (1981). *J. Solid State Chem.* **37**, 6–15.
 Choynet, J., N'Guyen, N., Groult, D. & Raveau, B. (1976). *Mat. Res. Bull.* **11**, 887–894.
 Evans, D. M. & Katz, L. (1973). *J. Solid. State Chem.* **8**, 150–158.
 Fischer, R. X. (1985). *J. Appl. Cryst.* **18**, 258–262.
 Groult, D., Chailleux, J. M., Choynet, J. & Raveau, B. (1976). *J. Solid State Chem.* **19**, 235–244.
 Shannon, J. R. & Katz, L. (1970). *Acta Cryst.* **B26**, 105–109.

Acta Cryst. (1993). **C49**, 571–573

Redetermination of the Structure of α -Tetraphosphorus Trisulfide Diiodide at 180 K

BRUCE W. TATTERSHALL, NIGEL L. KENDALL, ANDREW McCAMLEY AND WILLIAM CLEGG*

Department of Chemistry, University of Newcastle, Newcastle upon Tyne NE1 7RU, England

(Received 4 June 1992; accepted 27 October 1992)

Abstract

Redetermination of the structure of the title compound from data collected at 180 K gives considerably improved precision. The two independent molecules in the asymmetric unit are practically identical and have essentially C_2 symmetry unaffected by crystal packing. The greatest difference between the two molecules is in the 'book angles' between the fused five-membered rings; this is in accordance with chemical-shift variations observed in ^{31}P NMR spectra for this and related compounds.

Comment

Only one form of the most stable phosphorus sulfide iodide, α - $P_4S_3I_2$, is known in solution where it exists as discrete molecules shown by ^{31}P NMR to have C_2 symmetry. Two crystalline forms have been reported. The first (space group $P\bar{1}$) was obtained by controlled evaporation of the solvent from a solution in CS_2 at room temperature and contained two independent molecules in the asymmetric unit with C_2 molecular symmetry not crystallographically imposed (Wright & Penfold, 1959). The structure determination was of insufficient precision for the details of the molecular geometry and its distortion from exact C_2 symmetry to be explored. A recent study of the temperature dependence of the Raman spectrum of this crystalline form (Rollo & Burns, 1989) showed 'behaviour typical of a molecular solid' with only weak intra-intermolecular coupling. The second crystalline form, designated α' - $P_4S_3I_2$ and with space group $I\bar{4}2d$, was obtained along with the $P\bar{1}$ form when a solution in CS_2 was cooled to 250 K (Blachnik, Kurz & Wickel, 1984). The isomorphous α' - $P_4Se_3I_2$ contained molecules with their C_2 axes coincident with the crystallographic z axis, but for the sulfide, only unit-cell parameters were published.

Changes in NMR coupling constants and chemical shifts with chalcogen substitution for phosphorus chalcogenide cage molecules in solution depend mainly on small changes in molecular geometry (Tattershall, Blachnik & Baldus, 1989); further rationalization of NMR parameters for α - $P_4E_3I_2$ ($E = S, Se$; Blachnik, Loennecke & Tattershall, 1992) would benefit from a greater ability to predict accurate bond angles in solute α - $P_4S_3I_2$ as a result of more precise crystal structure data, which we present here.

Our results show that the previous structure determination was essentially correct, but we now have sufficient precision to draw further conclusions. Crystal packing appears not to distort the molecules significantly as the bond lengths and angles in the two independent molecules in the asymmetric unit are practically identical and the molecular symmetry is essentially C_2 . The bond angles showing the greatest differences between the two molecules are the 'book angles' between the two five-membered rings [e.g. P12—P14—S11 94.03(12) versus P22—P24—S21 92.91(11)°]. These angles are probably controlled, *inter alia*, by a balance of the interactions between corresponding P and S atoms in the five-membered rings [e.g. P11 and S12, which at a distance of 3.157(5) Å are within the sum of their van der Waals radii] and the interactions between the I and bridging S atoms [e.g. I11 and S13, at 3.877(5) Å just beyond the sum of their van der Waals radii]. Variation of these angles with exocyclic substitution is probably largely responsible for the wide range of ^{31}P NMR bridgehead chemical shifts and bridgehead-bridgehead 2J coupling constants observed for α - $P_4S_3R_2$ derivatives (Tattershall, 1987, 1991).

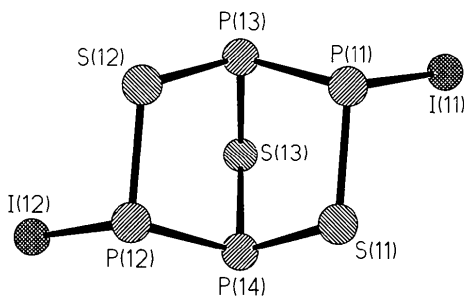


Fig. 1. View of one of the independent molecules of α - $P_4S_3I_2$ showing the labelling of the atoms. The second molecule follows an analogous scheme.

Experimental

Crystal data

$P_4S_3I_2$
 $M_r = 473.86$
 Triclinic
 $P\bar{1}$
 $a = 7.268$ (4) Å
 $b = 7.342$ (4) Å
 $c = 19.553$ (11) Å
 $\alpha = 94.43$ (6)°
 $\beta = 90.31$ (6)°
 $\gamma = 90.90$ (6)°
 $V = 1040.1$ (10) Å³
 $Z = 4$

$D_x = 3.026$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 32 reflections
 $\theta = 11.46$ – 12.43 °
 $\mu = 7.190$ mm⁻¹
 $T = 180.0$ (5) K
 Block crystal
 $0.70 \times 0.40 \times 0.36$ mm
 Yellow

Data collection

Stoe–Siemens diffractometer
 ω/θ scans, on-line profile fitting (Clegg, 1981)
 Absorption correction: empirical
 $T_{min} = 0.012$, $T_{max} = 0.048$
 3646 measured reflections
 3646 independent reflections

3523 observed reflections
 $[I > 2\sigma(I)]$
 $\theta_{max} = 25.01$ °
 $h = -8 \rightarrow 8$
 $k = -8 \rightarrow 8$
 $l = 0 \rightarrow 23$
 5 standard reflections
 frequency: 60 min
 intensity variation: none

Refinement

Refinement on F^2
 Final $R = 0.0403$
 $R(\text{obs.}) = 0.0393$
 $wR = 0.1114$
 $S = 1.238$
 3646 reflections
 164 parameters
 Calculated weights
 $w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 4.9236P]$ where
 $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 1.58$ e Å⁻³
 $\Delta\rho_{min} = -1.41$ e Å⁻³
 Extinction correction: SHELXL92 (Sheldrick, 1992)
 Extinction coefficient: 0.0116 (6)
 Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Refinement on F^2 for all reflections except those flagged for possible systematic errors; the observed threshold $I > 2\sigma(I)$ is used only for calculating $R(\text{obs.})$ given here for comparison with refinements on F .

Data collection: Stoe *DIF4*. Cell refinement: Stoe *DIF4*. Data reduction: local programs. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL92*. Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: local programs.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
I11	0.60757 (7)	0.95391 (7)	0.59843 (2)	0.0355 (3)
I12	-0.10433 (7)	0.28859 (8)	0.70853 (3)	0.0416 (3)
P11	0.3948 (3)	0.7214 (3)	0.54224 (9)	0.0300 (9)
P12	-0.0356 (3)	0.4498 (3)	0.60488 (10)	0.0336 (9)
P13	0.4298 (3)	0.5181 (3)	0.61856 (10)	0.0326 (9)
P14	0.0487 (3)	0.7136 (3)	0.65868 (10)	0.0328 (9)
S11	0.1336 (2)	0.8301 (3)	0.56735 (10)	0.0339 (9)
S12	0.2200 (3)	0.3403 (3)	0.57317 (11)	0.0396 (10)
S13	0.2974 (3)	0.6468 (3)	0.70389 (9)	0.0341 (10)
I21	0.92987 (7)	0.42035 (6)	0.09946 (2)	0.0345 (3)
I22	0.24888 (7)	1.15486 (7)	0.20126 (2)	0.0348 (3)
P21	0.7128 (3)	0.6192 (3)	0.04305 (10)	0.0304 (9)
P22	0.4409 (3)	1.0597 (3)	0.10047 (9)	0.0313 (9)
P23	0.4903 (3)	0.6036 (3)	0.11877 (11)	0.0341 (9)
P24	0.6897 (3)	0.9926 (3)	0.15833 (10)	0.0309 (9)
S21	0.8262 (2)	0.8836 (2)	0.06822 (10)	0.0329 (9)
S22	0.3291 (3)	0.7979 (3)	0.07082 (11)	0.0380 (9)
S23	0.6025 (3)	0.7582 (3)	0.20408 (9)	0.0353 (10)

Table 2. Geometric parameters (\AA , $^\circ$)

I11—P11	2.474 (3)	I21—P21	2.478 (3)
I12—P12	2.474 (3)	I22—P22	2.483 (3)
P11—S11	2.117 (3)	P21—S21	2.119 (3)
P11—P13	2.207 (3)	P21—P23	2.206 (3)
P12—S12	2.113 (3)	P22—S22	2.113 (3)
P12—P14	2.208 (4)	P22—P24	2.210 (3)
P13—S13	2.099 (3)	P23—S23	2.098 (4)
P13—S12	2.135 (3)	P23—S22	2.129 (4)
P14—S13	2.090 (3)	P24—S23	2.091 (3)
P14—S11	2.129 (3)	P24—S21	2.134 (3)
S11—P11—P13	102.49 (11)	S21—P21—P23	102.30 (11)
S11—P11—I11	102.43 (11)	S21—P21—I21	102.53 (11)
P13—P11—I11	96.00 (10)	P23—P21—I21	96.42 (10)
S12—P12—P14	102.00 (12)	S22—P22—P24	102.02 (12)
S12—P12—I12	102.80 (11)	S22—P22—I22	101.61 (11)
P14—P12—I12	96.84 (10)	P24—P22—I22	96.97 (10)
S13—P13—S12	102.91 (12)	S23—P23—S22	102.72 (12)
S13—P13—P11	101.15 (12)	S23—P23—P21	101.78 (12)
S12—P13—P11	93.25 (12)	S22—P23—P21	92.53 (12)
S13—P14—S11	103.17 (12)	S23—P24—S21	102.94 (12)
S13—P14—P12	101.65 (12)	S23—P24—P22	101.72 (12)
S11—P14—P12	94.03 (12)	S21—P24—P22	92.91 (11)
P11—S11—P14	106.64 (12)	P21—S21—P24	107.00 (12)
P12—S12—P13	107.14 (12)	P22—S22—P23	107.42 (12)
P14—S13—P13	100.19 (12)	P24—S23—P23	100.51 (12)

The following method, derived from published procedures (Topsom & Wilkins, 1956; Baudler & Mozaffar-Zanganeh, 1976) has been found to give pure α - $\text{P}_4\text{S}_3\text{I}_2$ though the course of the reaction remains obscure. All operations were carried out under nitrogen using Schlenk methods.

A mixture of I_2 (10g, 39.4 mmol) and recrystallized S_8 (3.8g, 14.8 mmol) was dissolved in dried CS_2 (50 cm^3). A solution of P_4 (4.9g, 39.5 mmol) in CS_2 (10 cm^3) was added, giving a clear orange-red solution. A brick-red precipitate appeared after 15 min; the mixture was then stirred for 20 h at 293 K. The solvent was distilled out at atmospheric pressure and the molten product then held at 393 K for 3 h. The yellow-brown mass obtained on cooling to room temperature was extracted with

CS_2 by a modified Soxhlett procedure. α - $\text{P}_4\text{S}_3\text{I}_2$ was crystallized from the extract at 203 K. Large crystals were obtained by the slow cooling of a saturated solution of this material from 333 to 293 K. A suitable single crystal was cleaved from the aggregate formed.

We thank SERC for financial support.

Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55800 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1018]

References

- Baudler, M. & Mozaffar-Zanganeh, H. (1976). *Z. Anorg. Allg. Chem.* **423**, 193–202.
- Blachnik, R., Kurz, G. & Wickel, U. (1984). *Z. Naturforsch. Teil B*, **39**, 778–782.
- Blachnik, R., Loennecke, P. & Tattershall, B. W. (1992). *J. Chem. Soc. Dalton Trans.* pp. 3105–3109.
- Clegg, W. (1981). *Acta Cryst.* **A37**, 22–28.
- Rollo, J. R. & Burns, G. R. (1989). *J. Phys. Chem. Solids*, **50**, 753–762.
- Sheldrick, G. M. (1990). *SHELXTL/PC User's Manual*. Siemens Analytical X-ray Instruments, Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1992). *SHELXL92*. Program for the refinement of crystal structures. Univ. of Göttingen, Germany.
- Tattershall, B. W. (1987). *J. Chem. Soc. Dalton Trans.* pp. 1515–1520.
- Tattershall, B. W. (1991). *J. Chem. Soc. Dalton Trans.* pp. 483–487.
- Tattershall, B. W., Blachnik, R. & Baldus, H.-P. (1989). *J. Chem. Soc. Dalton Trans.* pp. 977–984.
- Topsom, R. D. & Wilkins, C. J. (1956). *J. Inorg. Nucl. Chem.* **3**, 187–189.
- Wright, D. A. & Penfold, B. R. (1959). *Acta Cryst.* **12**, 455–460.

Acta Cryst. (1993). **C49**, 573–576

Bis[1,2-bis(diphenylphosphino)ethane]-platinum(II) Iodide Bis(deuteriochloroform) Solvate

GEORGE FERGUSON, ALAN J. LOUGH, ALAN J. McALEES
AND ROBERT McCRINDLE

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

(Received 17 June 1992; accepted 29 September 1992)

Abstract

In the $[(\text{Ph}_2\text{PCH}_2)_2\text{Pt}]^{2+}$ cation the Pt atom lies on a crystallographic inversion centre (and has necessarily planar coordination) with Pt—P = 2.3310(13) and 2.3250(14) \AA and intra-ring P—Pt—P = 82.09(5) $^\circ$. The unique five-membered PtP_2C_2 ring has close to an envelope conformation. The iodide ion lies in a general posi-