

References

- ALCOCK, N. W. (1975). *ABSCOR. A Fortran Crystallographic Absorption-Correction Program*. Private communication.
- AYDIN URAZ, A. & ARMAĞAN, N. (1975). *A Fortran Crystallographic Extinction Program*. Univ. of Ankara, Dept. of Physics, Ankara, Turkey.
- BAGGIO, S., AMZEL, L. M. & BECKA, L. N. (1969). *Acta Cryst.* **B25**, 2650–2653.
- BAUR, W. H. (1972). *Acta Cryst.* **B28**, 1456–1465.
- CRUICKSHANK, D. W. J. (1965). *Computing Methods in Crystallography*, p. 114. Oxford: Pergamon Press.
- EL SAFFAR, Z. M. (1968). *Acta Cryst.* **B24**, 1131–1133.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 202–203. Birmingham: Kynoch Press.
- KILLEAN, R. C. G., LAWRENCE, J. L. L. & SHARMA, V. C. (1972). *Acta Cryst.* **A28**, 405–407.
- MANOJLOVIĆ-MUIR, L. (1975). *Acta Cryst.* **B31**, 135–139.
- MORIMOTO, N. (1956). *Miner. J. (Sapporo)*, **2**, 1–3.
- PADMANABHAN, V. M., YADAVA, V. S., NAVARRO, Q. O., GARCIA, A., KARSONO, L., SUH, I.-H. & CHIEN, L. S. (1971). *Acta Cryst.* **B27**, 253–257.
- RUBEN, H. W., TEMPLETON, D. H., ROSENSTEIN, R. D. & OLOVSSON, I. (1961). *J. Amer. Chem. Soc.* **83**, 820–824.
- STOUT, G. H. & JENSEN, L. H. (1968). *X-ray Structure Determination*, p. 403. London: Macmillan.
- TARIMCI, Ç., SCHEMPP, E. & CHANG, S. C. (1975). *Acta Cryst.* **B31**, 2146–2149.
- TAYLOR, P. G. & BEEVERS, C. A. (1952). *Acta Cryst.* **5**, 341–344.
- ZACHARIASEN, W. H. (1967). *Acta Cryst.* **23**, 558–564.
- ZALKIN, A. (1967). *DRF. A Fortran Crystallographic Data-Reduction and Fourier Program*. Berkeley, Calif., USA.
- ZALKIN, A. (1968). *LALS. A Fortran Crystallographic Least-Squares Program*. Berkeley, Calif., USA.

Acta Cryst. (1977). **B33**, 1399–1404

The Crystal Structure of Chromium Thiophosphate, CrPS₄

BY ROLAND DIEHL* AND CLAUS-DIETER CARPENTIER

Kristallographisches Institut der Universität, D-7800 Freiburg/Breisgau, Hebelstrasse 25, Germany (BRD)

(Received 30 September 1976; accepted 24 October 1976)

Chromium thiophosphate, CrPS₄, is monoclinic with $a = 10.871(2)$, $b = 7.254(2)$, $c = 6.140(2)$ Å, $\beta = 91.88(4)^\circ$, $V = 483.9(4)$ Å³, space group $C2$ and $Z = 4$. The crystal structure has been determined by Fourier methods from the X-ray intensities of 911 independent reflexions measured on a four-circle automatic single-crystal diffractometer, and refined to $R = 0.019$. It is characterized by puckered hexagonally close-packed sulphur layers stacked parallel to (100) with Cr in octahedral and P in tetrahedral interstices. CrPS₄ is the first metal thiophosphate with the metal atom in octahedral sulphur coordination.

Introduction

Metal phosphorus sulphides of compositional type M_xPS_4 (x values so far known are 1.0, 1.5, 3.0) must be looked upon as thiophosphates. The determinations of the crystal structures of BPS₄ (Weiss & Schaefer, 1963), AlPS₄ (Weiss & Schaefer, 1960), GaPS₄ (Buck & Carpentier, 1973), InPS₄ (Carpentier, Diehl & Nitsche, 1970), BiPS₄ (Zimmerman, Carpentier & Nitsche, 1975), Pd₃(PS₄)₂ (Bither, Donohue & Young, 1971) and Cu₃PS₄ (Ferrari & Cavalca, 1948) have shown that the tetrahedral PS₄ group is a common feature of all M_xPS_4 compounds so far studied. This class of compounds has gained interest not only because of its manifold crystal chemistry but also for potential

applications in solid-state devices since many of the compounds crystallize in non-centrosymmetric space groups.

A new metal thiophosphate with $M = Cr$ and $x = 1.0$ has recently been synthesized. To obtain further information on the crystal chemistry of thiophosphates the crystal structure of CrPS₄ has been investigated by X-ray diffraction methods.

Experimental

CrPS₄ was synthesized from powdered stoichiometric amounts of the elements in evacuated quartz ampoules at a temperature of 700°C. Reaction velocity was enhanced by adding 5 mg of iodine per cm³ of the tube volume. Black, lustrous single crystals were obtained by chemical transport in a temperature gradient from

* Present address: Institut für Angewandte Festkörperphysik der Fraunhofer-Gesellschaft, D-7800 Freiburg/Breisgau, Eckerstrasse 4, Germany (BRD).

750 to 650°C. The very soft and plastic crystals were of ribbon-like or prismatic habit, slipping very easily parallel to the dominant crystal face, (001).

From Weissenberg photographs the crystals were found to be monoclinic. Systematic extinctions hkl with $h + k = 2n + 1$ indicated the possible space groups to be $C2/m$, $C2$, or Cm . A piezo test could not be performed because of the high conductivity of the crystal samples.

Precise lattice constants were obtained from Guinier powder photographs (Cu $K\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$) with cubic As₂O₃ ($a = 11.081 \text{ \AA}$) as an internal standard. It followed from an indexing of the crystal faces that the crystal form is built up by a combination of {100}, {001}, {101}, {201} and {120}. {001} is the dominant crystal form.

X-ray fluorescence analysis with InPS₄ and Cr₂S₃ as standards yielded atomic ratios P:S and Cr:S both of 1:4. The chemical formula was thus confirmed to be CrPS₄. By the suspension method with bromoform-methanol, a density $\rho_m = 2.88 (3) \text{ g cm}^{-3}$, was obtained resulting in four formulae per unit cell ($Z = 4$). All crystal data are summarized in Table 1.

For X-ray intensity measurements a prismatic crystal specimen of $0.32 \times 0.27 \times 0.24 \text{ mm}$ was used. Intensity data of 911 independent reflexions in the range $0.0 \leq (\sin \theta)/\lambda \leq 0.75 \text{ \AA}^{-1}$ were measured with a NaI(Tl) scintillation counter on a four-circle automatic single-crystal diffractometer (Enraf-Nonius CAD-4) using Zr-filtered Mo $K\alpha$ radiation ($\lambda = 0.71056 \text{ \AA}$) monochromatized by a graphite monochromator. The background-corrected intensities were further corrected for absorption ($\mu = 14.6 \text{ cm}^{-1}$) with the program ORABS (Busing, 1966). Corrections for long-time drift (standard reflexions: 211 and 421), Lorentz and

polarization factors were performed with the X-RAY 70 system (Stewart, Kundell & Badwin, 1970), which was also used for structure determination and refinement.

Determination and refinement of the crystal structure

A three-dimensional Patterson synthesis was calculated from all F_o^2 values giving a map with very sharp peaks on an extremely low background. Although the Wilson plot indicated centrosymmetry a complete interpretation of the Patterson map resulted in an atomic arrangement which was inconsistent with the centrosymmetric space group $C2/m$. Therefore, two Patterson-compatible structural models were established, one in space group $C2$, the other in Cm [No. 5 and No. 8, respectively, in *International Tables for X-ray Crystallography* (1965)].

For structure factor calculations, atomic scattering factors for Cr, P and S (neutral atoms) were taken from Cromer & Waber (1965). $\Delta f'$ and $\Delta f''$ correction factors for anomalous dispersion (Cromer & Liberman, 1970) were also included. A least-squares refinement was performed with the program CRYLSQ of the X-RAY 70 system (Stewart *et al.*, 1970). The function to be minimized was $\sum w ||F_o| - |F_c||^2$ with $w = 1/\sigma^2$ (F_o), σ being the estimated standard deviation (e.s.d.) which was derived from counting statistics. 101 reflexions having $F_o < 3\sigma$ were treated as 'less-thans'. Refinement was started with positional parameters as derived from the Patterson map, and individual isotropic temperature factors.

Refinement in space group $C2$ yielded a reliability index $R = \sum ||F_o| - |F_c||/\sum F_o$ of 0.085. For space group Cm , $R = 0.104$ was obtained. Hence, the $C2$ model was selected for further refinement. With individual anisotropic temperature coefficients (Cruickshank, 1956), dispersion correction factors, and an isotropic correction factor for secondary extinction (Larson, 1967) the reliability index converged to $R = 0.019$ with 'less-thans' omitted and $R = 0.022$ with 'less-thans' included. Different weighting schemes were

Table 1. Crystal data of CrPS₄

$a = 10.871 (2) \text{ \AA}$	$\rho_m = 2.88 (3) \text{ g cm}^{-3}$
$b = 7.254 (2)$	$\rho_x = 2.898$
$c = 6.140 (2)$	$Z = 4$
$\beta = 91.88 (4)^\circ$	FW 211.2258
$V = 483.9 (4) \text{ \AA}^3$	$F(000) = 412 e$

Table 2. Atomic positional parameters and anisotropic thermal coefficients ($\times 10^4$)

Position	Cr(1) 2(a)	Cr(2) 2(a)	P 4(c)	S(1) 4(c)	S(2) 4(c)	S(3) 4(c)	S(4) 4(c)
x	0	0	2971 (1)	1335 (3)	1347 (3)	1062 (1)	1303 (1)
y	0	5095 (2)	2588 (6)	-84 (6)	5248 (6)	2594 (5)	7575 (5)
z	0	0	1655 (1)	7007 (5)	6993 (5)	1934 (1)	1452 (1)
U_{11}	65 (10)	71 (11)	64 (03)	101 (13)	134 (14)	64 (03)	80 (03)
U_{22}	86 (09)	82 (09)	100 (03)	141 (09)	120 (12)	105 (03)	110 (03)
U_{33}	148 (11)	104 (10)	118 (03)	161 (14)	142 (13)	132 (03)	108 (03)
U_{12}	0	0	17 (12)	44 (10)	-15 (10)	32 (13)	16 (13)
U_{13}	18 (08)	00 (08)	02 (02)	20 (09)	36 (09)	03 (02)	04 (02)
U_{23}	0	0	30 (11)	49 (09)	-27 (09)	-22 (13)	-17 (12)

applied to the observed structure factors. Best agreement between the sets of F_o and F_c was obtained with unit weights.* The final atomic positional and anisotropic thermal parameters are summarized in Table 2.

A difference Fourier map was completely featureless, the highest 'peak' being about 1% of the smallest peak of the F_o synthesis.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32253 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Discussion

As is shown on Fig. 1 viewed normal to (001), the structure of CrPS_4 is characterized by puckered S layers arranged in hexagonal close-packing parallel to (100), the stacking sequence being shown on the left-hand side of the figure. Both symmetrically inequivalent Cr atoms are coordinated each by six S atoms in the form of a slightly distorted octahedron. The P atoms are located in the centres of rather regular S tetrahedra. One of the characteristic coordination polyhedra around Cr and P is outlined.

Bonding distances and angles of the pertinent coor-

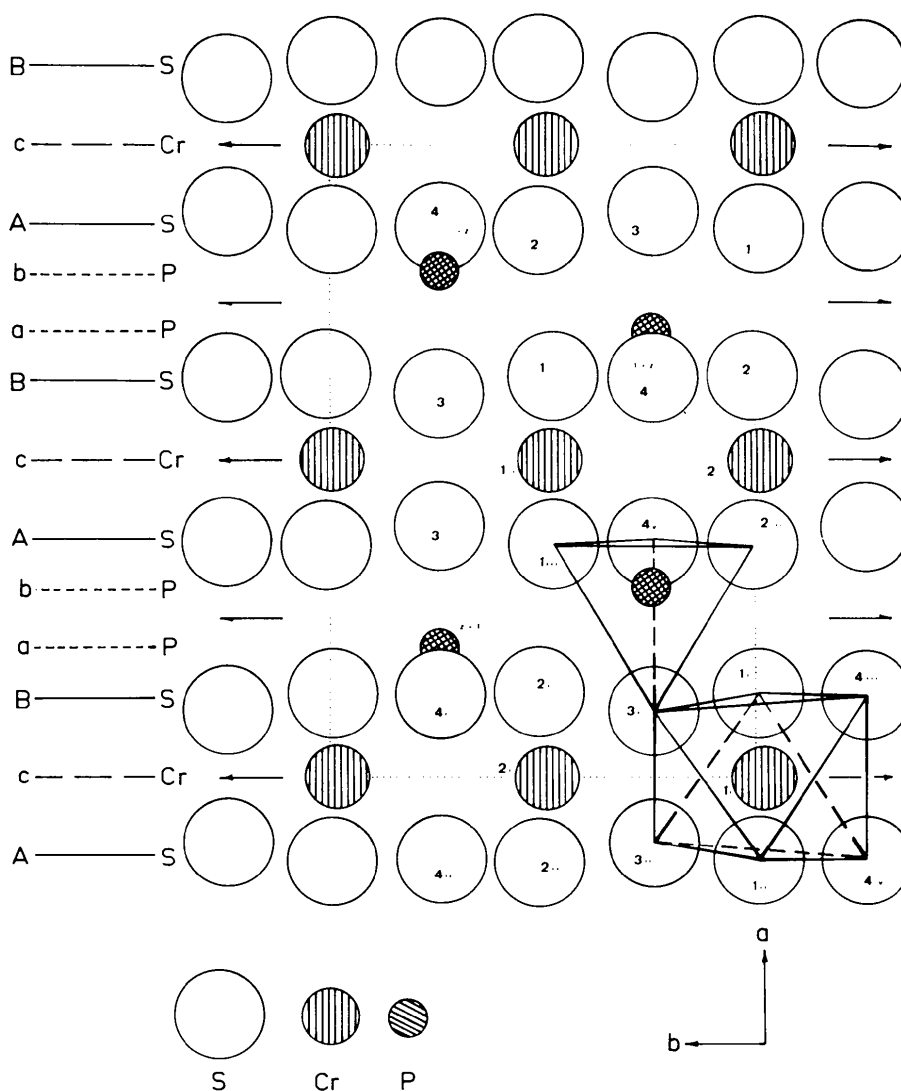


Fig. 1. Layer-like atomic arrangement of the CrPS_4 crystal structure viewed along $[00\bar{1}]$, with stacking sequence.

Table 3. Bond distances (Å) and angles (°)

Coordinates of bonding atoms (see Fig. 1)

Cr(1 ⁱ)	x, y, z	S(1 ⁱⁱ)	$\bar{x}, y, 1 - z$	S(3 ⁱⁱ)	\bar{x}, y, \bar{z}
Cr(1 ⁱⁱ)	$\frac{1}{2} + x, \frac{1}{2} + y, z$	S(1 ⁱⁱⁱ)	$\frac{1}{2} - x, y + \frac{1}{2}, 1 - z$	S(4 ⁱ)	x, y, z
Cr(2 ⁱ)	x, y, z	S(2 ⁱ)	$x, y, z - 1$	S(4 ⁱⁱ)	\bar{x}, y, \bar{z}
Cr(2 ⁱⁱ)	$\frac{1}{2} + x, y - \frac{1}{2}, z$	S(2 ⁱⁱ)	$\bar{x}, y, 1 - z$	S(4 ⁱⁱⁱ)	$x, y - 1, \bar{z}$
P ⁱ	x, y, z	S(2 ⁱⁱⁱ)	$\frac{1}{2} - x, y - \frac{1}{2}, 1 - z$	S(4 ^{iv})	$\bar{x}, y - 1, \bar{z}$
S(1 ⁱ)	$x, y, z - 1$	S(3 ⁱ)	x, y, z	S(4 ^v)	$\frac{1}{2} - x, y - \frac{1}{2}, \bar{z}$

P ⁱ -Cr(1 ⁱ)	3.844 (17)	P ⁱ -Cr(2 ⁱⁱ)	3.052 (15)	S(3 ⁱ)-S(3 ⁱⁱ)	3.257 (34)	
-Cr(2 ⁱ)	3.815 (17)	Cr(2 ⁱ)-Cr(1 ⁱ)	3.696 (2)	S(3 ^{i,ii})-S(4 ^{i,ii})	3.636 (05)	
-Cr(1 ⁱⁱ)	3.018 (15)	-Cr(1 ⁱⁱ)	3.558 (1)	S(3 ^{i,ii})-S(2 ^{i,ii})	3.615 (07)	
Cr(1 ⁱ)-S ₆ octahedron				S(3 ^{i,ii})-S(2 ^{ii,i})	3.333 (11)	
Cr(1 ⁱ)-S(1 ⁱ)-S(1 ⁱⁱ)	2.380 (23)			S(4 ⁱ)-S(4 ⁱⁱ)	3.298 (31)	
-S(3 ⁱ)-S(3 ⁱⁱ)	2.488 (11)			S(4 ^{i,ii})-S(2 ^{i,ii})	3.218 (04)	
-S(4 ⁱⁱⁱ)-S(4 ^{iv})	2.411 (11)			S(4 ^{i,ii})-S(2 ^{ii,i})	3.499 (16)	
S(3 ⁱ)-Cr(1 ⁱ)-S(1 ⁱ)	95.91 (09)			S(4 ^{i,ii})-S(2 ^{i,ii})-S(3 ^{i,ii})	63.98 (09)	
-S(4 ⁱⁱⁱ)	96.74 (08)			S(2 ^{i,ii})-S(4 ^{i,ii})-S(3 ^{i,ii})	63.32 (09)	
-S(1 ⁱⁱ)	86.33 (09)			S(2 ^{i,ii})-S(3 ^{i,ii})-S(4 ^{i,ii})	52.69 (08)	
-S(3 ⁱⁱ)	81.76 (09)			S(4 ^{ii,i})-S(4 ^{i,ii})-S(2 ^{i,ii})	64.96 (07)	
-S(4 ^{iv})	170.32 (03)			S(4 ^{ii,i})-S(2 ^{i,ii})-S(4 ^{i,ii})	58.64 (06)	
S(1 ⁱ)-Cr(1 ⁱ)-S(4 ⁱⁱⁱ)	84.31 (09)			S(4 ^{i,ii})-S(4 ^{ii,i})-S(2 ^{i,ii})	56.42 (07)	
-S(4 ^{iv})	93.53 (09)			S(4 ^{i,ii})-S(2 ^{ii,i})-S(3 ^{i,ii})	64.25 (09)	
-S(1 ⁱⁱ)	177.05 (14)			S(2 ^{ii,i})-S(4 ^{i,ii})-S(3 ^{i,ii})	55.67 (08)	
S(4 ⁱⁱⁱ)-Cr(1 ⁱ)-S(4 ^{iv})	86.30 (09)			S(2 ^{ii,i})-S(3 ^{i,ii})-S(4 ^{i,ii})	60.09 (09)	
				S(2 ^{i,ii})-S(3 ^{i,ii})-S(3 ^{i,i})	57.75 (07)	
				S(3 ^{i,ii})-S(3 ^{ii,i})-S(2 ^{i,ii})	66.52 (07)	
				S(3 ^{i,ii})-S(2 ^{i,ii})-S(3 ^{ii,i})	55.73 (06)	
S(3 ⁱ)-S(3 ⁱⁱ)	3.257 (34)			P ⁱ -S ₄ tetrahedron		
S(1 ^{i,ii})-S(3 ^{i,ii})	3.616 (06)			P ⁱ -S(3 ⁱ)	2.089 (04)	
S(1 ^{i,ii})-S(3 ^{ii,i})	3.331 (11)			-S(1 ⁱⁱⁱ)	2.014 (08)	
S(1 ^{i,ii})-S(4 ^{iii,iv})	3.216 (04)				P ⁱ -S(2 ⁱⁱⁱ)	2.019 (08)
S(4 ⁱⁱⁱ)-S(4 ^{iv})	3.298 (31)				-S(4 ^v)	2.088 (14)
S(1 ^{i,ii})-S(4 ^{iii,iv})	3.491 (16)					
S(3 ^{i,ii})-S(4 ^{iii,iv})	3.663 (05)			S(3 ⁱ)-P ⁱ -S(1 ⁱⁱⁱ)	108.93 (20)	
				-S(2 ⁱⁱⁱ)	108.68 (20)	
S(3 ^{i,ii})-S(1 ^{i,ii})-S(4 ^{iii,iv})	64.53 (09)			-S(4 ^v)	108.77 (05)	
S(1 ^{i,ii})-S(3 ^{i,ii})-S(4 ^{iii,iv})	52.43 (08)			S(1 ⁱⁱⁱ)-P ⁱ -S(2 ⁱⁱⁱ)	114.18 (14)	
S(1 ^{i,ii})-S(4 ^{iii,iv})-S(3 ^{i,ii})	63.04 (09)			-S(4 ^v)	103.24 (18)	
S(1 ^{ii,i})-S(3 ^{ii,i})-S(3 ^{i,ii})	57.70 (07)					
S(1 ^{ii,i})-S(3 ^{i,ii})-S(3 ^{ii,i})	66.56 (07)			S(3 ⁱ)-S(1 ⁱⁱⁱ)	3.339 (12)	
S(3 ^{i,ii})-S(1 ^{ii,i})-S(3 ^{ii,i})	55.74 (06)			-S(2 ⁱⁱⁱ)	3.338 (12)	
S(3 ^{i,ii})-S(1 ^{ii,i})-S(4 ^{iii,iv})	64.90 (09)			-S(4 ^v)	3.595 (33)	
S(1 ^{ii,i})-S(3 ^{i,ii})-S(4 ^{iii,iv})	59.65 (09)			S(1 ⁱⁱⁱ)-S(2 ⁱⁱⁱ)	3.868 (06)	
S(3 ^{i,ii})-S(4 ^{iii,iv})-S(1 ^{ii,i})	63.04 (09)			-S(4 ^v)	3.216 (04)	
S(1 ^{ii,i})-S(4 ^{iv,iii})-S(4 ^{iii,iv})	64.79 (07)			S(2 ⁱⁱⁱ)-S(4 ^v)	3.218 (04)	
S(4 ^{iv,iii})-S(1 ^{ii,i})-S(4 ^{iii,iv})	58.75 (06)					
S(4 ^{iv,iii})-S(4 ^{iii,iv})-S(1 ^{ii,i})	56.46 (07)			S(1 ⁱⁱⁱ)-S(4 ^v)-S(2 ⁱⁱⁱ)	63.51 (10)	
				S(4 ^v)-S(1 ⁱⁱⁱ)-S(2 ⁱⁱⁱ)	58.28 (10)	
				S(4 ^v)-S(2 ⁱⁱⁱ)-S(1 ⁱⁱⁱ)	58.21 (10)	
				S(3 ⁱ)-S(4 ^v)-S(2 ⁱⁱⁱ)	58.36 (07)	
				S(4 ^v)-S(3 ⁱ)-S(2 ⁱⁱⁱ)	55.17 (07)	
				S(4 ^v)-S(2 ⁱⁱⁱ)-S(3 ⁱ)	66.47 (07)	
				S(3 ⁱ)-S(4 ^v)-S(1 ⁱⁱⁱ)	58.39 (07)	
				S(3 ⁱ)-S(1 ⁱⁱⁱ)-S(4 ^v)	66.49 (07)	
				S(4 ^v)-S(3 ⁱ)-S(1 ⁱⁱⁱ)	55.12 (07)	
				S(1 ⁱⁱⁱ)-S(3 ⁱ)-S(2 ⁱⁱⁱ)	60.95 (10)	
				S(3 ⁱ)-S(1 ⁱⁱⁱ)-S(2 ⁱⁱⁱ)	59.52 (10)	
				S(1 ⁱⁱⁱ)-S(2 ⁱⁱⁱ)-S(3 ⁱ)	59.54 (10)	
Cr(2 ⁱ)-S ₆ octahedron						
Cr(2 ⁱ)-S(3 ⁱ)-S(3 ⁱⁱ)	2.438 (12)					
-S(4 ⁱ)-S(4 ⁱⁱ)	2.440 (11)					
-S(2 ⁱ)-S(2 ⁱⁱ)	2.396 (23)					
S(3 ⁱ)-Cr(2 ⁱ)-S(4 ⁱ)	96.36 (09)					
-S(2 ⁱ)	96.79 (09)					
-S(2 ⁱⁱ)	87.17 (09)					
-S(3 ⁱⁱ)	83.82 (10)					
-S(4 ⁱⁱ)	170.54 (03)					
S(4 ⁱ)-Cr(2 ⁱ)-S(2 ⁱ)	83.41 (09)					
-S(2 ⁱⁱ)	92.67 (09)					
-S(4 ⁱⁱ)	85.02 (09)					
S(2 ⁱ)-Cr(2 ⁱ)-S(2 ⁱⁱ)	174.69 (15)					

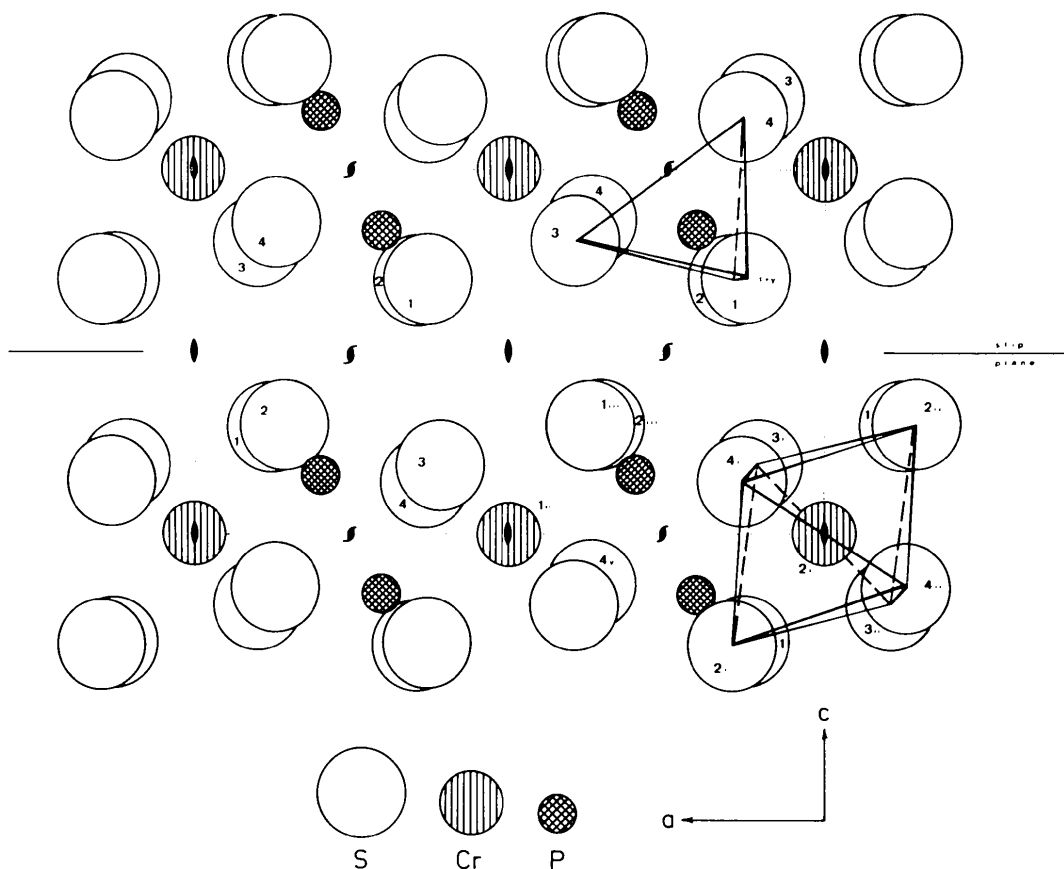


Fig. 2. Atomic arrangement of the CrPS_4 crystal structure viewed along $[0\bar{1}0]$; the slip plane is indicated.

Table 4. *Crystal chemistry of $M\text{PS}_4$ thiophosphates*

Compound	Space group <i>Z</i>	Lattice constants	Transformation	Close-packing of S atoms	Coordination of <i>M</i> by S
BPS_4	$I222$	$a = 5.60 \text{ \AA}$	$\mathbf{a} = \frac{1}{2}(\bar{\mathbf{a}}' + \mathbf{b}' + \mathbf{c}')$	cubic	tetrahedral
	2	$b = 5.25$ $c = 9.04$	$\mathbf{b} = \frac{1}{2}(\bar{\mathbf{a}}' - \mathbf{b}' - \mathbf{c}')$ $\mathbf{c} = \mathbf{c}' - \frac{\mathbf{a}'}{2}$		
AlPS_4	$P222$ 2	$a = 5.61 \text{ \AA}$ $b = 5.67$ $c = 9.05$	same as for BPS_4	cubic	tetrahedral
GaPS_4	$P2_1/c$ 4	$a = 8.603 \text{ \AA}$ $b = 7.778$ $c = 11.858$ $\beta = 135.46^\circ$	$\mathbf{a} = \mathbf{c}' - \frac{\mathbf{a}'}{2}$ $\mathbf{b} = \mathbf{c}'$ $\mathbf{c} = \mathbf{a}'$ $\beta = 3\beta'/2$	hexagonal	tetrahedral
InPS_4	$I\bar{4}$ 2	$a = 5.60 \text{ \AA}$ $b = a$ $c = 9.02$	same as for BPS_4	cubic	tetrahedral
CrPS_4	$C2$ 4	$a = 10.871$ $b = 7.254$ $c = 6.140$ $\beta = 91.88^\circ$	$\mathbf{a} = \mathbf{a}'$ $\mathbf{b} = \mathbf{b}'$ $\mathbf{c} = \mathbf{c}'$ $\beta = \beta'$	hexagonal	octahedral

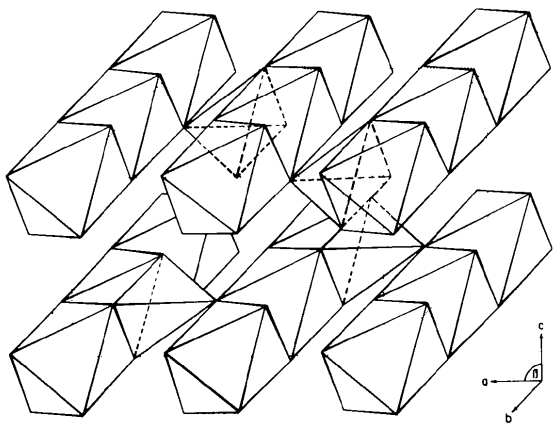


Fig. 3. Schematic illustration of the CrPS₄ crystal structure showing connected coordination polyhedra.

dination polyhedra are comprehensively listed in Table 3. As can be derived from the mean bonding distance of Cr–S (2.426 Å) and P–S (2.053 Å) the bonding of Cr to S is to a great extent ionic (ionic radii: Cr³⁺ 0.64, S²⁻ 1.84 Å) whereas the mean P–S bond length is considerably shorter than the sum of the ionic radii (P⁵⁺ 0.34 Å). Because of this strong bonding of covalent character (covalent radii: P 1.06, S 1.02 Å) CrPS₄ must be classified as a thiophosphate. Altogether, the S atoms are considerably polarized which is indicated by a mean S–S distance of 3.457 Å.

The Cr atoms are concentrated on plane (001) as is illustrated on Fig. 2, which is viewed along [010]. Again, one octahedron and one tetrahedron are outlined. There is a cation-free region parallel to (001) around $z = \frac{1}{2}$ explaining the easy slipping mentioned above. The slip plane is indicated on Fig. 2.

Fig. 3 gives a schematic illustration of the CrPS₄ structure in the form of connected coordination polyhedra, only occupied polyhedra being shown (as on all figures the unit cell is outlined by dotted lines). Chains of edge-sharing CrS₆ octahedra run along [010]. Connexion of the chains along [100] is achieved via PS₄ tetrahedra. The PS₄ tetrahedron is linked by corner-sharing to a common corner of two CrS₆ octahedra of one chain and by edge-sharing to two CrS₆ octahedra of an adjacent chain.

Apart from the crystal structure of BiPS₄ (Zimmermann *et al.*, 1975), which exhibits a rather strange coordination of Bi by S, and which is not characterized by a close-packed arrangement of S atoms, the crystal structures of all other MPS₄ compounds so far known are geometrically related (Buck & Carpentier, 1973). If

CrPS₄ is included into a similar scheme, the geometric relations given in Table 4 are evident. The transformations of the lattice vectors of the Group III thiophosphates into those of CrPS₄ (a'b'c') are shown in the fourth column. Packing type as well as the coordination of M by S are also included. In contrast to the M^{III} thiophosphates incorporated in Table 4 the metal atom of CrPS₄ is octahedrally coordinated by S.

Finally, it should be stated that the arrangement of the S and Cr atoms is practically centrosymmetric. The non-centrosymmetry of the crystal structure is mainly induced by the P atoms. Since the contribution of the P atoms to the total scattering power of the structure is only of about 10% it can be reasoned that the crystal form of CrPS₄ (each crystal face having a parallel counterface) as well as the Wilson plot indicate the pseudo-centrosymmetry mentioned above.

Thanks are due to W. Littke (Chemisches Institut der Universität Freiburg) for his permission to use the single-crystal diffractometer. All numerical calculations were performed on the Univac-1106 computer of the Rechenzentrum der Universität Freiburg. Financial support by the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

References

- BITHER, T. A., DONOHUE, P. C. & YOUNG, H. S. (1971). *J. Solid State Chem.* **3**, 300–304.
- BUCK, P. & CARPENTIER, C. D. (1973). *Acta Cryst.* **B29**, 1864–1868.
- BUSING, W. R. (1966). Oak Ridge National Laboratory, Tennessee, USA.
- CARPENTIER, C. D., DIEHL, R. & NITSCHKE, R. (1970). *Naturwissenschaften*, **57**, 393–394.
- CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
- CROMER, D. T. & WABER, J. T. (1965). *Acta Cryst.* **18**, 104–109.
- CRUICKSHANK, D. W. J. (1956). *Acta Cryst.* **9**, 747–753.
- FERRARI, A. & CAVALCA, L. (1948). *Gazz. Chim. Ital.* **78**, 283–285.
- International Tables for X-ray Crystallography* (1965). Vol. 1, 2nd ed. Birmingham: Kynoch Press.
- LARSON, A. C. (1967). *Acta Cryst.* **26**, 664–666.
- STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). The X-RAY 70 system – version of July 1970. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- WEISS, A. & SCHAEFER, H. (1960). *Naturwissenschaften*, **47**, 495.
- WEISS, A. & SCHAEFER, H. (1963). *Z. Naturforsch.* **18**, 81–82.
- ZIMMERMANN, H., CARPENTIER, C. D. & NITSCHKE, R. (1975). *Acta Cryst.* **B31**, 2003–2006.