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The High Pressure Synthesis, Crystal Structure, and Properties of CrP₄ and MoP₄

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The new compounds CrP₄ and MoP₄ have been prepared by reaction of the elements at pressures of 15 to 65 kbar in a tetrahedral anvil high-pressure device. They have isotypic monoclinic crystal structures, space group *C2/c*, and four formula units per unit cell. The cell dimensions are, for CrP₄: $a = 5.1914$ (5), $b = 10.7600$ (8), $c = 5.7712$ (6) Å, $\beta = 110.648$ (6)°, and for MoP₄: $a = 5.313$ (2), $b = 11.139$ (7), $c = 5.820$ (2) Å, $\beta = 110.64$ (4)°. The structure of CrP₄ was determined from three-dimensional single-crystal counter data, and refined by a full-matrix least-squares method with isotropic thermal parameters, yielding a conventional *R* value of 0.034 for 1017 observed reflections. Two nonequivalent P atoms are tetrahedrally coordinated, one by three P atoms and one Cr atom, the other by two P atoms and two Cr atoms. All P–P distances are within 2.21 ± 0.02 Å. The Cr atom is coordinated by six P atoms, forming a distorted octahedron. Cr–P distances vary between 2.32 and 2.39 Å. The [CrP₆] octahedra share edges, forming zigzag chains along the *c* direction. Temperature-dependent resistivity measurements of CrP₄ and MoP₄ samples indicate metallic conductivity. CrP₄ is Pauli paramagnetic. The structure and bonding of CrP₄ are discussed and compared with those of other phosphorus-rich compounds.

Introduction

The binary systems chromium–phosphorus and molybdenum–phosphorus have been investigated repeatedly in the past (Årstad & Nowotny, 1937; Nowotny & Henglein, 1938; Vogel & Kasten, 1939; Faller, Biltz, Meisel & Zumbusch, 1941; Schönberg, 1954; Bachmayer, Nowotny & Kohl, 1955; Lundström, 1962; Rundqvist, 1962*a,b*; Rundqvist & Lundström, 1963; Rundqvist, 1965; Sellberg & Rundqvist, 1965; Baurecht, Boller & Nowotny, 1971). Reviews have been given by Rundqvist (1962*c*) and Lundström (1969). There was agreement that the compounds CrP₂ and MoP₂ were the compounds richest in phosphorus found so far in the respective systems. The present study was undertaken to explore the influence of high pressure on the formation of phosphorus-rich compounds in these systems. The compounds CrP₄ and MoP₄ were prepared for the first time, and their crystal structure and physical properties are reported.

Sample preparation

The samples were prepared in a tetrahedral anvil press of National Bureau of Standards design (Lloyd, Hut-

ton & Johnson, 1959), using a cylindrical boron nitride crucible of 0.6 cm length and 0.13 cm⁻³ volume, surrounded by a graphite sleeve resistance heater inserted in a pyrophyllite tetrahedron. The temperature was measured with a Pt, Pt–Rh thermocouple uncorrected for pressure effects and placed at the center of the cylinder surface. Detailed operating procedures have been described by Bither, Gillson & Young (1966).

High-purity Mo, Cr, and red P powders were ground together in the metal:phosphorus ratio 1:4, and pressed into a pellet, which was placed in the boron nitride crucible. Pressure was applied and then the temperature was raised. Optimum conditions are from 15–65 kbar and 900–1200°C. These conditions were generally held for two hours; the samples were cooled over a period of about two hours to 700–1000°C and then quenched.

To investigate the stability of CrP₄ at lower pressures, CrP₄ was also prepared by reaction of a 1:4 mixture of Cr and P sealed in a Pyrex tube (10 mm outside diameter, 6 mm inside diameter) held in a Pt jacket and heated to 700°C under 200 atm; the temperature and pressure were then raised to 1000°C and 3 kbar. Under these conditions, the Pyrex tube is soft, so that the external pressure equals the internal pressure. The reaction product was identified, through its X-ray

* Contribution No. 1847.

pattern, as being identical to the CrP₄ phase prepared at 65 kbar.

Characterization of CrP₄

CrP₄ obtained in the 65 kbar experiments had the form of large, black, shiny, brittle crystals with glass-like fracture surfaces. Chemical analysis gave the following results: 30.7% Cr, 72.7% P; calculated values for CrP₄: 29.5% Cr, 70.5% P. Electrical measurements were made on a single crystal of unknown orientation with the four-probe technique. CrP₄ is a good metallic conductor: $\rho_{298^\circ\text{K}} = 2.3 \times 10^{-4}$ ohm.cm, $\rho_{4.2^\circ\text{K}} = 2.6 \times 10^{-6}$ ohm.cm. Magnetic measurements between 4.2 and 300°K show weak, and slightly field- and temperature-dependent paramagnetic behavior, indicating diamagnetism with superimposed Pauli paramagnetism.

Unit cell and space group

Single crystals of the crushed material were investigated with a Buerger precession camera. The diffraction patterns could be indexed with a monoclinic unit cell. The conditions for observed reflections are hkl with $h+k=2n$ and $h0l$ with $l=2n$. They lead to space groups $C2/c$ or Cc , of which $C2/c$ was found to be correct through the structure determination. A Guinier-Hagg powder pattern (Table 1) of CrP₄ was indexed on the monoclinic cell, and the lattice constants were refined by a least-squares procedure, using high-purity KCl ($a=6.29310$ Å) as an internal standard. Lattice constants are given in Table 2. The measured density was 3.88 g.cm⁻³; the X-ray density was 3.873 g.cm⁻³, assuming four formula units.

Structure determination of CrP₄

The single crystal used for the measurement of the diffraction intensities approximated the shape of a needle, with an irregular cross-section and dimensions $50 \times 30 \times 250 \mu$. It was mounted with the needle-axis – which turned out to be close to the [110] direction – parallel to the ϕ axis of an automated Picker diffractometer. Zr-filtered Mo radiation was used with scintillation counter and pulse-height discriminator. The θ - 2θ scan technique was used; the scan angle was $1.8^\circ 2\theta$ and the scan speed $1^\circ 2\theta \text{ min}^{-1}$. Background counts of 15 sec were taken at the beginning and end of each scan. The intensity of a standard reflection was taken every three hours. It remained constant, within $\pm 2\%$, during the period of the data collection. All reflections within the asymmetric quadrant up to $(\sin \theta)/\lambda = 0.98$ were measured. The usual Lorentz-polarization correction was applied. No absorption

correction was made, since approximate transmission values calculated for the crystal shape varied only between 79 and 88%, which amounts to relative errors of less than $\pm 2.5\%$ in structure factors.

A three-dimensional Patterson synthesis was computed with a program written by Fritchie & Guggenberger (1967), and the structure was found through the interpretation of this Patterson function. The structure was refined on a Univac 1108 computer, using a full-

Table 1. Evaluation of a Guinier-Hagg pattern of CrP₄ and of a Debye-Scherrer pattern of MoP₄

Both patterns were taken with Cu K α radiation.

CrP ₄						MoP ₄					
hk l	d _c	d _o	I _c	I _o		hk l	d _c	d _o	I _c	I _o	
02 0	5.3800	-	1	-		02 0	5.5693	5.575	15	m	
11 0	4.4275	4.4250	44	vs		11 0	4.5405	4.543	91	vvvs	
11-1	4.1375	-	2	-		11-1	4.2189	4.222	7	v	
02 1	3.8114	-	1	-		02 1	3.8940	3.898	14	m	
11 1	2.9856	2.9844	6	vw		11 1	3.0395	3.038	9	v	
13 0	2.8854	2.8843	6	vw		13 0	2.9750	2.975	9	m	
13-1	2.8004	2.8003	100	vvvs		13-1	2.8788	2.880	100	vvvs	
11-2	2.7278	-	0	-		04 0	2.7845	-	0	-	
00 2	2.7002	2.7000	58	vvvs		11-2	2.7500	2.751	5	vw	
04 0	2.5900	-	0	-		00 2	2.7234	2.725	60	vs	
20 0	2.4289	2.4286	10	w		20 0	2.4862	2.489	1	vvw	
02 2	2.4133	-	1	-		04 1	2.4794	-	1	-	
04 1	2.4078	2.4078	4	vvw		02 2	2.4455	2.447	5	vw	
13 1	2.3487	-	2	-		13 1	2.4061	2.407	10	v	
22-1	2.3277	2.3275	18	m		22-1	2.3859	2.388	21	s	
20-2	2.2410	-	0	-		20-2	2.2733	-	2	-	
13-2	2.2168	2.2147	10]		22 0	2.2702	2.267	21]	
22 0	2.2138	2.2147	18]	s	13-2	2.2502	2.250	10]	s
22-2	2.0587	2.0588	11	w		22-2	2.1094	2.1097	13	m	
11 2	2.0331	2.0330	25	s		11 2	2.0611	2.0613	28	s	
15 0	1.9575	-	1	-		15 0	2.0330	2.0325	2	vvw	
15-1	1.9400	1.9405	5	vw		15-1	2.0015	2.0031	10	w	
04 2	1.9057	-	0	-		04 2	1.9470	-	0	-	
11-3	1.8934	-	0	-		24-1	1.9160	1.9166	34	vs	
24-1	1.8627	1.8527	35	s		11-3	1.9112	-	0	-	
22 1	1.8502	1.8502	12	m		22 1	1.8905	1.8898	12	w	
24 0	1.8028	-	0	-		06 0	1.8564	1.8578	14	m	
06 0	1.7933	1.7933	17	m		24 0	1.8546	-	0	-	
13 2	1.7931	-	0	-		13 2	1.8251	-	0	-	
15 1	1.7592	1.7593	6	vw		15 1	1.8205	1.8215	9	v	
24-2	1.7218	-	0	-		24-2	1.7638	-	0	-	
15-2	1.7107	-	0	-		05 1	1.7572	1.7585	15	m	
02 3	1.7071	1.7061	2]	vw	15-2	1.7549	-	1	-	
31-1	1.7059	1.7059	3]	vw	31-1	1.7459	-	3	-	
06 1	1.7019	1.7022	18	m		02 3	1.7252	-	4	-	
13-3	1.6950	1.6951	47	vs		13-3	1.7194	1.7205	35	s	
22-3	1.6871	-	2	-		22-3	1.7120	-	3	-	
31-2	1.6533	1.6534	21	s		31-2	1.6886	1.6882	19	m	
31 0	1.6013	1.6015	9	w		31 0	1.6394	1.6396	11	w	
24 1	1.5896	1.5897	31	s		24 1	1.6297	1.6315	25	s	
33-1	1.5565	1.5571	2	vvw		33-1	1.5958	-	0	-	
20 2	1.5538	1.5536	2	vvw		20 2	1.5797	-	0	-	
33-2	1.5153	-	0	-		33-2	1.5519	-	0	-	
11 3	1.5071	1.5070	2	vvw		06 2	1.5339	1.5335	10	v	
04 3	1.4961	-	1	-		15 2	1.5270	-	1	-	
05 2	1.4939	1.4937	12]	m	11 3	1.5251	-	2	-	
22 2	1.4928	1.4937	6]	m	04 3	1.5209	-	3	-	
15 2	1.4920	-	1	-		22 2	1.5197	1.5191	6	vvw	
24-3	1.4825	1.4830	4	vw		26-1	1.5186	-	0	-	
31-3	1.4798	1.4799	3	vvw		17 0	1.5155	-	3	-	
33 0	1.4758	-	0	-		33 0	1.5135	-	0	-	
26-1	1.4729	-	0	-		24-3	1.5111	-	6	-	
17 0	1.4655	1.4657	1	vvw		31-3	1.5056	-	2	-	
17-1	1.4540	-	0	-		17-1	1.5023	-	0	-	
26 0	1.4427	1.4429	3	vvw		26 0	1.4875	-	0	-	
15-3	1.4341	-	1	-		15-3	1.4630	1.4635	3	vvw	
11-4	1.4255	-	0	-		26-2	1.4394	-	1	-	
20-4	1.4099	1.4099	5	vw		11-4	1.4379	-	1	-	
31 1	1.4073	-	1	-		31 1	1.4376	-	1	-	
13 3	1.4012	1.4015	3	vvw		20-4	1.4244	1.4243	5	vvw	

Table 2. Unit-cell dimensions of CrP₄ and MoP₄

	a(Å)	b(Å)	c(Å)	β (°)	V(Å ³)
CrP ₄	5.1914 (5)	10.7600 (8)	5.7712 (6)	110.648 (6)	301.67 (6)
MoP ₄	5.313 (2)	11.139 (7)	5.820 (2)	110.64 (4)	322.4 (4)

Jeitschko & Parthé, 1969), using positional parameters of CrP_4 , gave very good agreement between calculated and observed intensities (Table 1), confirming the CrP_4 -type structure for MoP_4 .

Conductivity measurements on a compact, multiple-crystal sample with the four-probe technique showed metallic conductivity ($\rho_{298^\circ\text{K}} = 2.0 \times 10^{-3}$ ohm.cm, $\rho_{4.2^\circ\text{K}} = 1.2 \times 10^{-3}$ ohm.cm).

Discussion

Fig. 1 shows the densities of the new high-pressure phases, CrP_4 and MoP_4 , as compared with calculated densities of other Cr and Mo phosphides prepared under 'ambient' (in quartz capsules) pressure. It can be seen that the densities of CrP_4 and MoP_4 fit well into the function given by the ambient pressure phases in the systems Mo-P and Cr-P. The question arises whether CrP_4 and MoP_4 might not also be stable at pressures much lower than 65 kbar. Indeed, as mentioned in the experimental section, CrP_4 could also be

prepared in sealed Pyrex tubes at 1000°C and 3 kbar. However, attempts to synthesize CrP_4 or MoP_4 from the elemental components in sealed, evacuated quartz capsules at 600°C resulted in multiple-phase products, whose X-ray patterns did not show the presence of CrP_4 or MoP_4 . Furthermore, single-phase CrP_4 prepared under high pressure formed white phosphorus when annealed in an evacuated quartz capsule at 400°C . Thus, while CrP_4 might still be a stable modification at ambient pressure at temperatures lower than 400°C , our results agree with those of Faller *et al.* (1941), who found CrP_2 and MoP_2 to be the compounds richest in P at ambient pressure.

The structure of CrP_4 is shown in Figs. 2 and 3. It can best be described as a three-dimensional framework structure, although it can be visualized as a layered structure with atoms at $z \approx \frac{1}{4}$ and $\frac{3}{4}$. The Cr atom is surrounded by six P atoms, forming a distorted octahedron. These octahedra share edges and thus form zigzag chains in the z direction. The P atoms are in two nonequivalent sites. Both have four nearest

Table 4. Final positional and thermal parameters of the CrP_4 structure

Numbers in parentheses are e.s.d.'s in the least significant digits.

	x	y	z	$B(\text{\AA}^2)$
Cr in 4(e)	0	0.06241 (3)	$\frac{1}{4}$	0.266 (7)
P(1) in 8(f)	0.27377 (8)	0.08859 (4)	0.67797 (7)	0.367 (8)
P(2) in 8(f)	0.27388 (7)	0.22115 (4)	0.18996 (7)	0.349 (8)

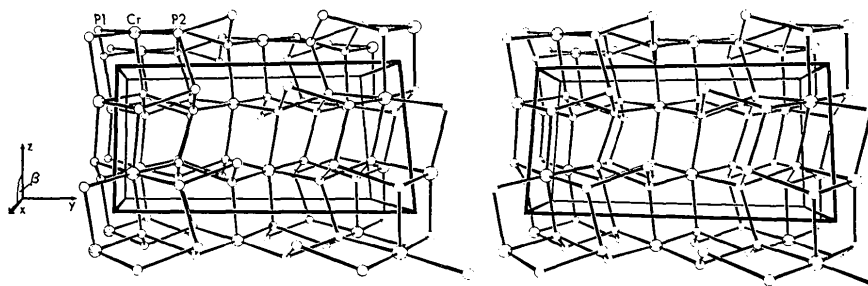


Fig. 2. Stereodiagram of the CrP_4 structure.

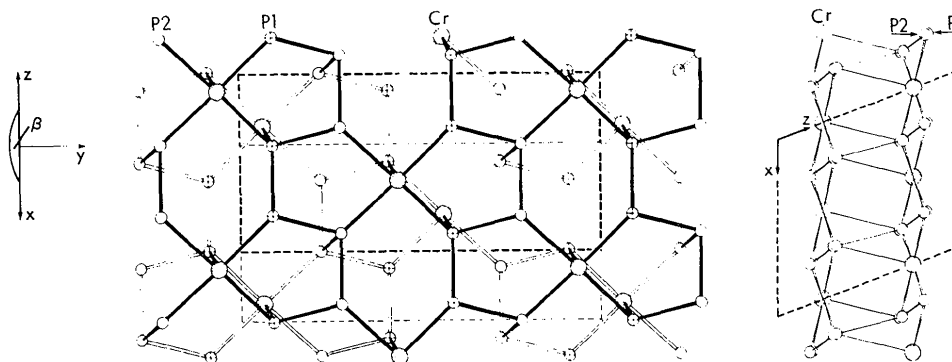


Fig. 3. Normal projections of the CrP_4 structure. In the projection on (001), atoms at $z \approx \frac{1}{4}$ are connected by full lines and atoms $z \approx \frac{3}{4}$ are connected by double lines.

neighbors in approximately tetrahedral configuration: P(1) has two P atoms and two Cr atoms as neighbors while P(2) is surrounded by one Cr atom and three P atoms.

Interatomic distances and angles for CrP_4 are given in Table 5. Fig. 4 shows nearest-neighbor environments. It can be seen that P–P distances vary within the limits 2.21 ± 0.02 Å. These distances are similar to the covalent bonding distances of about 2.22 Å found for Hittorf's phosphorus (Thurn & Krebs, 1969) and the average P–P distance of 2.23 Å found for the black phosphorus modification (Brown & Rundqvist, 1965). In both these phosphorus modifications, the P atom is bound to three P neighbors at three corners of a distorted tetrahedron, while the fourth corner can be thought of as accommodating a nonbonding electron pair.

Table 5. *Interatomic distances and angles in the CrP_4 structure*

Standard deviations were computed from e.s.d.'s of positional parameters and lattice constants; they are all less than 0.001 Å and 0.1° , respectively.

	Cr:	2P(1)	2.3925 Å		
		2P(1)	2.2912		
		2P(2)	2.3252		
		2Cr	3.1828		
P(1):	1Cr	2.3925 Å	P(2):	1Cr	2.3252 Å
	1Cr	2.2912		1P(1)	2.2285
	1P(1)	2.1980		1P(2)	2.2011
	1P(2)	2.2285		1P(2)	2.2070
P(1)–Cr–P(1)	94.41° (2 ×)		Cr–P(1)–Cr	85.59°	
P(1)–Cr–P(1)	166.47		Cr–P(1)–P(1)	123.85	
P(1)–Cr–P(1)	95.17 (2 ×)		Cr–P(1)–P(2)	111.35	
P(1)–Cr–P(2)	84.00 (2 ×)		Cr–P(1)–P(1)	125.44	
P(1)–Cr–P(2)	86.07 (2 ×)		Cr–P(1)–P(2)	116.01	
P(1)–Cr–P(1)	89.67		P(1)–P(1)–P(2)	95.93	
P(1)–Cr–P(2)	177.45 (2 ×)				
P(1)–Cr–P(2)	92.46 (2 ×)		Cr–P(2)–P(1)	118.45°	
P(2)–Cr–P(2)	85.46		Cr–P(2)–P(2)	119.62	
Cr–Cr–Cr	130.08		Cr–P(2)–P(2)	126.40	
			P(1)–P(2)–P(2)	95.41	
			P(1)–P(2)–P(2)	97.30	
			P(2)–P(2)–P(2)	92.67	

CrP_4 and MoP_4 have the highest phosphorus content of known transition metal phosphides. Among non-transition metal phosphides the compounds HgPbP_{14} (Krebs & Ludwig, 1958) and CdP_4 (Krebs, Müller & Zürn, 1956) have been reported. In the HgPbP_{14} structure, most P atoms have a coordination similar to the coordination found in elemental P modifications, while the CdP_4 structure is surprisingly closely related to the CrP_4 structure. As in CrP_4 , the Cd atom is octahedrally coordinated by P atoms, and the two non-equivalent P atoms have tetrahedral environments with three P plus one Cd and two P plus two Cd atoms respectively. The average P–P distance is again 2.21 Å. However, in CdP_4 the $[\text{CdP}_6]$ octahedra are linked over corners in all three dimensions. This difference in the

linkage of octahedra can be understood through the presence of a positive partial charge on Cd, caused by the difference in electronegativity of Cd and P. Since the Cd–Cd distances are larger for corner-sharing octahedra than for edge-sharing octahedra, corner-sharing is more stable from an electrostatic point of view. Conversely, edge-sharing in CrP_4 can be taken as an indication of metal–metal bonding, especially since the composition would permit corner-sharing. Metal–metal bonding can also be inferred from the deviations from ideal tetrahedral and octahedral bond angles around the Cr–Cr bond (Fig. 4): the ideally tetrahedral angle of 109° for Cr–P(1)–Cr is reduced to 86° , and the ideally octahedral angle of 90° for P(1)–Cr–P(1) is increased to 94° , to allow for shorter Cr–Cr contacts. The Cr–Cr distance of 3.18 Å is larger than that of about 2.5 Å in elemental Cr, but may still be considered as bonding.

Assigning a formal valence of zero to each P atom bonded to three P atoms and one Cr atom, and a formal valence of -1 to each P atom bonded to two P and two Cr atoms, the formal valence of Cr in CrP_4 is $+2$ resulting in a d^4 configuration. Alternatively, one arrives at the same result by accounting for 22 out of the total of 26 valence electrons per formula unit CrP_4 , through filling the interacting four sp^3 orbitals (on P) and one d^2sp^3 orbital (on Cr). The remaining four valence electrons can be accommodated in the t_{2g} orbitals of Cr. One of these orbitals – extending in directions perpendicular to the neighboring Cr atoms – can be filled with two spin-compensating electrons. The other two electrons can be accommodated in the remaining two equivalent t_{2g} orbitals, where they can overlap with the corresponding orbitals of the neighboring Cr atoms, thus accounting for the diamagnetic (or Pauli paramagnetic) behavior. The Cr–Cr–Cr angle of 130° compares favorably with the ideal angle of 120° for these assignments.

In this context, the homologous series TX_2 ($T = \text{Fe, Ru, Os}$; $X = \text{P, Sb, As}$) with marcasite structure (Hulliger, 1963) is of interest. In these compounds, the metalloid elements can be considered as forming X_2^{2-} pairs; therefore, the VIIIa metals have formal valence $+4$, resulting again in a d^4 configuration, and the compounds are essentially diamagnetic (Hulliger & Mooser, 1965a). The VIIIa metal is again surrounded by six metalloid atoms in octahedral coordination, and these octahedra share edges. However, these edge-shared octahedra form straight strings in the marcasite-type structure, whereas zigzag chains are formed in the CrP_4 structure. As mentioned above, the zigzag linkage of edge-sharing octahedra is ideal for maximal overlap of two t_{2g} orbitals of the central atoms. The linear linkage of edge-sharing octahedra in marcasites allows maximal overlap for only one t_{2g} orbital. Hulliger & Mooser (1965b) have cautiously denied the presence of metal–metal bonds in d^4 marcasites, while Goodenough (1965) allows for σ and π metal–metal bonding.

Our interpretation of bonding in CrP_4 does not necessarily indicate metallic conductivity. We believe that CrP_4 is essentially a semimetal.

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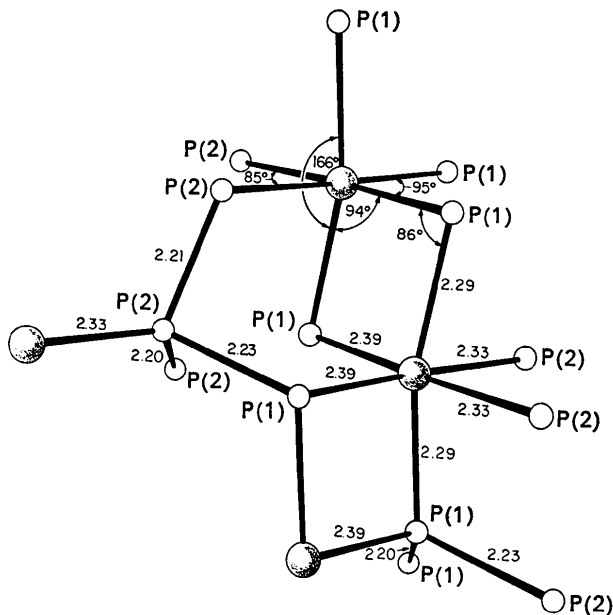


Fig. 4. Nearest-neighbor environments in the CrP_4 structure.