

Stacking Variants of MnP_4 : Preparation and Structure of 6- MnP_4

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Abstract

Two new polymorphs of MnP_4 were prepared by reaction of the elemental components in a tin flux or by chemical transport in the presence of iodine. They can be considered as stacking variants (2- MnP_4 and 6- MnP_4) of a previously reported modification of this composition which is now called 8- MnP_4 . The structure of 6- MnP_4 was determined from single-crystal counter data. It is triclinic, space group $P\bar{1}$, with $a = 16.347$ (3), $b = 5.847$ (4), $c = 5.108$ (3) Å, $\alpha = 115.66$ (2), $\beta = 95.15$ (5), $\gamma = 89.21$ (3)°, and $Z = 6$. Refinement resulted in a final $R = 0.060$ for 1227 structure factors and 63 variable parameters. The near-neighbor environments are very similar to those of 8- MnP_4 : The P atoms are tetrahedrally coordinated by Mn and P atoms, and the Mn atoms are octahedrally coordinated by P atoms. The MnP_6 octahedra are linked *via* edges thus forming infinite zigzag chains. The Mn atoms with formal oxidation number +2 (d^5 system) are displaced from the centers of their octahedra to form pairs with Mn–Mn bonding distances of 2.92 and 2.96 Å. In agreement with a simple bonding description based on classical two-electron bonds, 6- MnP_4 is diamagnetic and semiconducting. As is the case for all transition-metal tetraphosphides the P atoms form a two-dimensionally infinite net of condensed, ten-membered rings. A puckered net of pentagons and hexagons formed by transition-metal and P atoms can be considered as the basic building element of the structures of CrP_4 , 2-, 6-, 8- MnP_4 , and $\beta\text{-FeP}_4$. The different stacking possibilities of this net are described in a systematic way.

Introduction

The polyphosphides of the transition metals (T) with the highest P content known so far have the composition TP_4 . Although one or other of these had probably been prepared by Biltz (1941) and co-workers, structurally they were not well characterized and their compositions were usually given with a somewhat lower P content. The tensimetric studies of Biltz and co-workers showed that these compounds

were not stable at higher temperatures under normal pressure and therefore it is difficult to prepare them in single phase by direct reaction of the elemental components. The first of these compounds, CrP_4 , was prepared in a well crystallized form at high pressure ($15\text{--}65 \times 10^2$ MPa) but could also be obtained at 3×10^2 MPa (Jeitschko & Donohue, 1972) and, more recently, by the tin-flux technique (Braun, 1976; Braun & Jeitschko, 1978). A compound with the composition MnP_4 was also first prepared at high pressure (Jeitschko & Donohue, 1975) but was synthesized later at lower pressure (Braun, 1976; Braun & Jeitschko, 1978; von Schnering, 1976). More recently, the preparations, crystal structures and properties of $\alpha\text{-FeP}_4$ (Jeitschko & Braun, 1978; Grandjean, Gérard, Krieger, Heiden, Braun & Jeitschko, 1980), $\beta\text{-FeP}_4$ (Sugitani, Kinomura, Koizumi & Kume, 1978), RuP_4 and OsP_4 (Braun & Jeitschko, 1978), and ReP_4 (Jeitschko & Rühl, 1979) have been described.

In the present paper we report on two new modifications of MnP_4 (2- MnP_4 and 6- MnP_4) and on the structure determination of one of these (6- MnP_4). They can be considered as stacking variants of the earlier reported modification (Jeitschko & Donohue, 1975) which will be called 8- MnP_4 here.

Sample preparation and properties

In the course of this study we have prepared the three modifications of MnP_4 under a variety of reaction conditions but the exact thermodynamic stability ranges of each stacking variant are not known. Frequently, two and sometimes all three modifications were obtained in the same preparation. Our best preparation procedures for single-phase products are as follows.

6- MnP_4 is obtained best by the tin-flux technique (Jolibois, 1910; Goryunova, Orlov, Sokolova, Shpenkov & Tsvetkova, 1968; Baghdadi, Finley, Russo, Arnott & Wold, 1974; Jeitschko & Braun, 1977). Powders of the elements (all from Merck 'rein') with the atomic ratio Mn:P:Sn = 1:10:6 were annealed in evacuated silica tubes for one or two weeks at temperatures between 820 and 920 K. After

quenching, the samples were treated with moderately diluted hydrochloric acid (1:1) to dissolve the matrix of tin phosphides. The resulting crystals of 6- MnP_4 were not visibly attacked by this procedure. They were analyzed by X-ray fluorescence spectroscopy. No elements other than Mn and P were found. The detectability limit for tin was <0.1 wt %.

The previously characterized modification of MnP_4 (Jeitschko & Donohue, 1975; Braun & Jeitschko, 1978) – now called 8- MnP_4 – can also be prepared in single phase by the tin-flux technique with the same starting composition and the preparation conditions as described above for 6- MnP_4 except that the annealing temperatures are higher: 1020 to 1200 K. 2- MnP_4 is obtained by this technique with starting composition $\text{Mn}:\text{P}:\text{Sn} = 1:10:20$ and with annealing for three weeks at 820 K.

With iodine as catalyst and/or transporting agent we have obtained all three modifications. Here the starting compositions were varied between $\text{Mn}:\text{P} = 1:2$ and $1:4$. About 1 at.% of iodine was added. The samples were annealed in sealed evacuated silica tubes for 6 to 8 weeks. Usually there was a temperature gradient in the tubes with the hot end at temperatures ranging between 770 and 970 K; the cool end was between 50 and 100 K lower. Single-phase 2- MnP_4 was obtained only at the colder parts of the tubes *via* a transport reaction. At the hot ends of the tubes mostly 6- MnP_4 was observed, but 2- MnP_4 and 8- MnP_4 were usually also present in smaller amounts.

In addition to the three modifications of MnP_4 , other manganese phosphides with lower P content were observed in various preparations. Of these, MnP (Rundqvist & Nawapong, 1965) was identified, but we have also obtained a compound with higher P content, the powder patterns of which appear to be similar to the pattern given by Biltz, Wiechmann & Meisel (1937) for the compound MnP_3 .

Similarly to 8- MnP_4 , crystals of 2- and 6- MnP_4 are shiny black, stable in air, and not attacked by non-oxidizing acids. Magnetic measurements with the Faraday technique indicate diamagnetism for all three modifications. The electrical conductivities of 2- and 6- MnP_4 were determined between 4 and 400 K with a four-probe technique (Grandjean, Gérard, Krieger, Heiden, Braun & Jeitschko, 1980). They increase with temperature; thus both compounds are semi-conducting.

Cell dimensions and space group

Single crystals of 6- MnP_4 were examined with $\text{Mo } K\alpha$ radiation in Weissenberg and precession cameras. They have triclinic diffraction symmetry. The structure determination resulted in the centrosymmetric space group $P\bar{1}$. Lattice constants were refined from Guinier

Table 1. Powder diagram of 6- MnP_4

The calculated pattern was generated by a computer program (Yvon, Jeitschko & Parthé, 1977) with data of the refined structure. [Guinier camera, $\text{Cu } K\alpha$ radiation, $Q = 10^4/d^2$ (\AA^{-2}).]

<i>h</i>	<i>k</i>	<i>l</i>	Q_c	Q_o	I_c	I_o	<i>h</i>	<i>k</i>	<i>l</i>	Q_c	Q_o	I_c	I_o
0	0	1	476	477	8	} <i>vw</i>	2	0	-2	1955	1955	5	<i>vw</i>
0	1	-1	477				9	1	-2	2	1983	1984	5
1	-1	1	533	533	20	<i>vw</i>	6	0	1	1985	2963		
1	0	1	538	539	18	<i>vw</i>	2	2	-2	1986		5	
2	-1	1	665	665	11	<i>vw</i>	3	2	-2	2138	2137	4	<i>vw</i>
2	0	1	677	677	14	<i>vw</i>	7	-1	1	2456	2456	10	<i>vw</i>
3	-1	1	872	873	3	<i>vw</i>	7	0	1	2500	2499	10	<i>w</i>
0	2	-1	1199	1199	2	<i>vw</i>	1	-1	-2	2963	2963	3	} <i>m</i>
2	-1	1	1283	1282	78	<i>vs</i>	6	0	-2	2964			
2	2	-1	1326	1325	76	<i>vs</i>	3	3	-1	2965	2963	3	} <i>m</i>
6	0	0	1359	1358	100	<i>vs</i>	7	2	-1	2965			
3	2	-1	1503	1504	5	<i>vw</i>	1	3	-2	2999	2999	20	<i>m</i>
2	-1	2	1783	1783	17	<i>w</i>	8	0	1	3092	3090	11	<i>w</i>
1	0	-2	1891	1891	6	<i>vw</i>	0	3	0	3243	3241	25	<i>m</i>
0	0	2	1903	1905	14	} <i>m</i>	1	3	0	3300	3361	39	} <i>vs</i>
0	2	-2	1908				8	8	-1	-1			
1	2	-2	1909	5	8	-2	-2	3489	3491	8	<i>w</i>		
6	-1	-1	1947	1948	4	<i>vw</i>	8	2	-1	3520	3521	34	<i>s</i>

powder data (Table 1) with α -quartz as standard ($a = 4.9130$, $c = 5.4046$ \AA): $a = 16.347$ (3), $b = 5.847$ (4), $c = 5.108$ (3) \AA , $\alpha = 115.66$ (2), $\beta = 95.15$ (5), $\gamma = 89.21$ (3) $^\circ$, $V = 438.1$ (1) \AA^3 . Lattice constants obtained from samples with different preparation conditions were within the error limits given above for the least significant digits in parentheses. This suggests that the compound has only a limited homogeneity range. With $Z = 6$ the calculated density is 4.07 Mg m^{-3} .

The single-crystal diffraction patterns of 2- MnP_4 usually have systematic non-space-group extinctions which indicate twinning. They could be indexed with a triclinic cell. The cell dimensions refined from Guinier data are: $a = 5.861$ (2), $b = 5.104$ (1), $c = 5.836$ (2) \AA , $\alpha = 93.82$ (1), $\beta = 107.31$ (2), $\gamma = 115.81$ (1) $^\circ$, $V = 146.1$ (1) \AA^3 . These agree well with those obtained independently for this modification by Nöläng & Tergenius (1980). The results of our single-crystal structure determination will be reported shortly (Jeitschko, Rühl, Krieger & Heiden, 1980).

Structure determination

The single crystal of 6- MnP_4 used for the collection of the intensities was taken from a sample prepared with a tin flux with the starting composition $\text{Mn}:\text{P}:\text{Sn} = 1:5:6$ which was heated within a few hours to 1100 K. After one week at this temperature the sample was cooled slowly to room temperature within a week.

The crystal was mounted in random position on a four-circle diffractometer with graphite-monochromatized $\text{Mo } K\alpha$ radiation, a scintillation counter, and a pulse-height discriminator. ω scans were taken over a scan angle of 1° with a speed of $0.05^\circ \text{ s}^{-1}$. Background was counted for 22 s at both ends of each scan.

All reflections within a half-sphere of reciprocal space up to $2\theta = 60^\circ$ were measured. After averaging for equivalent reflections, 2445 unique reflections were obtained for the centrosymmetric space group. No absorption correction was made because of the small size of the crystal ($35 \times 35 \times 50 \mu\text{m}$); $\mu_{\text{MoK}\alpha} = 6.05 \text{ mm}^{-1}$. This yields a value of $\mu r = 0.14$ for the average half-diameter of the crystal.

A Patterson function yielded the locations of the Mn atoms, and the positions of the P atoms were deduced from difference syntheses. The structure was refined with a full-matrix least-squares program (Sheldrick, 1976) using scattering factors for neutral atoms (Cromer & Mann, 1968), corrected for anomalous dispersion (Cromer & Liberman, 1970). Weights were assigned according to $w = 1/[\sigma^2(F_o) + kF_o^2]$ where k is a least-squares parameter which refined to $k = 0.00038$ in the final cycles. An isotropic extinction correction parameter was refined and applied to the F_c values. Because of systematic errors for weak reflections (small F_o values were always greater than their corresponding F_c values) caused by imperfections of the graphite monochromator (ω scans were taken), all reflections with $F_o < 5\sigma$ were assigned zero weight in the final cycles. A final $R = 0.060$ was obtained for the 1227 structure factors with non-zero weight in a refinement with isotropic thermal parameters and a total of 63 variable parameters. For all 2445 reflections $R = 0.128$.* A final difference synthesis showed no features less than -1.6 or greater than $+2.1 \text{ e } \text{Å}^{-3}$. The atom parameters are listed in Table 2, interatomic distances in Table 3.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35648 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Atomic parameters of 6-MnP₄*

All atoms are in the general position of space group $P\bar{1}$. Numbers in parentheses are e.s.d.'s in the least significant digits. Positional parameters are multiplied by 10^4 .

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å ²)
Mn(1)	757 (1)	8781 (4)	8697 (5)	0.20 (3)
P(1)	651 (2)	5709 (7)	119 (8)	0.28 (5)
P(2)	1000 (2)	1727 (7)	7146 (8)	0.30 (5)
P(3)	563 (2)	1916 (7)	3103 (8)	0.24 (5)
P(4)	1160 (2)	5696 (7)	4306 (8)	0.19 (5)
Mn(2)	2586 (1)	5498 (4)	5093 (5)	0.15 (3)
P(5)	2301 (2)	2465 (7)	6560 (8)	0.28 (5)
P(6)	2738 (2)	2403 (7)	734 (8)	0.32 (5)
P(7)	2716 (2)	8589 (7)	3654 (8)	0.23 (5)
P(8)	2200 (2)	8538 (7)	9450 (8)	0.30 (5)
Mn(3)	4067 (1)	8194 (4)	4995 (5)	0.15 (3)
P(9)	4002 (2)	1235 (7)	9538 (8)	0.24 (5)
P(10)	4342 (2)	5283 (7)	562 (8)	0.36 (5)
P(11)	3907 (2)	5043 (7)	6289 (8)	0.27 (5)
P(12)	4503 (2)	1373 (7)	3813 (8)	0.20 (5)

Table 3. *Bond distances (Å) in 6-MnP₄*

The shortest non-bonding Mn–Mn, Mn–P, and P–P distances are: Mn(1)–Mn(2) 3.712, Mn(3)–P(5) 3.700, P(12)–P(12) 2.819 Å. E.s.d.'s are 0.004 Å for Mn–Mn, 0.005 Å for Mn–P, and 0.006 Å for P–P distances.

Mn(1)–P(1)	2.224	P(5)–Mn(2)	2.272
P(2)	2.238	P(6)	2.202
P(3)	2.239	P(7)	2.241
P(3)	2.251	P(2)	2.247
P(4)	2.334	P(6)–Mn(2)	2.212
P(8)	2.368	P(5)	2.202
Mn(1)	2.963	P(9)	2.221
Mn(2)–P(6)	2.212	P(8)	2.231
P(11)	2.235	P(7)–Mn(2)	2.245
P(7)	2.245	Mn(3)	2.291
P(5)	2.272	P(8)	2.223
P(8)	2.303	P(5)	2.241
P(4)	2.339	P(8)–Mn(2)	2.303
Mn(3)	2.923	Mn(1)	2.368
Mn(3)–P(11)	2.236	P(7)	2.223
P(9)	2.241	P(6)	2.231
P(10)	2.247	P(9)–Mn(3)	2.241
P(7)	2.291	P(6)	2.221
P(12)	2.327	P(12)	2.230
P(12)	2.351	P(10)	2.258
Mn(2)	2.923	P(10)–Mn(3)	2.247
P(1)–Mn(1)	2.224	P(11)	2.179
P(4)	2.227	P(9)	2.258
P(2)	2.260	P(10)	2.259
P(1)	2.269	P(11)–Mn(2)	2.235
P(2)–Mn(1)	2.238	Mn(3)	2.236
P(3)	2.172	P(10)	2.179
P(5)	2.247	P(12)	2.228
P(1)	2.260	P(12)–Mn(3)	2.327
P(3)–Mn(1)	2.239	Mn(3)	2.351
Mn(1)	2.251	P(11)	2.228
P(2)	2.172	P(9)	2.230
P(4)	2.234		
P(4)–Mn(1)	2.334		
Mn(2)	2.339		
P(1)	2.227		
P(3)	2.234		

Discussion

Near-neighbor environments in 6-MnP₄ are very similar to those in 8-MnP₄. The Mn atoms are surrounded by six P atoms in an approximately octahedral arrangement. The P atoms are tetrahedrally coordinated either by two Mn and two P atoms or by one Mn and three P atoms. Bonding Mn–P distances vary between 2.212 and 2.368 Å; the P–P distances cover the range from 2.172 to 2.269 Å. The average distances are very similar to those in 8-MnP₄ (in parentheses): Mn–P 2.275 (2.282), and P–P 2.228 (2.225 Å).

Bonding in 6-MnP₄ can again be rationalized with a simple covalent model where all near-neighbor interactions are considered as classical two-electron bonds. By

counting the electrons of the Mn–P bonds as belonging to the P atoms, the Mn atoms obtain the oxidation number +2 (d^5 system). All d orbitals of the Mn atoms can be considered as utilized. The $d_{x^2-y^2}$ and d_{z^2} orbitals participate in the Mn–P bonding ('octahedral $d^2 sp^3$ hybrid') and the remaining three $\sim t_{2g}$ orbitals hold the five electrons which are not involved in Mn–P bonding. Four of these are non-bonding and localized in the (say) d_{xy} and d_{xz} orbitals while the fifth electron uses the remaining d_{yz} orbital which overlaps with the corresponding orbital of a neighboring Mn atom, thus forming a two-electron Mn–Mn bond. This simple rationalization of the bonding situation is supported by the diamagnetism and the semiconductivity of the compound. The bonding Mn–Mn interaction is also evident from the distortions of the coordination polyhedra which allow short Mn–Mn interactions of 2.923 and 2.963 Å (Fig. 1). The corresponding distance in $8-MnP_4$ is 2.941 (2) Å, and in $2-MnP_4$ 2.936 (2) Å.

In counting the electrons of the Mn–P bonds as belonging to the P atoms, the P atoms may be considered as forming a two-dimensionally infinite polymeric P polyanion. It extends parallel to the x and z directions and consists of condensed ten-membered rings (Fig. 2). The other MP_4 compounds ($M = \text{metal}$) also have such ten-membered P rings.* The differences

* References to MP_4 compounds not mentioned in the Introduction have been given earlier (Jeitschko & Rühl, 1979).

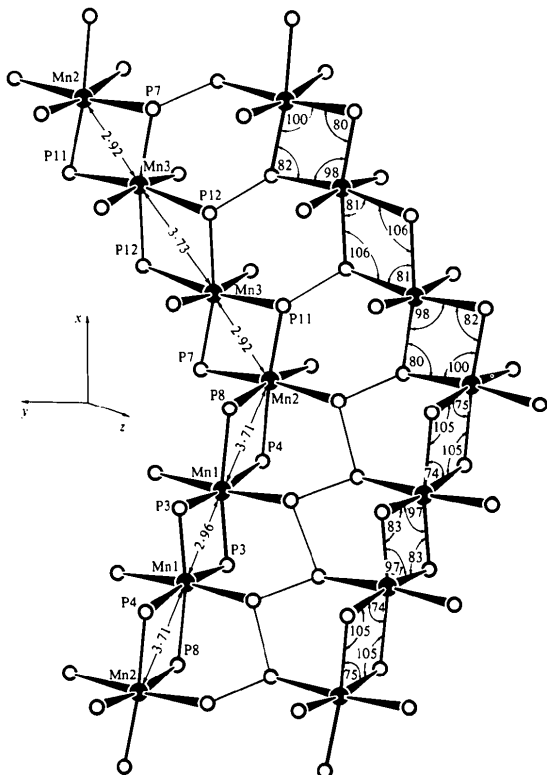


Fig. 1. Near-neighbor environments of the Mn atoms in $6-MnP_4$.

in the structures arise through different modes of condensation. These differences are reflected in the different ways the MP_6 octahedra are linked with each other. In $6-MnP_4$ linear arrays of four edge-sharing octahedra are further linked *via* edges, thus forming infinite zigzag chains. In $8-MnP_4$ linear arrays of four edge-sharing octahedra are connected with each other *via* corners.

The structure of $6-MnP_4$ may also be viewed as a stacking of identical two-dimensionally infinite nets, although bonding within and between the nets is of equal strength. Such nets (Fig. 3) were first outlined to describe the topology of CrP_4 and $8-MnP_4$ and were later also found in $\beta-FeP_4$ and $2-MnP_4$. The differences in the structures arise through the different ways these identical nets are stacked on top of each other. Although the nets are identical within themselves their interactions with neighboring nets are not. The differences in near-neighbor interactions of adjacent nets can (aside from distortions of coordination

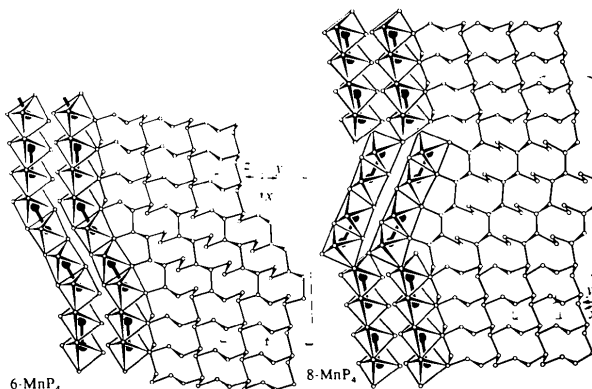


Fig. 2. Comparison of the crystal structures of $6-MnP_4$ and $8-MnP_4$. On the left-hand sides the arrangements of the MnP_6 octahedra are shown. The right-hand sides of the drawings show the condensed ten-membered rings of the phosphorus polyanions. The projection directions are chosen such that the P atoms of the puckered rings do not overlap; the projections are not perpendicular to the planes of the phosphorus polyanions.

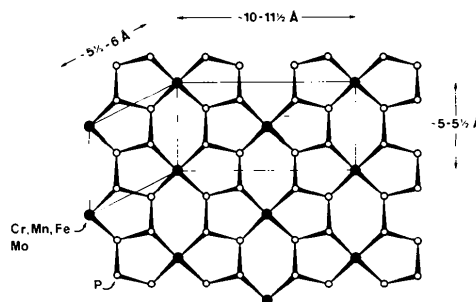
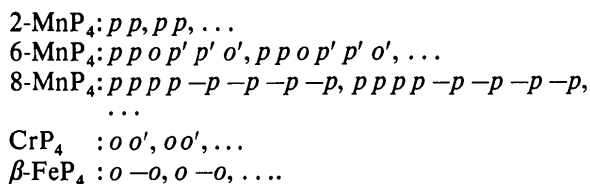


Fig. 3. Puckered net of pentagons and hexagons which can be considered as the basic building element of several MP_4 compounds. The cell dimensions a and b of CrP_4 , $8-MnP_4$, and $\beta-FeP_4$ correspond to the centered rectangular mesh. The cell dimensions a and b of $2-MnP_4$ and $6-MnP_4$ correspond to the primitive mesh outlined on the left-hand side of the figure.

polyhedra) all be described if the near neighbors of the P atoms are considered. All P atoms have three neighbors within one net. Their fourth neighbor belongs to an adjacent net and is either a P or a metal atom. In the latter case the P atom has two metal neighbors: one of its own net and one of the adjacent net above and below. These P atoms are marked with a cross in Fig. 4. All possible ways of connecting adjacent nets can be described with the eight orientations of the nets symbolized by the hexagons and the letters *o* and *p* augmented by primes and minus signs. With these symbols the five crystal structures known so far to be built up with such nets can be described as follows:



It is now clear why we have chosen arabic numbers to differentiate between the three known forms of MnP_4 : the numbers indicate how many nets need to be stacked on top of each other to complete one translation period. It is obvious that the stacking

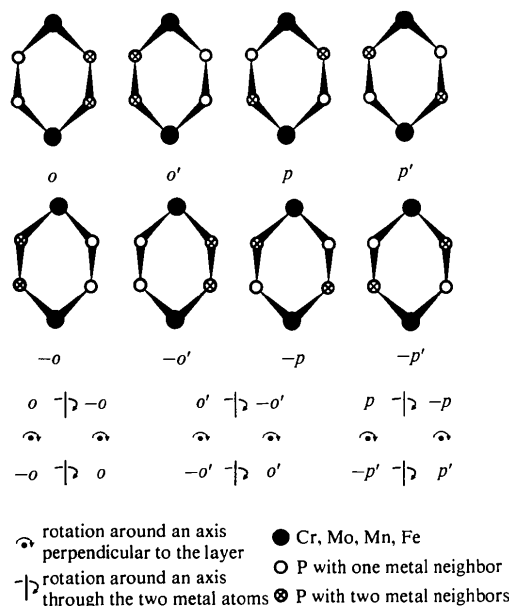


Fig. 4. Six-membered rings indicating different orientations of the net of Fig. 3 and its linkages with adjacent nets. A total of eight different possibilities (all with the rings in chair conformations) have to be considered to describe all known stacking variants of such nets: four where the P atoms with two metal neighbors are in *ortho* (*o*) positions, and four where these P atoms are in *para* (*p*) positions. In the lower part of the drawing it is shown how rotations transform certain orientations of the rings into each other. Only three basically different possibilities remain: one with a *para* form, and two with *ortho* forms which are related like mirror images.

sequence $p p, p p, \dots$ might equally well be described with $p' p', p' p', \dots$ or with $-p -p, -p -p, \dots$. Therefore we have indicated in the lower part of Fig. 4 how these symbols are transformed into each other when one structure is looked at from different viewpoints. Thus 6-MnP_4 can also be described by, for instance, $-p' -p' -o -p -p -o', -p' -p' -o -p -p -o', \dots$ if the structure is thought of as being rotated by 180° around an axis perpendicular to the nets.

It is unfortunate that these stacking symbols do not immediately indicate whether adjacent nets have edge-shared or corner-shared MP_6 octahedra. However, even when the nets are all approximately parallel to each other, as in 2-MnP_4 , the distortions of the polyhedra allow alternating short and long (bonding and non-bonding) Mn–Mn interactions.

It is obvious that further stacking variants are possible. In particular, they should occur in 'solid solutions' of MP_4 compositions with more than one kind of metal.

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