Preparation, Physical Properties and Crystal Structure of $MoNiP_8$ and $WNiP_8$

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Dewalsky, M. V. and Jeitschko, W., 1991. Preparation, Physical Properties and Crystal Structure of $MoNiP_8$ and $WNiP_8$. – Acta Chem. Scand. 45: 828–832.

The title compounds were prepared by reacting powders of the binary transition metal alloys with phosphorus in a tin melt. The crystal structure of the two isotypic polyphosphides was determined from single-crystal diffractometer data of $MoNiP_8$. It is trigonal, with space group $P\bar{3}1c$ (No. 163), a = 623.5(2), c = 874.7(3) pm, Z = 2 and R = 0.015 for 387 structure factors and 18 variable parameters. The Mo atoms have eight P neighbours forming an almost perfect cube; the Ni atoms have slightly distorted octahedral coordination by phosphorus. The P atoms form novel P_8 units the form of which can be derived from a cube. Considering the additional metal neighbours all P atoms obtain the coordination number four. Chemical bonding is discussed on the basis of classical two-electron bonds. A comparison of the interatomic distances suggests that two excess electrons per formula unit occupy antibonding Ni–P states. $MoNiP_8$ is Pauli paramagnetic and has metallic conductivity. The lattice constants of $WNiP_8$ are a = 622.1(1) and c = 874.9(1) pm.

Dedicated to Professor Sten Andersson on the occasion of his 60th birthday.

The transition metals (T) form numerous polyphosphides with the composition TP_4.[1] Ternary compounds with a T:P ratio of 1:4 are also known, e.g. $MoFe_2P_{12}$,[2] $TiMn_2P_{12}$,[3] $NbMn_2P_{12}$[4] and $NbFe_2P_{12}$.[5,6] In these polyphosphides the early transition metals have square-antiprismatic phosphorus coordination, while the late transition metals are surrounded octahedrally by phosphorus atoms. The new polyphosphide $MoNiP_8$ reported here is the first in which the (early) transition metal atoms have eight phosphorus neighbours forming an almost perfect cube. A preliminary account of the structure determination of this compound has been given previously.[7]

Experimental

Sample preparation. Many transition metal polyphosphides are easily prepared by reacting the elemental components in a tin flux.[8] From the ingots thus obtained the transition metal polyphosphides are separated by dissolving the tin-rich matrix in hydrochloric acid. Starting materials were powders of the transition metals (stated purities > 99.9 %), red phosphorus (Hoechst, ultrapure) and tin (Merck, rein). The components were mixed in the atomic ratio Mo(W):Ni:P:Sn = 1:1:40:50, annealed in evacuated, sealed silica tubes at 650 °C for 4 weeks and quenched in air. After the tin-rich matrix had been dissolved the ternary polyphosphides could be identified in the Guinier powder diagrams together with binary polyphosphides and (in samples containing tungsten) the new ternary compound WNi_4P_{16}.[9]

$MoNiP_8$ could be prepared in a pure and well-crystallized form by starting with the binary alloy MoNi,[10] which was prepared by arc melting. This alloy was crushed to a fine powder and reacted in the same ratio as stated above with phosphorus and tin in silica tubes. The annealing conditions were also the same. The analogous procedure with the tungsten alloy also gave much better results; however, after treatment with hydrochloric acid the sample was still not a single phase.

The products were investigated in a scanning electron microscope. Energy dispersive X-ray analyses of the crystals did not reveal any impurities such as silicon or tin.

Chemical and physical properties. The powders of $MoNiP_8$ and $WNiP_8$ are black and stable in air. The $MoNiP_8$ crystals have a metallic lustre. Electrical condutivity measurements of a cold-pressed pellet of $MoNiP_8$ which had been annealed for 7 days with an excess of phosphorus indicated metallic behaviour. The four-probe measurements resulted in an increase of the specific resistivity from 1800 μΩ cm at liquid-helium temperature to 2400 μΩ cm at room temperature. Magnetic measurements in a SQUID magnetometer showed low and weakly temperature-dependent susceptibility, suggesting Pauli paramagnetism.

Structure determination. Single crystals of $MoNiP_8$ were investigated with a precession camera. They had Laue symmetry $\bar{3}m$. The systematic extinctions (*hhl* only with $l = 2n$) led to the space groups $P31c$ *and* $P\bar{3}1c$, of which the higher symmetry group $P\bar{3}1c$ was found to be correct during the structure determination. The lattice constants were

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Table 1. Guinier powder pattern of $WNiP_8$.

hkl	Q_c	Q_o	I_c	I_o
100	344	347	7	w
101	475	475	100	vs
002	523	525	17	m
102	867	866	43	s
110	1033	1032	64	vs
200	1377	1378	12	w
201	1508	1506	66	vs
103	1520	1521	66	vs
112	1556	1555	36	s
202	1900	1899	23	m
004	2090	2092	3	vw
210	2411	2409	5	vw
104	2434	2429	4	vw
211	2541	2537	32	s
203	2553	2551	26	s
212	2933	2930	24	m
300	3100	3096	60	vs
114	3123	3119	79	vs
213	3586	3583	42	s
105	3610	3614	8	m
302	3622		6	
220	4132	4132	14	m
214	4501	4502	3	vw
311	4607	4610	9	w
222	4655	4657	5	vw
312	4999	5004	8	w
106	5047	5050	9	w
304	5189	5193	10	w
313	5653	5652	31	s
215	5676		8	
116	5736	5735	13	m

The Q values are defined by $Q = 100/d^2$ nm^{-2}. The diagram was recorded with Cu $K\alpha_1$ radiation. For the intensity calculation[11] the positional parameters of $MoNiP_8$ were used. Very weak reflections with $I_c < 3$ were omitted. Observed intensities I_o are abbreviated as follows: vs, very strong; s, strong; m, medium; w, weak; vw, very weak.

refined from the Guinier powder data using α-quartz as a standard (a = 491.30 and c = 540.46 pm). The evaluation of such a pattern for the isotypic compound $WNiP_8$ is shown in Table 1. The lattice constants of $MoNiP_8$ are given in Table 2; for $WNiP_8$ they are a = 622.1(1) and c = 874.9(1) pm.

Table 2. Crystal data for $MoNiP_8$.

Diffractometer	Enraf–Nonius CAD-4	
Radiation	Mo $K\alpha$ (graphite monochromated)	
Space group	$P\bar{3}1c$ (No. 163)	
Cell parameter	single-crystal	powder
a/pm	622.2(7)	623.5(2)
c/pm	873(1)	874.7(3)
V/nm^3	0.2927	0.2945
Calculated density/g cm^{-3}	4.54	
Z	2	
Crystal size/mm^3	0.05 × 0.05 × 0.01	
Scan type	θ/2θ	
Scan width θ/°	1.5 × (0.6 + 0.35 × tan θ)	
Minimum scan speed/° min^{-1}	0.4	
2θ limits/°	4–80	
Octants collected	$\pm h \pm k\, l$	
No. of data measured	3921	
Absorption correction	from ψ scan data	
Ratio of transmission factors max/min	1.089	
No. of unique data	688	
Inner residual, R_i	0.029	
No. with $I_o > 3\sigma(I_o)$	387	
No. of variable parameters	18	
Final residual (on Fs), R	0.015	
Weighted residual, R_w	0.017	

Details of the data collection with the single-crystal diffractometer are given in Table 2. The structure was solved by interpretation of the Patterson function and through difference Fourier syntheses. The atomic scattering factors[12] were corrected for anomalous dispersion.[13] An isotropic extinction parameter was optimized during the full-matrix least-squares refinements. A final residual of R = 0.015 was obtained for 387 structure factors and 18 variable parameters. The highest peak in the final difference Fourier synthesis was 1.1 e Å^{-3}.* The atomic positions and interatomic distances are given in Tables 3 and 4. As a check on the composition we also refined occupancy parameters. No deviation from the ideal composition was found: the occupancy parameters varied between 99.7 ± 0.2 % for the Ni position and 100.1 ± 0.1 % for the Mo position.

* Lists of observed and calculated structure factors are available from the authors on request.

Table 3. Atomic parameters of $MoNiP_8$.[a]

Atom	$P\bar{3}1c$	x	y	z	B
Mo	2d	2/3	1/3	1/4	0.289(3)
Ni	2b	0	0	0	0.309(5)
P1	12i	0.045 60(7)	0.321 35(8)	0.153 49(6)	0.362(5)
P2	4f	1/3	2/3	0.037 06(8)	0.385(7)

[a] Standard deviations in the position of the least significant digit are given in parentheses. The program STRUCTURE TIDY[14] was used to standardize the positional parameters. The last column contains the equivalent isotropic B values (×100 in units of nm^2) of the anisotropic thermal parameters.

Table 4. bonds lengths (in pm) and bond angles (in °) in $MoNiP_8$.

Mo:	2 P2	251.1	P1:	1 P1	221.6
	6 P1	254.5		1 P2	224.3
				1 Ni	230.8
				1 Mo	254.5
Ni:	6 P1	230.8	P2:	3 P1	224.3
				1 Mo	251.1

P–Mo–P:	180.00, 3×177.09, 6×109.57, 6×109.38, 3×72.98, 6×70.62, 3×67.93		
P–Ni–P:	3×180.00, 6×90.44, 6×89.56		
P–P1–P:	97.99	P–P2–P:	3×100.98
P–P1–Mo:	115.55, 110.96	P–P2–Mo:	3×117.02
P–P1–Ni:	105.15, 104.01		
Mo–P1–Ni:	120.35		

The shortest nonbonding distances are 393 pm (Mo–P), 421 pm (Mo–Ni), 566 pm (Mo–Mo), 357 pm (Ni–P), 437 pm (Ni–Ni), 284 pm (P–P). The standard deviations of the distances result essentially from the uncertainty of the lattice constants. They are all smaller than 0.1 pm. The standard deviations of the angles are all equal to or smaller than 0.02°.

Discussion

The crystal structure of $MoNiP_8$ is shown in Fig. 1. Considering other polyphosphide structures it is relatively simple, with only four atomic positions (Fig. 2). The Mo atoms have eight P neighbours forming a bicapped trigonal antiprism. The interatomic distances and angles of this coordination polyhedron deviate only slightly from a cube. To our knowledge this is the first example of such an environment for a metal atom in a polyphoshide. In MoP_4, which like $MoNiP_8$ has a metal:phosphorus ratio of 1:4, the Mo atoms have six P neighbours in an octahedral arrangement.[15] Eight-coordination is found for the Mo atoms in $MoFe_2P_{12}$; however, there the phosphorus atoms form a square antiprism.[2]

The Ni atoms have almost perfect octahedral phosphorus coordination. This coordination is also found in NiP_3[16] and in the high-pressure modification of NiP_2,[17] while in the ambient-pressure modification of NiP_2[18] the Ni atoms have four P neighbours forming a square.

Both of the two independent P atoms have distorted tetrahedral coordination, one with one Mo and three P neighbours, and the other one with one Mo, one Ni and two P neighbours. Tetrahedral environments are very common for the phosphorus atoms in transition metal polyphosphides.[1,19] In emphasizing the P–P bonding we obtain two enantiomorphic P_8 units (Fig. 2). They can be derived from a cube by breaking three of the twelve cube edges in such a way that only one three-fold axis of the cube is maintained, with two-fold axes perpendicular to the three-fold axis (point symmetry D_3-32). To our knowledge these P_8 units have not been observed in polyphosphides before.[20]

Chemical bonding in transition metal polyphosphides can usually be well accounted for by the classical concept of

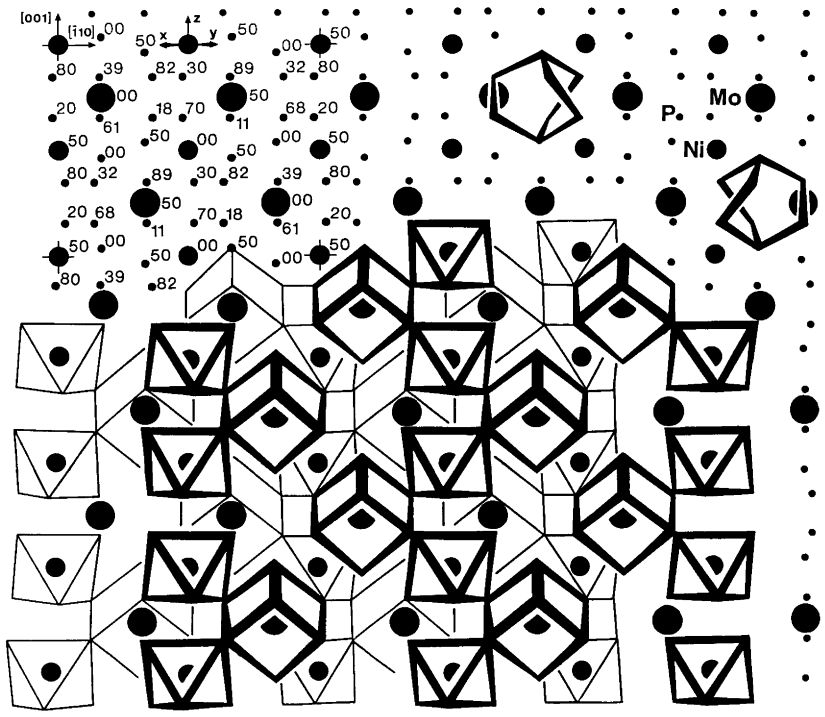

Fig. 1. Crystal structure of $MoNiP_8$ projected along the [110] direction. In the upper left-hand corner the heights of the atoms in the projection direction are given in hundredths. The P_8^{6-} polyanions are shown in the upper right-hand corner. The linkage of the distorted MoP_8 cubes and NiP_6 octahedra is shown below.

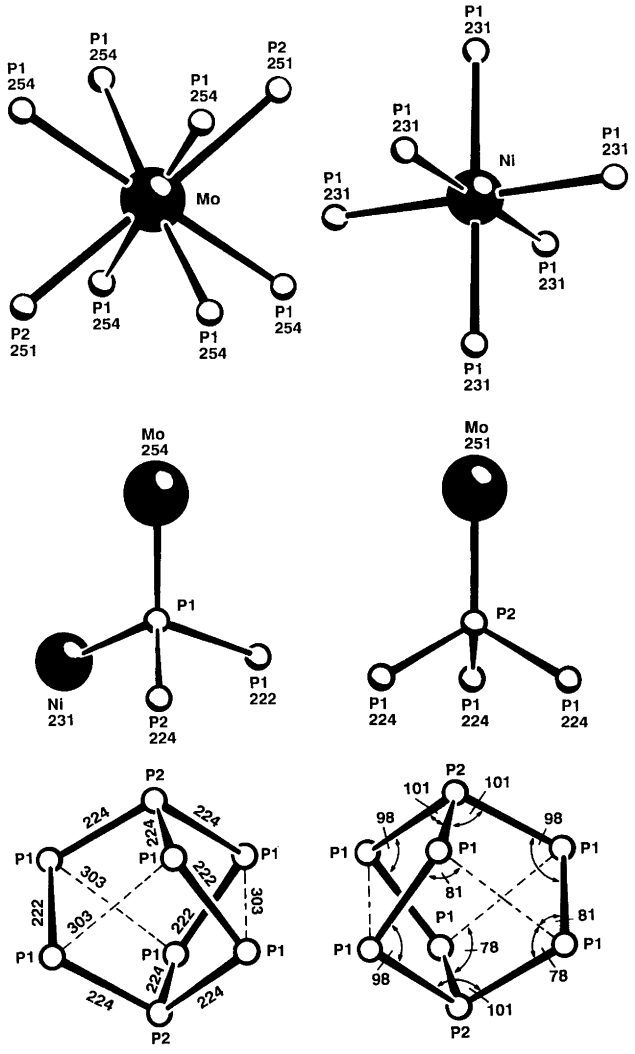

Fig. 2. Near-neighbour environments and the chiral P_8^{6-} polyanions in $MoNiP_8$. Interatomic distances are given in units of pm, interatomic angles in degrees of arc.

the two-electron bond, where two electrons are counted for all T–P and P–P interactions. The two-electron bond model is also the basis for our discussion of bonding in $MoNiP_8$, although we will see that some difficulty arises in this case: not all valence electrons can be accommodated in bonding molecular ('crystal') orbitals.

We reminded the reader how we use oxidation numbers to count electrons. One assumes that the octet rule is valid for the phosphorus atoms. Each phosphorus atom then shares eight electrons with its four neighbours. For P–P bonds we count one electron at each P atom, for T–P bonds we count (this is not in contradiction to the more-or-less covalent character of this bond) both electrons at the phosphorus atom. In this way we establish oxidation numbers for the P atoms which have to be matched by the oxidation numbers of the metal atoms. The important result is that we obtain the number of electrons on the metal atoms which do not participate in the bonding to the phosphorus atoms.

In this way the P1 and P2 atoms of $MoNiP_8$ obtain the oxidation numbers (formal charges) of -1 and 0, respectively. Since there are six P1 and two P2 atoms per formula unit, the P_8 polyanion obtains the oxidation number -6. We thus have to distribute $+6$ formal charges to the two metal atoms. In remaining with the two-electron bond model we need eight atomic orbitals (AOs) of the Mo atoms ("d^4sp^3 hybrid", we will return to this later) and six AOs of the Ni atoms ("d^2sp^3 hybrid") to form the eight Mo–P and six Ni–P bonds of each metal atom. The metal atoms have six (Mo) and ten (Ni) valence electrons; of these six are involved in T–P bonding. The remaining ten valence electrons should be accommodated in nonbonding AOs of the metal atoms. The metal atoms have only one (Mo) and three (Ni) AOs that are not involved in T–P bonding. These four AOs can hold eight electrons, but ten electrons need to be accommodated: thus, we encountered an unexpected difficulty.

If two of the eight P atoms per formula unit were Si atoms (the samples were prepared in silica tubes) no problem would arise. The crystal used for the structure determination was checked again by EDAX; no indication of any silicon content was observed. Even though the atomic scattering factors of silicon and phosphorus are similar, any substantial silicon content can be ruled out. Any significant deviation from the ideal composition could also have been detected by the refinements of the occupancy parameters (see above). Finally, however, the comparison of interatomic distances suggested that the additional two valence electrons per formula unit are accommodated in Ni–P antibonding orbitals.

The average Mo–P distance of the 253.65 pm in $MoNiP_8$ compares quite well with the average Mo–P distance of 253.75 pm in $MoFe_2P_{12}$ (even though in $MoNiP_8$ the eight P atoms form a distorted cube, while they are square antiprismatic in $MoFe_2P_{12}$). The Ni–P bond distance of 230.8 pm in $MoNiP_8$, however, is rather long when compared to the T–P bond distances of 228.1 ± 0.1 pm in NiP_3[16,21] and 222.5 ± 0.1 pm in isotypic CoP_3.[16,22] In all three compounds the Co and Ni atoms, respectively, have octahedral P coordination. The two-electron bond model works quite well for CoP_3, which is semiconducting.[23–25] There the Co atoms obtain an oxidation number of $+3$, i.e. a d^6 system, and all bonding ('crystal') orbitals are occupied. The additional electron in isotypic NiP_3 apparently occupies a delocalized orbital which is antibonding with respect to the Ni–P interactions. This can be concluded from the metallic conductivity of this compound and from the greater bond length of the Ni–P interactions when compared to the Co–P interactions. In $MoNiP_8$ the Ni–P distances are even greater. This correlates with the fact that there are two electrons per Ni atom which have to be accommodated in apparently degenerate antibonding Ni–P orbitals which are not completely filled. This is compatible with the Pauli paramagnetism and the metallic conductivity of the compound. In contrast to the Ni–P bonding electrons, which are counted at the P atoms, the Ni–P antibonding electrons need to be counted

at the Ni atoms (in any case they occupy a band which is mainly composed of the AOs of the nickel atoms) to arrive at a formula with conventional oxidation numbers: $Mo^{4+}Ni^{2+}(P_8)^{6-}$. Even though we have used the two-electron bond model to (at least roughly) rationalize chemical bonding in $MoNiP_8$ we realize that the "extended 8-N" Mooser–Pearson rule[23,26–29] cannot be used to predict possible near-neighbour coordinations for $MoNiP_8$. Furthermore, we note that the 18-electron rule as usually applied is not valid for the Ni atoms in NiP_3 and $MoNiP_8$. In NiP_3 the formal count leads to 19 and in $MoNiP_8$ it leads to 20 electrons per Ni atom.

We conclude with a remark about the almost cubic P coordination of the Mo atoms in $MoNiP_8$. An sp^3d^3f hybridization would be necessary for perfect cubic coordination,[30] however, the $4f$ orbitals are energetically too high in a Mo compound to be available for bonding interactions. In the solid state, packing effects may distort the energetically most favourable bonding situation. In maintaining the two-electron bond model as the most useful first approximation for rationalizing chemical bonding in polyphosphides, we believe that the Mo atoms 'take what they get' i.e. they utilize their d^4sp^3-hybridized orbitals without maximal overlap, and thus for the given composition the structure of $MoNiP_8$ is the best compromise. In this down-to-earth spirit we appreciate Sten Andersson, to whom this paper is dedicated.

Acknowledgements. We thank Mrs. U. Rodewald and Dr. M. H. Möller for data collection on the four-circle diffractometer, Mrs. J. Nowitzki and Dipl.-Chem. K. Zeppenfeld for the magnetic susceptibility measurements, Dipl.-Phys. U. Wortmann for the electrical conductivity measurements, Mr. K. Wagner for the EDAX investigations and Mrs. U. Göcke for competent help with the drawings. Dr. G. Höfer (Heraeus Quarzschmelze) and the Hoechst AG, Werk Knapsack have supported our work through gifts of silica tubes and ultrapure red phosphorus. We also thank the *Fonds der Chemischen Industrie* and the *Deutsche Forschungsgemeinschaft* for financial help.

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Received January 14, 1991.