Crystal Structure Refinements of some MnP-type Phosphides

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Studies of the crystal-chemical as well as other physical and chemical properties of transition metal phosphides affords a rough division of these compounds into two classes.[1,2] The first class comprises the metal-rich phosphides. Structurally, these compounds are characterized by high coordination numbers for both the metal and the phosphorus atoms. The phosphorus atoms tend to be located as far apart as possible in the structures, and the P—P distances generally exceed 3 Å. In phosphides belonging to the second class, the coordination numbers of the atoms are comparatively low. Bonding occurs between the phosphorus atoms which are thereby linked into pairs, four-membered rings, infinite chains or infinite twodimensional networks.

The transition metal monophosphides form an interesting borderline group between two above-mentioned classes of phosphides. The borderline character is manifested by, for example, a tendency towards the formation of P—P bonds in the structures. It appears that the P—P distances in the monophosphides are related to the group number of the metal constituent, the P—P distances becoming shorter as the group number increases. Thus, in the structure of NiP (recently determined by Larsson [3]) the shortest P—P distance is 2.4 Å, which exceeds the normal covalent P—P distance by only 0.2 Å.

The compounds of the 3d transition metals are particularly suitable for studies of this trend in P—P distances, since these metals form an unbroken series of monophosphides. So far, CrP is the only member of this series for which accurate structural information is not available. A structure determination of CrP has therefore been undertaken and the results are reported below.

Polycrystalline CrP was prepared as described in Ref. 4. This material was arc-melted, and single-crystals suitable for X-ray examination were obtained from the melts. The single-crystal used in the structure determination was rotated about the crystallographic *b* axis and had a rather uniform cross-section of about 0.05 mm. Intensities were recorded in a Weissenberg camera with zirconium-filtered Mo*K* radiation using the multiple-film technique with thin iron foils interleaved between successive films. The intensities were estimated visually. Correction of the intensities for absorption was considered unnecessary. The electronic computers BESK and FACIT EDB were used for the following calculations: corrections for Lorentz and polarisation factors,[5] Fourier series summations,[6] structure factor calculations,[6] least squares refinement,[7] and calculation of

Table 1. Atomic parameters, individual isotropic temperature factors (in $Å^2$) and standard deviations for the structures of CrP, MnP, FeP, and CoP.

Phosphide	x	$\sigma(x)$	z	$\sigma(z)$	B	$\sigma(B)$
Parameters for the metal atoms						
CrP	0.0073	0.0003	0.1929	0.0003	0.29_7	0.011
MnP	0.0049	0.0003	0.1965	0.0002	0.22_6	0.009
FeP	0.0019	0.0003	0.2004	0.0002	0.26_8	0.008
CoP	0.0007	0.0003	0.1976	0.0003	0.29_4	0.010
Parameters for the phosphorus atoms						
CrP	0.1853	0.0005	0.5653	0.0005	0.37	0.03
MnP	0.1879	0.0005	0.5684	0.0004	0.34	0.03
FeP	0.1915	0.0005	0.5686	0.0005	0.38	0.03
CoP	0.1913	0.0006	0.5816	0.0006	0.36	0.03

Table 2. Interatomic distances (Å) in CrP, MnP, FeP, and CoP. (Distances shorter than 3.5 Å listed).

Type of distance	Number of equivalent distances	CrP	MnP	FeP	CoP
Me—Me	2	2.768	2.704	2.658	2.605
	2	2.796	2.816	2.791	2.751
	2	3.113	3.172	3.099	3.281
Me—P	1	2.323	2.288	2.241	2.214
	2	2.368	2.341	2.280	2.272
	1	2.436	2.402	2.349	2.354
	2	2.394	2.387	2.349	2.357
P—P	2	2.644	2.660	2.643	2.701
	2	3.113	3.172	3.099	3.281
	2	3.483	3.396	3.339	3.160
	4	3.458	3.420	3.340	3.294

interatomic distances.[6] Atomic scattering factors were interpolated from the values given in Ref. 8.

CrP is known to crystallize with the MnP-type structure (for a full description see, *e.g.*, Ref. 4). The MnP-type structure is generally assumed to possess the symmetry of space group *Pnma*. However, the symmetry might possibly be $Pn2_1a$, and the CrP structure was therefore refined with the least squares method on the basis of this lower symmetry. A total of 70 $F(h0l)$ and 74 $F(h1l)$ values was used in the refinement. The weights assigned were set equal to $1/F_o^2$. Initial x and z parameters were obtained for the atoms from preliminary electron density projections along the b axis. The y parameter of chromium was arbitrarily set equal to $\frac{1}{4}$ and kept fixed, while the y parameter of phosphorus (initial value 0.25) was varied. The refinement converged satisfactorily. It was found, however, that the CrP structure did not deviate significantly from the *Pnma* symmetry. The final y parameter for phosphorus differed from $\frac{1}{4}$ by less than the calculated standard deviation. Accordingly, the structure data for CrP are reported on the basis of space group *Pnma* symmetry.

In connection with the work on CrP it was thought worth while making least-squares refinements of the MnP, FeP, and CoP structures using the intensity material already obtained in a previous investigation.[4] These refinements were carried out in a similar manner as described for CrP, and the results of all four structure refinements are presented in Table 1. The values obtained for MnP, FeP, and CoP do not differ significantly from those reported in Ref. 4. The final R-values for CrP, MnP, FeP, and CoP were 0.074, 0.068, 0.061, and 0.064, respectively. Interatomic distances, based on unit cell dimensions as given in Ref. 4, are listed in Table 2. The standard deviations of the Me—Me distances are calculated to be 0.002—0.003 Å, and those of the Me—P and P—P distances 0.003—0.004 Å.

The results obtained will be the subject of a general crystal-chemical discussion to be published later.

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Homoserine and its Lactone in Pea Seedlings

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The presence of L-homoserine in the pea plant was demonstrated in this laboratory in 1953 when its lactone, α-amino-γ-butyrolactone, was isolated as the hydrochloride in crystalline form from an ethanol extract of pea plants.[1] The extract was boiled first under reflux with 1 N hydrochloric acid for 3 h. Subsequently the unusually vigorous formation of L-homoserine in germinating pea seeds was found[2] and the presence of this amino acid in many different plants established.[3] It was always found in pea seedlings as the free amino acid, and not as the lactone, when the amino acids in the neutral ethanol extract were separated on an Amberlite-IR 120 column and then eluted with ammonia. Also on some paper chromatograms prepared directly from the ethanol extract of the bleeding sap of pea plant only the spot of homoserine but not of its lactone could be observed.

Staron *et al.*[4] have recently published a study according to which the lactone of homoserine is the natural compound in germinating pea seeds and not homoserine itself. This is not in accordance with the findings in this laboratory. In order to elucidate the reason for the different results we have performed the following experiment. Pea seeds ("Thursday II") partially sterilized by sublimate solution ($HgCl_2$) were germinated in the light at room temperature for five days. The germination was slower than usual. The shoots (about 2.5 cm), with small roots attached, were separated from the cotyledons and 5 g was extracted four times with 90 % ethanol (80, 30, 30, 30 ml). The extract was taken to dryness *in vacuo* at about 35° and the residue was dissolved in 12 ml 40 % ethanol. A two-dimensional paper chromatogram (butanol-acetic acid-water and phenol-water) was run, using a volume of solution corresponding to 25 mg

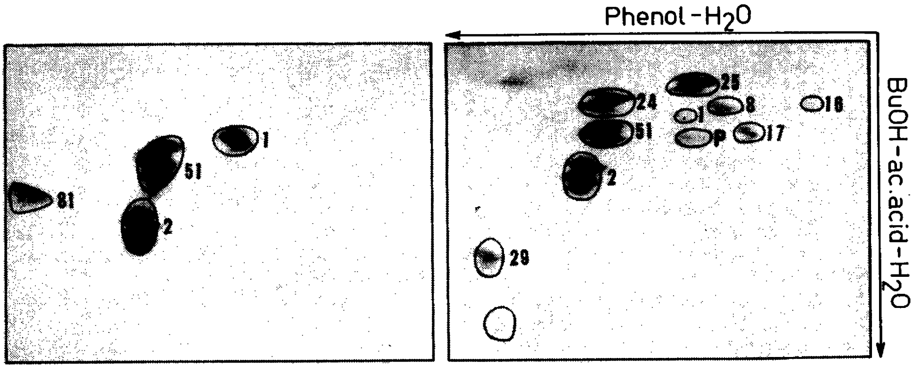

Fig. 1. 2-Dimensional chromatograms of the free amino acids extracted from pea seedlings (minus cotyledones)

left: Control with homoserine 51, its lactone 81, glycine 1 and alanine 2 added

right: Ethanol extract of the seedlings: homoserine 51, gly 1, ala 2, glu NH_2 24, glu 17, asp NH_2 25, asp 16, serine 8, γ-NH_2-butyric acid 29.