

Diphosphides of the Group VIII Transition Metals

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The existence of phosphides with the composition MeP_2 (Me = transition metal) has been established for all Group VIII transition metals¹⁻⁷ except cobalt⁸. The unit cell dimensions and structure types have been determined⁹⁻¹² for FeP_2 , RuP_2 , OsP_2 and PtP_2 , but no X-ray data have so far been published for RhP_2 , IrP_2 , NiP_2 and PdP_2 .

During investigations of transition metal phosphides at this Institute, the above mentioned diphosphides have been synthesised by heating mixtures of metal powder and red phosphorus in evacuated and sealed silica tubes at temperatures between 800°C and 1 100°C. All attempts to grow single-crystals suitable for X-ray work were unsuccessful. However, an analysis of the X-ray powder patterns of RhP_2 , IrP_2 , NiP_2 and PdP_2 showed that the diffraction lines can be indexed on the basis of monoclinic unit cells. The powder data, taken with a Guinier-type focussing camera in $CrK\alpha_1$ radiation (internal calibration standard silicon, $a = 5.4305 \text{ \AA}$) are collected in Tables 1 and 2. Variable unit cell dimensions indicating extended homogeneity

Table 1a. Powder data for RhP_2 . ($CrK\alpha_1$ radiation).

<i>hkl</i>	I_0	$\sin^2\theta_0 \times 10^4$	$\sin^2\theta_c \times 10^4$
100	w—	468	468.4
011	w	843.8	843.8
11 $\bar{1}$	v.st	953.0	953.3
020	st	1 561.4	1 561.6
10 $\bar{2}$	st		1 564.3
111	m	1 670.8	1 671.2
002	st	1 813.1	1 813.8
200	st	1 873.9	1 873.6
11 $\bar{2}$	v.w.	1 954	1 954.7
120	v.w.	2 030	2 030.0
12 $\bar{1}$	m	2 125.2	2 124.5
012	w	2 203.2	2 204.2
20 $\bar{2}$	w+	2 251.8	2 251.6
210	w	2 263.8	2 264.0
21 $\bar{2}$	w	2 642.5	2 642.0
102	m—	3 000.1	3 000.1
12 $\bar{2}$	w	3 125.6	3 125.8
022	m+	3 375.3	3 375.3
220	st	3 435.9	3 435.2
211	st	3 435.4	3 435.4
22 $\bar{2}$	m+	3 812.8	3 813.2
113	st—	3 861.9	3 862.9
031	v.w	3 968	3 967.0
130	st	3 983.1	3 981.9
31 $\bar{1}$	st	3 982.7	3 982.7
13 $\bar{1}$	st	4 076.5	4 076.4
21 $\bar{3}$	m	4 191.3	4 191.3
300	v.w	4 217	4 215.7
013	m	4 471.3	4 471.4
122	m—	4 561.5	4 561.6
131	st	4 795.3	4 794.3

Table 1b. Powder data for IrP_2 . ($CrK\alpha_1$ radiation).

<i>hkl</i>	I_0	$\sin^2\theta_0 \times 10^4$	$\sin^2\theta_c \times 10^4$
100	w—	460	459.2
011	w+	833.9	833.9
11 $\bar{1}$	v.st	961.3	961.0
020	st	1 564.2	1 563.4
10 $\bar{2}$	st		1 567.0
111	st	1 625.5	1 625.2
002	st	1 772.4	1 772.0
200	st	1 836.9	1 836.9
11 $\bar{2}$	v.w	1 959	1 957.9
120	v.w	2 023	2 022.7
12 $\bar{1}$	w+	2 134.4	2 133.6
012	v.w	2 165	2 162.8
210	w	2 227.7	2 227.8
20 $\bar{2}$	m+	2 280.9	2 280.6
21 $\bar{2}$	v.w	2 673	2 671.4
102	m	2 895.0	2 895.4
12 $\bar{2}$	w+	3 130.7	3 130.5
211	st	3 335.6	3 334.9
022	st	3 335.6	3 335.4
220	st	3 400.5	3 400.4
11 $\bar{3}$	st		3 840.8
22 $\bar{2}$	st+	3 843.0	3 844.0
031	st		3 960.7
31 $\bar{1}$	st	3 970.8	3 970.7
130	st		3 977.0
13 $\bar{1}$	st	4 087.8	4 087.9
21 $\bar{3}$	m	4 222.4	4 222.2
013	m	4 377.7	4 377.8
122	m	4 458.3	4 458.8
131	st	4 752.2	4 752.0
202	m	4 937.5	4 937.2

Table 2a. Powder data for NiP₂. (CrK α ₁ radiation).

<i>hkl</i>	<i>I</i> ₀	sin ² Θ ₀ × 10 ⁴	sin ² Θ _c × 10 ⁴
11 $\bar{1}$	w	843.1	843.0
110	m	912.5	912.6
020	m	1 662.6	1 662.6
20 $\bar{2}$	st	1 709.1	1 709.6
11 $\bar{2}$	m	1 866.0	1 866.1
200	m	1 987.9	1 987.6
111	m	2 074.7	2 074.6
002	v.w	2 186	2 185.0
021	m	2 208.1	2 208.9
2 $\bar{2}$ $\bar{1}$	v.w	2 966	2 965.0
2 $\bar{2}$ $\bar{2}$	m	3 371.9	3 372.2
31 $\bar{2}$			3 378.3
31 $\bar{1}$	w	3 586.1	3 586.8
220	m	3 649.8	3 650.2
022	m	3 846.3	3 847.6
11 $\bar{3}$	v.w	3 982	3 981.6
130	st	4 238.1	4 237.8
31 $\bar{3}$	v.w	4 261	4 262.3
112	st	4 329.0	4 329.1
2 $\bar{2}$ $\bar{3}$	v.w	4 874	4 872.0
310	m	4 888.0	4 887.8

Table 2b. Powder data for PdP₂. (CrK α ₁ radiation).

<i>hkl</i>	<i>I</i> ₀	sin ² Θ ₀ × 10 ⁴	sin ² Θ _c × 10 ⁴
11 $\bar{1}$	v.w	778	776.9
110	v.st	823.0	822.9
020	m+	1 528.4	1 528.6
20 $\bar{2}$	st	1 578.9	1 578.9
200	st	1 762.9	1 763.0
11 $\bar{2}$	st	1 782.1	1 782.0
111	w	1 919.6	1 920.0
021	w	2 054.6	2 054.1
002	w	2 102.0	2 102.2
31 $\bar{2}$	w	3 021.8	3 021.7
2 $\bar{2}$ $\bar{2}$	m	3 107.7	3 107.5
31 $\bar{1}$	v.w	3 161	3 159.7
220	m	3 290.9	3 291.6
022	m	3 631.1	3 630.8
13 $\bar{1}$			3 834.0
11 $\bar{3}$	v.w	3 838	3 838.1
130	st	3 880.2	3 880.0
31 $\bar{3}$	v.w	3 933	3 934.7
112	st	4 067.7	4 068.2
310	m	4 348.9	4 348.9
40 $\bar{2}$	m	4 581.9	4 581.6
2 $\bar{2}$ $\bar{3}$	v.w	4 590	4 592.1
13 $\bar{2}$	m	4 840.2	4 839.1
221	v.w	4 960	4 960.3

Table 3. Unit cell data for RhP₂, IrP₂, NiP₂ and PdP₂. (Estimated accuracy of the cell dimensions \pm 0.02 %).

Phosphide	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	β °	<i>U</i> (Å ³)
RhP ₂	5.742 ₂	5.794 ₂	5.837 ₀	112° 91 ₁	178.9
IrP ₂	5.745 ₇	5.790 ₆	5.850 ₀	111° 60 ₀	181.0
NiP ₂	6.365 ₅	5.615 ₂	6.071 ₅	126° 22 ₄	175.1
PdP ₂	6.777 ₁	5.856 ₃	6.206 ₃	126° 42 ₇	198.2

ranges were not observed. The unit cell dimensions are given in Table 3.

It has been hinted that RhP₂ and IrP₂ are isostructural^{3,4,10}. A comparison of the data in Tables 1a and 1b shows that this is undoubtedly true. Furthermore, it seems probable that these two phases are isostructural with RhSb₂, the unit cell dimensions of which are reported to be¹³ $a = 6.6$ Å; $b = 6.4$ Å; $c = 6.7$ Å; $\beta = 117^\circ$; probable space-group $P 2_1/c$ with four formula units in the cell.

NiP₂ and PdP₂ are also isostructural as seen from Tables 2a and 2b. The data indicate that the unit cells are face-centred, and this is not contradicted by powder data taken with CuK α radiation up to $\Theta = 45^\circ$. The space-group might possibly be $C 2/c$ or Cc , and the unit cells contain four formula units.

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1. Franke, W., Meisel, K., Juza, R. and Biltz, W. *Z. anorg. Chem.* **218** (1934) 346.
2. Biltz, W., Ehrhorn, H. J. and Meisel, K. *Ibid.* **240** (1939) 117.
3. Faller, F. E., Strotzer, E. F. and Biltz, W. *Ibid.* **244** (1940) 317.
4. Söfge, K. H., Heimbrecht, M. and Biltz, W. *Ibid.* **243** (1940) 297.
5. Biltz, W. and Heimbrecht, M. *Ibid.* **237** (1938) 132.
6. Wiehage, G., Weibke, F., Biltz, W., Meisel, K. and Wiechmann, F. *Ibid.* **228** (1936) 357.
7. Biltz, W., Weibke, F., May, E. and Meisel, K. *Ibid.* **223** (1935) 129.
8. Biltz, W., Heimbrecht, M. and Meisel, K. *Ibid.* **241** (1939) 349.
9. Meisel, K. *Ibid.* **218** (1934) 360.
10. Rundqvist, S. *Nature* **185** (1960) 31.

11. Thomassen, L. *Z. physik. Chem.* **B 4** (1929) 277.
12. Kjekshus, A. *Acta Chem. Scand.* **14** (1960) 1450.
13. Zhuravlev, N. N., Pak Gvan, O. and Kuz'min, R. N. *Vest. Mosk. Univ. Ser. mat., mekhan., astron., fiz., khim.*, No. 5 (1958) 79. (See The Abstracts Journal for Metallurgy, Part A, Nr. 9/10 (1959) 50).

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Reactivity of Coordinated Substances

I. The Oxidation of EDTA Bound in the Cr(III)EDTA Complex by Permanganate Ion

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Earlier observations showed that free EDTA is oxidised by permanganate ion in acidic solution. Addition of Bi(III) in excess to EDTA results in a marked decrease of the reaction rate: the complex formation with Bi(III) protects the EDTA¹ against the oxidising effect of MnO₄⁻.

This qualitative result suggests that it is possible to decide by a direct chemical method between the different types of coordination of EDTA to different metal ions. For this purpose we compared the oxidation of EDTA in the presence of excess Bi(III) and that of the inert Cr(III)EDTA complex by MnO₄⁻. The reaction was studied in perchloric acid medium at 20 ± 1–2°C by means of spectrophotometric investigations.

As is shown in Fig. 1, the Bi(III)EDTA complex is oxidised very slowly (curve 1), while the oxidation of Cr(III)EDTA takes place much faster (curve 2). Under

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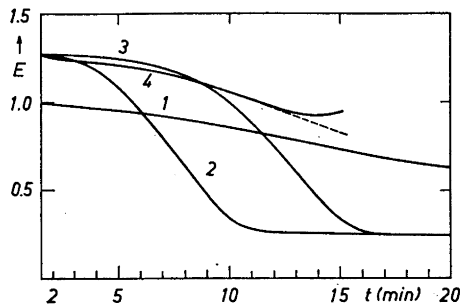


Fig. 1. Change of extinction (E) with time (t) of the following solutions: Curve 1. 2×10^{-3} M Bi(III), 10^{-3} M EDTA, 2.12×10^{-4} M MnO₄⁻, 0.23 M HClO₄. Curve 2. 10^{-3} M Cr(III)EDTA, 2.12×10^{-4} M MnO₄⁻, 0.23 M HClO₄. Curve 3. 10^{-3} M Cr(III)EDTA, 2×10^{-3} M Bi(III), 2.12×10^{-4} M MnO₄⁻, 0.23 M HClO₄. Curve 4. 10^{-3} M Cr(III)EDTA, 2.12×10^{-3} M Mn(II), 2.12×10^{-4} M MnO₄⁻, 0.23 M HClO₄. Wavelength 525 mμ, cell length 2 cm.

similar conditions the reduction of MnO₄⁻ by free EDTA is completed within 30 sec. This characteristic behaviour may be explained most simply by the existence of at least one free functional group in the Cr(III)EDTA compound, i.e. the pentadentate nature of EDTA in this complex².

If Bi(III) is added to the Cr(III)EDTA the oxidation rate decreases (curve 3). This effect can be interpreted by an interaction of free Bi(III) and Cr(III)EDTA. It must be mentioned, however, that so far this interaction could not be demonstrated by other methods.

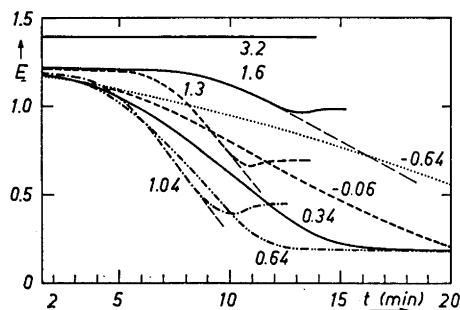


Fig. 2. The effect of pH on the reduction of MnO₄⁻ by Cr(III)EDTA complex. Numbers indicate pH values of solutions: 10^{-3} M Cr(III)EDTA, 2.12×10^{-4} M MnO₄⁻. Wavelength 525 mμ, cell length 2 cm.