distorted Cd/NaO_4 tetrahedron (see Table 2) considerably exceeds the predicted distance of 2·255 Å. The resulting 'loose' fit in this tetrahedron is reflected in the appreciably larger amplitudes of vibration of the Cd/Na composite atom as compared with the nearly equally massive V atom: the r.m.s. amplitudes of the former are 0·153, 0·141 and 0·122 Å along the crystal axes, the latter are 0·086, 0·115 and 0·088 Å.

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Structure Refinement of Hafnium Phosphide, Hf_3P

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Abstract. $M_r = 566·4$, Ti_3P-type tetragonal structure, $P4_2/n$, $a = 10·6654$ (4), $c = 5·2925$ (3) Å, $U = 602·02$ Å^3, $Z = 8$, $D_x = 12·49$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 109·3$ mm^{-1}, room temperature, $F(000) = 1848$. The crystal structure has been refined from visually estimated intensity data obtained from Weissenberg X-ray photographs [$R(F) = 0·072$ for 341 reflections]. The atomic coordination follows rules formulated earlier for representatives of the Fe_3P–Ti_3P–V_3S–Hf_3As family of structures.

Introduction. The atomic coordination in compounds crystallizing with the Fe_3P-, Ti_3P-, α-V_3S- and β-V_3S-type structures was thoroughly discussed by Rundqvist, Andersson & Pramatus (1979). Some interesting coordination trends were observed, suggesting an empirical rule for the coordination of metal neighbours about the non-metal atoms. Later, the structure of Hf_3As was determined by Willerström, Carlsson & Rundqvist (1980) and classified as a new member of the Fe_3P–Ti_3P–V_3S structure family. The atomic coordination in Hf_3As was consistent with the empirical coordination rule proposed, and more recent structure refinements of Hf_3Sb and h-Ta_3Ge (Willerström & Rundqvist, 1981) and Tc_3P (Rühl, Jeitschko & Schwochau, 1982) also supported the validity of the rule. In connection with these studies it seemed worthwhile to refine the structure of Hf_3P. The occurrence of this compound was first reported by Ganglberger, Nowotny & Benesovsky (1966). They found that Hf_3P crystallizes with the Ti_3P-type structure, which was later confirmed by Lundström & Tansuriwongs (1968). In the present work, the Hf_3P structure was refined using a single crystal selected from material provided by Professor S. Rundqvist of the Inorganic Chemistry Department of Uppsala University, Sweden.

Experimental. An Hf_3P powder diffraction photograph obtained using a Guinier–Hägg-type focusing camera (Philips XDC-700), Cu $K\alpha_1$ radiation (Deslattes & Henins, 1973), silicon SRM-640 ($a = 5·43088$ Å) (Hubbard, Swanson & Mauer, 1975) as internal calibration standard; unit-cell dimensions refined by the least-squares method, the result being in satisfactory agreement with that reported by Lundström & Tan-

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suriwongs (1968). An Hf_3P single crystal in the form of a flat plate of irregular shape with approximate dimensions 0·04 × 0·09 × 0·02 mm was mounted; the c axis, which was almost parallel to the long edge of the crystal, taken as the rotation axis; Weissenberg photographs ($l = 0,1,2,3$) recorded, Zr-filtered Mo $K\alpha$ radiation, multiple-film technique, thin silver or iron foils between successive films; intensities measured by visual comparison with an intensity scale obtained by timed exposures of one reflection from the crystal; Lorentz and polarization corrections, as well as an absorption correction using the Gaussian grid method applied; atomic scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); absorption coefficients from *International Tables for X-ray Crystallography* (1962), transmission factors between 0·0165 and 0·1712. Full-matrix least-squares refinement of scale factors, one isotropic-extinction parameter, atomic positional parameters and isotropic temperature factors performed using standard crystallographic programs (Lundgren, 1976) on an IBM 370/138 computer; Cruickshank's weighting scheme (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961), $w = 1/(c_1 + |F_o| + c_2 \times |F_o|^2)$, applied with $c_1 = 105{\cdot}86$ and $c_2 = 0{\cdot}00233$; $R_w = 0{\cdot}090$;* a δR normal probability plot (Abrahams & Keve, 1971) was an almost straight line with a slope of 1·01 and an intercept at −0·08; isotropic-extinction parameter 1·6 (2).

Discussion. The structure data obtained are given in Table 1, and the interatomic distances in Table 2.

In the structures of Fe_3P- and Ti_3P-type compounds, the non-metal atoms are surrounded by nine near-neighbour transition-metal atoms. As first observed by Nawapong (1966) in the case of Nb_3P, and later by Rundqvist *et al.* (1979) in a further number of cases, one metal neighbour can occasionally be much more distant from the central non-metal atom than the remaining eight. For phosphides, where a fairly large number of accurate structure determinations was available, an empirical rule was found: the greater the cohesive strength of the parent metal, the smaller the coordination number for P in the corresponding phosphide (Rundqvist *et al.*, 1979). In the series V_3P, Nb_3P, α-Ta_3P (all crystallizing with the Ti_3P-type structure), for instance, the ninth metal neighbour moves progressively further away from the central P atom, consistent with the increasing cohesive energy in the series V, Nb, Ta.

The metal-atom coordination about P in the series Ti_3P, Zr_3P, Hf_3P is illustrated histographically in Fig. 1.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38413 (4 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Structure data for* Hf_3P

Space group $P4_2/n$ (No. 86), origin at $\bar{1}$; all atoms in positions 8(g). Standard deviations are in parentheses.

	x	y	z	B(Å^2)
Hf(1)	0·1652 (2)	0·6422 (2)	0·7195 (10)	0·40 (4)
Hf(2)	0·1120 (2)	0·2780 (2)	0·5268 (11)	0·44 (5)
Hf(3)	0·0694 (2)	0·5343 (2)	0·2380 (11)	0·46 (5)
P	0·0426 (15)	0·2877 (14)	0·027 (6)	0·24 (21)

Table 2. *Interatomic distances* (Å) *in* Hf_3P

Distances shorter than 5·0 Å are listed. Standard deviations are in parentheses.

Hf(1)—2P	2·70 (2)	Hf(3)—1P	2·65 (2)
—1Hf(1)	2·926 (4)	—1P	2·76 (2)
—1Hf(3)	2·977 (7)	—1P	2·87 (2)
—1Hf(3)	3·139 (3)	—1Hf(1)	2·977 (7)
—1Hf(3)	3·146 (7)	—1Hf(3)	3·012 (10)
—1Hf(2)	3·256 (4)	—1Hf(2)	3·050 (4)
—1Hf(3)	3·299 (3)	—1Hf(2)	3·058 (5)
—1Hf(2)	3·341 (4)	—1Hf(1)	3·139 (3)
—4Hf(1)	3·359 (2)	—1Hf(1)	3·146 (7)
—1Hf(3)	3·379 (3)	—1Hf(2)	3·165 (5)
—1Hf(2)	4·056 (4)	—1Hf(3)	3·228 (10)
—1P	4·32 (2)	—1Hf(1)	3·299 (3)
—1P	4·49 (2)	—1Hf(1)	3·379 (3)
—1P	4·52 (2)	—1Hf(2)	3·958 (4)
—1P	4·59 (3)	—1P	4·11 (2)
—1P	4·64 (3)	—1P	4·49 (3)
—1Hf(2)	4·939 (7)	—1Hf(2)	4·674 (7)
		—1P	4·74 (3)
Hf(2)—1P	2·69 (2)	—1Hf(2)	4·746 (7)
—1P	2·74 (2)	—1Hf(2)	4·913 (7)
—2P	2·75 (3)	—1P	4·94 (3)
—1Hf(2)	3·004 (4)	—1Hf(2)	4·990 (4)
—1Hf(3)	3·050 (4)	—1Hf(2)	4·998 (4)
—1Hf(3)	3·058 (5)		
—1Hf(3)	3·165 (5)	P—1Hf(3)	2·65 (2)
—2Hf(2)	3·177 (9)	—1Hf(2)	2·69 (2)
—1Hf(1)	3·256 (4)	—2Hf(1)	2·70 (2)
—1Hf(1)	3·341 (4)	—1Hf(2)	2·74 (2)
—2Hf(2)	3·619 (10)	—2Hf(2)	2·75 (3)
—1Hf(3)	3·958 (4)	—1Hf(3)	2·76 (2)
—1Hf(1)	4·056 (4)	—1Hf(3)	2·87 (2)
—2P	4·59 (2)	—2P	3·96 (4)
—1Hf(3)	4·674 (7)	—1Hf(3)	4·11 (2)
—1Hf(3)	4·746 (7)	—1Hf(1)	4·32 (2)
—1P	4·86 (2)	—2P	4·33 (5)
—1Hf(3)	4·913 (7)	—1Hf(3)	4·49 (3)
—1Hf(1)	4·939 (7)	—1Hf(1)	4·49 (2)
—1Hf(3)	4·990 (4)	—1P	4·50 (3)
—1Hf(3)	4·998 (4)	—1Hf(1)	4·52 (2)
		—2Hf(2)	4·59 (2)
		—1Hf(1)	4·59 (3)
		—1P	4·63 (3)
		—1Hf(1)	4·64 (3)
		—1Hf(3)	4·74 (3)
		—1Hf(2)	4·86 (2)
		—1Hf(3)	4·94 (3)

The histograms indicate the number of metal—phosphorus distances within given intervals of D/d, where D is the sum of the Goldschmidt radius for 12-coordination for the transition-metal atoms (1·45, 1·60 and 1·58 Å, respectively, for Ti, Zr and Hf) and the covalent radius for P (1·10 Å), and d is the distance from the central P atom to a metal neighbour.

It is evident from the histograms in Fig. 1 that the P coordination exhibits the same trend as in the series V_3P, Nb_3P, α-Ta_3P (compare Fig. 2 of Rundqvist *et*

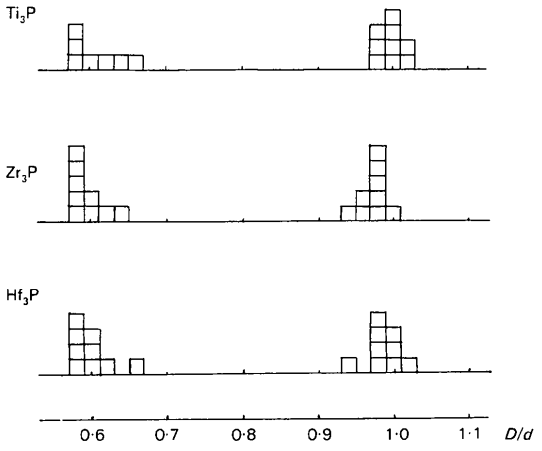

Fig. 1. Histographic representation of the coordination of metal (Hf, Zr, Ti) atoms about the P atoms in the structures of Hf_3P, Zr_3P, and Ti_3P. Each square corresponds to one interatomic distance. D is the sum of the Goldschmidt radius for the metal atom and the covalent radius for the P atom, and d is the metal–phosphorus interatomic distance.

al., 1979). The tendency towards eight-coordination is more pronounced in the latter case. This is again in agreement with the empirical rule, since the cohesive energies of the V-group metals are larger than those of the corresponding metals in the Ti group.

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Structure de l'Hydroxyborate de Thallium Hydraté, $Tl[B_3O_4(OH)_2].0{,}5H_2O$

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Abstract. $M_r = 343{\cdot}8$, orthorhombic, *Pnma*, $a = 13{\cdot}41$ (2), $b = 16{\cdot}17$ (3), $c = 5{\cdot}43$ (1) Å, $V = 1177$ Å^3, $Z = 8$, $D_m = 3{\cdot}68$, $D_x = 3{\cdot}87$ Mg m^{-3}, Mo $K\bar{\alpha}$, $\lambda = 0{\cdot}71069$ Å, $\mu = 275$ cm^{-1}, $F(000) = 1208$, $T = 293$ K, $R_w = 0{\cdot}055$ for 1154 independent reflexions. The structure contains a $[B_3O_4(OH)_2]^-$ unit formed by one tetrahedron and two triangles. These units are linked together to form an infinite $[B_3O_4(OH)_2]_n^{n-}$ chain twisted around and along the 2_1 axes; between these chains linked by hydrogen bonds, Tl^+ and H_2O are localized. Dehydration occurs in two steps and leads to an amorphous phase; annealing gives crystalline

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