the Sn···F interactions as being secondary bonds (Alcock, 1972).

The observed N—N distance in the $[N_2H_6]^{2+}$ ion of 1·428 (4) Å is as expected for the hydrazinium(2+) ion (*International Tables for X-ray Crystallography*, 1962). The $[N_2H_6]^{2+}$ cation forms six N—H···F hydrogen bonds. A projection of the $[N_2H_6]^{2+}$ ion down the N—N bond is shown in Fig. 2. The hydrogen-bond distances are in the usual range of 2·620 (4) to 2·707 (5) Å (Table 2) (Anderson *et al.*, 1973; Kojić-Prodić, Šćavničar & Matković, 1971; Golič & Lazarini, 1974; Golič *et al.*, 1980). There are some additional N···F contact distances [2·850 (4), 2·956 (4) Å], which suggest bifurcated hydrogen bonds. The tetrahedral H—N—H and H—N—N angles range from 106 (3) to 114 (7)° (Table 2).

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The Synthesis and Structure of Heptacobalt Tetrakis(hydrogenphosphate) Bis(phosphate)

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Abstract. $Co_7(PO_4)_2(HPO_4)_4$, $M_r = 986·4$, triclinic, $P\bar{1}$, $a = 6·466$ (4), $b = 9·480$ (2), $c = 7·871$ (2) Å, $\alpha = 104·29$ (2), $\beta = 101·35$ (3), $\gamma = 109·10$ (3)°, $V = 421·0$ Å³, $D_x = 3·884$ g cm⁻³, $Z = 1$, $\lambda(\text{Mo } K\alpha) = 0·7107$ Å, $\mu = 74·1$ cm⁻¹, $F(000) = 475$, room temperature, $R = 0·017$, $wR = 0·021$ for 2122 unique reflections, $I > 3\sigma(I)$. The new phase was synthesized hydrothermally, and is isostructural with $Mn_7(PO_4)_2(HPO_4)_4$. The structure is based on a framework of edge- and corner-sharing CoO_6, CoO_5 and PO_4 polyhedra, isotypic with that found in the mixed-valence iron phosphate $Fe_7(PO_4)_6$. In the present case, the cobalt is found purely in the divalent state, the

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necessary charge balance being maintained by the addition of H atoms in the form of bridging Co—OH—P groups.

Introduction. During the course of our studies on the exploratory synthesis of some first-row transition-metal phosphates by hydrothermal methods, we have previously reported the synthesis and structure of $Mn_7(PO_4)_2(HPO_4)_4$ (Lightfoot & Cheetham, 1986). The structure was found to be related to that of the mixed-valence iron phosphate $Fe_3^{II}Fe_4^{III}(PO_4)_6$ (Gorbunov, Maksimov, Kabalov, Ivaschenko, Mel'nikov & Belov, 1980), and has been independently reported by Cudennec, Riou & Gerault (1986) and Riou, Cudennec & Gerault (1987). Manganese is present in the divalent state only, hydrogen atoms making up the required charge balance in the form of Mn—OH—P linkages, which do not alter the basic $Fe_7(PO_4)_6$ framework. In an attempt to extend the range of phases which adopt this basic structure type, reactions analogous to that used to prepare $Mn_7(PO_4)_2(HPO_4)_4$ were carried out using cobalt- or iron-containing starting materials. This paper describes the results of these reactions, in particular the synthesis and structure of the new divalent cobalt phase $Co_7(PO_4)_2(HPO_4)_4$.

Experimental. Crystals of $Co_7(PO_4)_2(HPO_4)_4$ were prepared by a hydrothermal method. A 1:1 molar mixture of $CoCl_2.6H_2O$ and $NH_4H_2PO_4$ (5 g total) was added to 15 ml distilled H_2O, and the resultant mixture was sealed in a Teflon-lined stainless steel autoclave. The bomb was placed in an air oven at 493 K and held for 48 h, whence it was removed and allowed to cool naturally to room temperature. Well formed bright purple crystals were isolated by suction filtration, washed with water and dried in air. X-ray powder diffraction revealed the product to be monophasic and to possess obvious structural similarities to that of $Fe_7(PO_4)_6$ (Gorbunov et al., 1980). The observed powder diffraction pattern recorded on a Philips PW 1710 diffractometer, using KCl as an internal standard, is given in Table 1. A pattern calculated on the basis of the single-crystal results presented herein is given for comparison.

A suitable crystal ($0.15 \times 0.10 \times 0.05$ mm) was mounted on an Enraf–Nonius CAD-4 diffractometer. The unit-cell constants were determined on the basis of 25 carefully centred reflections in the angular range $15 < 2\theta < 20°$. Data were collected in the ω–2θ scan mode, with ω scan width $1.2 + 0.35\tan\theta$, scan speed 0.70–$5.50°$ min^{-1} in the range $0.2 < \theta < 30°$. A total of 2933 reflections (h -9 to 9, k -13 to 13, l -1 to 11) were measured, which were merged to a unique set of 2340. Of these, 2122 were regarded as observed according to the criterion $I > 3\sigma(I)$. Data were corrected for Lorentz and polarization effects, and a semi-empirical absorption correction, based on the ψ scans

Table 1. *Observed and calculated X-ray powder diffraction patterns for* $Co_7(PO_4)_2(HPO_4)_4$

Owing to the complexity of the pattern lines with $I_{calc} < 5$ are not included.

h	k	l	d_{obs}	d_{calc}	I_{obs}*	I_{calc}
0	0	1	7.20	7.274	13	13
0	1	−1	6.76	6.741	18	18
1	0	0	5.85	5.831	9	12
1	−1	−1	4.80	4.821	13	29
0	2	−1	4.33	4.335	24	5
1	1	−1		4.333		30
0	1	−2	3.85	3.841	9	6
0	0	2	3.63	3.637	15	5
2	−1	0	3.161	3.168	25	36
1	2	−1		3.154		25
2	0	−1	3.038	3.041	18	29
0	1	2	2.992	2.994	162	100
0	3	−1	2.977	2.981		62
1	2	0	2.915	2.914	9	11
1	2	−2	2.864	2.873	19	15
2	−2	−1		2.863		17
2	−2	1		2.721		22
2	−1	1	2.713	2.712	13	11
2	0	−2		2.707		11
2	1	−1	—	2.641	—	8
1	−3	2	2.620	2.617	14	20
1	0	−3	2.526	2.525	7	5
0	2	2	2.493	2.494	21	20
2	1	0	—	2.470	—	5
0	0	3		2.424		10
2	−3	−1	2.421	2.418	24	11
2	−2	−2		2.411		6
0	4	−2	2.166	2.167	8	7
2	−3	2	—	2.159	—	6
0	1	3	2.146	2.147	17	8
3	−2	−1	2.118	2.119	12	14
3	−2	0		2.110		7
1	−2	−3	—	2.014	—	9
3	−3	−1	1.977	1.978	7	5
0	4	−3	1.948	1.948	24	8
1	2	2	1.942	1.941	5	8
0	4	1	1.864	1.866	14	10
2	−1	−4	1.736	1.735	7	8
3	−3	−3	1.606	1.607	8	5
4	−1	−1	1.593	1.594	22	15
3	2	−3		1.593		14
1	5	−2	1.583	1.584	16	9

* I_{obs} values are based on peak heights rather than integrated intensities.

Table 2. *Final atomic coordinates and isotropic/ equivalent isotropic temperature factors for* $Co_7(PO_4)_2(HPO_4)_4$

	x	y	z	U(iso)/U(eq)*
Co(1)	0	0	0	0.0075
Co(2)	0.38612 (3)	0.11007 (2)	0.45711 (3)	0.0069
Co(3)	0.28549 (3)	0.28506 (2)	−0.18742 (3)	0.0081
Co(4)	0.05190 (3)	−0.48521 (2)	−0.28517 (3)	0.0074
P(1)	0.08549 (6)	−0.17344 (4)	−0.42163 (5)	0.0055
P(2)	0.41036 (6)	0.37297 (4)	0.23105 (5)	0.0067
P(3)	0.22564 (6)	−0.22195 (4)	0.14347 (5)	0.0057
O(1)	0.2620 (2)	0.2381 (1)	0.0505 (1)	0.0094
O(2)	0.3034 (2)	−0.0864 (1)	−0.4636 (1)	0.0081
O(3)	0.2714 (2)	0.4744 (1)	0.2954 (2)	0.0108
O(4)	0.4804 (2)	0.3115 (1)	0.3847 (2)	0.0107
O(5)	0.4484 (2)	−0.2278 (1)	0.2455 (1)	0.0084
O(6)	0.0537 (2)	−0.3474 (1)	−0.4577 (1)	0.0076
O(7)	0.1081 (2)	−0.0977 (1)	−0.2173 (1)	0.0095
O(8)	0.1259 (2)	0.1649 (1)	−0.4579 (1)	0.0081
O(9)	−0.0157 (2)	0.3365 (1)	−0.1711 (2)	0.0089
O(10)	0.3803 (2)	−0.4903 (1)	−0.2052 (2)	0.0101
O(11)	0.2237 (2)	−0.0544 (1)	0.1861 (1)	0.0081
O(12)	0.2063 (2)	−0.2745 (1)	−0.0671 (1)	0.0082
H(1)	0.373 (8)	0.562 (6)	0.406 (7)	0.09 (1)
H(2)	0.826 (5)	0.202 (4)	0.125 (4)	0.035 (8)

* $U(eq) = (U_1U_2U_3)^{1/3}$, where U_1, U_2, U_3 are the mean square displacements (in Å^2) along the principal axes of the thermal ellipsoid.

Table 3. *Selected bond distances (Å) and angles (°) for*
$Co_7(PO_4)_2(HPO_4)_4$

Co(1)—O(1)	2 ×	2·217 (1)	P(1)—O(2)		1·528 (1)
Co(1)—O(7)	2 ×	2·093 (1)	P(1)—O(6)		1·539 (1)
Co(1)—O(11)	2 ×	2·131 (1)	P(1)—O(7)		1·547 (1)
			P(1)—O(8)		1·544 (1)
Co(2)—O(2)		2·049 (1)			
Co(2)—O(2)		2·086 (1)	P(2)—O(1)		1·531 (1)
Co(2)—O(4)		2·062 (1)	P(2)—O(3)		1·578 (1)
Co(2)—O(5)		2·196 (1)	P(2)—O(4)		1·522 (1)
Co(2)—O(8)		2·096 (1)	P(2)—O(10)		1·532 (1)
Co(2)—O(11)		2·121 (1)			
			P(3)—O(5)		1·532 (1)
Co(3)—O(1)		2·051 (1)	P(3)—O(9)		1·530 (1)
Co(3)—O(5)		2·065 (1)	P(3)—O(11)		1·545 (1)
Co(3)—O(8)		2·018 (1)	P(3)—O(12)		1·576 (1)
Co(3)—O(9)		2·178 (1)			
Co(3)—O(10)		2·063 (1)	O(3)—O(4)		2·609 (2)
			O(3)—H(1)		0·97 (5)
Co(4)—O(3)		2·115 (1)	O(4)—H(1)		1·65 (5)
Co(4)—O(6)		2·103 (1)			
Co(4)—O(6)		2·061 (1)	O(7)—O(12)		2·448 (1)
Co(4)—O(9)		2·067 (1)	O(12)—H(2)		0·97 (3)
Co(4)—O(10)		2·116 (1)	O(7)—H(2)		1·48 (3)
Co(4)—O(12)		2·065 (1)			

O(1)—Co(1)—O(1)		180·00	O(6)—Co(4)—O(3)	81·99 (4)
O(7)—Co(1)—O(1)	2 ×	90·38 (4)	O(6)—Co(4)—O(3)	95·93 (4)
O(7)—Co(1)—O(1)	2 ×	89·62 (4)	O(6)—Co(4)—O(6)	77·86 (4)
O(7)—Co(1)—O(7)		180·00	O(9)—Co(4)—O(3)	92·23 (4)
O(11)—Co(1)—O(1)	2 ×	93·33 (4)	O(9)—Co(4)—O(6)	165·73 (4)
O(11)—Co(1)—O(1)	2 ×	86·67 (4)	O(9)—Co(4)—O(6)	89·86 (4)
O(11)—Co(1)—O(7)	2 ×	90·75 (4)	O(10)—Co(4)—O(3)	165·55 (5)
O(11)—Co(1)—O(7)	2 ×	89·25 (5)	O(10)—Co(4)—O(6)	109·17 (4)
O(11)—Co(1)—O(11)		180·00	O(10)—Co(4)—O(6)	95·43 (4)
			O(10)—Co(4)—O(9)	78·90 (4)
			O(12)—Co(4)—O(3)	89·70 (4)
O(2)—Co(2)—O(2)		84·91 (4)	O(12)—Co(4)—O(6)	86·94 (4)
O(4)—Co(2)—O(2)		177·95 (4)	O(12)—Co(4)—O(6)	162·84 (4)
O(4)—Co(2)—O(2)		93·75 (4)	O(12)—Co(4)—O(9)	106·15 (4)
O(5)—Co(2)—O(2)		81·34 (4)	O(12)—Co(4)—O(10)	81·98 (4)
O(5)—Co(2)—O(2)		83·06 (4)		
O(5)—Co(2)—O(4)		96·97 (4)	O(6)—P(1)—O(2)	108·68 (6)
O(8)—Co(2)—O(2)		91·09 (4)	O(7)—P(1)—O(2)	109·93 (6)
O(8)—Co(2)—O(2)		161·49 (4)	O(7)—P(1)—O(6)	108·74 (6)
O(8)—Co(2)—O(4)		89·70 (4)	O(8)—P(1)—O(2)	110·98 (6)
O(8)—Co(2)—O(5)		78·47 (4)	O(8)—P(1)—O(6)	109·95 (6)
O(11)—Co(2)—O(2)		84·93 (4)	O(8)—P(1)—O(7)	108·53 (6)
O(11)—Co(2)—O(2)		92·27 (4)		
O(11)—Co(2)—O(4)		96·69 (4)	O(3)—P(2)—O(1)	109·75 (6)
O(11)—Co(2)—O(5)		165·83 (4)	O(4)—P(2)—O(1)	112·02 (6)
O(11)—Co(2)—O(8)		105·40 (4)	O(4)—P(2)—O(3)	107·35 (7)
			O(10)—P(2)—O(1)	111·33 (6)
O(5)—Co(3)—O(1)		104·97 (4)	O(10)—P(2)—O(3)	104·63 (6)
O(8)—Co(3)—O(1)		134·94 (4)	O(10)—P(2)—O(4)	111·42 (6)
O(8)—Co(3)—O(5)		83·39 (4)		
O(9)—Co(3)—O(1)		82·75 (4)	O(9)—P(3)—O(5)	111·65 (6)
O(9)—Co(3)—O(5)		171·29 (4)	O(11)—P(3)—O(5)	114·71 (6)
O(9)—Co(3)—O(8)		88·28 (4)	O(11)—P(3)—O(9)	110·81 (6)
O(10)—Co(3)—O(1)		123·52 (5)	O(12)—P(3)—O(5)	106·61 (6)
O(10)—Co(3)—O(5)		100·86 (4)	O(12)—P(3)—O(9)	108·57 (6)
O(10)—Co(3)—O(8)		96·98 (4)	O(12)—P(3)—O(11)	103·94 (6)
O(10)—Co(3)—O(9)		77·58 (4)		

of three reflections, was applied; the minimum/ maximum corrections were 1·00/1·37. Final coordinates for $Mn_7(PO_4)_2(HPO_4)_4$ (Lightfoot & Cheetham, 1986) in the space group $P\bar{1}$ were used as a starting model for the structure refinement. Several cycles of full-matrix least-squares refinement on F led to final R factors $R = 0·017$, $wR = 0·021$. Weights were calculated according to a three-term Chebyshev weighting scheme (Carruthers & Watkin, 1979) with parameters 4·0, −1·6 and 3·2. Corrections were also made for anomalous-dispersion and secondary-extinction effects. All non-hydrogen atoms were refined with anisotropic temperature factors, hydrogen atoms isotropically. During the final refinement cycle, the r.m.s. shift/e.s.d.

was 0·05. The final difference Fourier map showed no features higher than $0·7\,e\,Å^{-3}$. All structure analysis and refinement was carried out using the Oxford *CRYSTALS* package (Watkin, Carruthers & Betteridge, 1985). Scattering factors were taken from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic coordinates and isotropic/ equivalent isotropic temperature factors are given in Table 2, and selected bond distances and angles in Table 3.* The structure is isomorphous with that of $Mn_7(PO_4)_2(HPO_4)_4$ and contains four crystallographically distinct metal sites (Fig. 1). $M(1)$ is on the inversion centre at (0,0,0) and has an almost regular octahedral environment. Of the other three metal sites, $M(2)$ and $M(4)$ display distorted octahedral coordination and $M(3)$ has a five-coordinated geometry, best described as distorted trigonal bipyramidal. Five-coordinate Co^{II} is not unusual, and has been observed in the phosphates $Co_3(PO_4)_2$ (Nord, 1974), $Co_2P_2O_7$ (Krishamachari & Calvo, 1972) and $Co_3(PO_4)_2.H_2O$ (Anderson, Kostiner & Ruszala, 1976). Bond-strength bond-length calculations (Brown & Shannon, 1973) confirm the cobalt in the present case to be purely divalent, valence sums for the four metal sites being 1·88, 2·09, 1·87 and 2·07, respectively.

The geometry of the PO_4 groups is almost regular, the only marked deviations being to accommodate the P—O—H groups. The extension of the P(2)—O(3) and P(3)—O(12) bonds to 1·578 and 1·576 Å respectively is typical of such linkages, and confirms the location of the H atoms. Very strong hydrogen bonds occur *via*
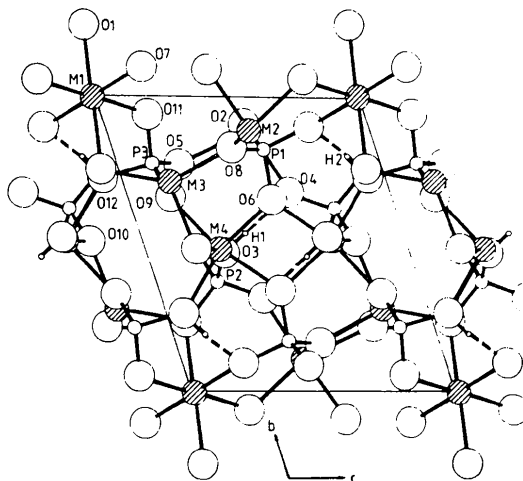

Fig. 1. View of the structure along [100].

O(3)—H(1)···O(4) and O(12)—H(2)···O(7) (see Table 3). In particular, the donor–acceptor distance O(12)—O(7) is remarkably short, at 2·448 Å. The corresponding distance in the Mn analogue is 2·500 Å, whereas the shortest distance reported in hydrates, as studied by neutron diffraction, is 2·546 Å (Chiari & Ferraris, 1982). However, shorter distances have been observed in the compounds $K_3Cu_2H(P_2O_7)_2$ (Effenberger, 1987) and $Na_5Cu_3H(PO_4)_4$ (Effenberger, 1985) where symmetric P—O···H···O—P bonds lead to donor–acceptor distances of 2·437 and 2·388 Å respectively.

Our attempts to prepare a purely divalent iron analogue of $Mn_7(PO_4)_2(HPO_4)_4$ led to the formation of dark green–grey crystals, perhaps indicative of some degree of oxidation, though not as far as $Fe_7(PO_4)_6$ itself. Single-crystal X-ray analysis of this phase (Lightfoot & Cheetham, 1986) does indeed suggest some degree of mixed-valence character, an approximate composition $Fe_6^{II}Fe^{III}(PO_4)_3(HPO_4)_3$ being deduced on the basis of bond-length bond-strength calculations. It was apparent from this experiment that Fe^{III} showed a marked preference for the $M(2)$ and $M(4)$ sites, which are found to be fully occupied by Fe^{III} in $Fe_7(PO_4)_6$ (Gorbunov et al., 1980).

It is possible that a solid solution $Fe_7(PO_4)_2$-$(HPO_4)_4$–$Fe_7(PO_4)_6$ may exist, with subtle control of experimental conditions governing the degree of oxidation. Mössbauer spectroscopy would clearly be of great value in studying this possibility in detail. Our own studies in these systems have now been extended to the solid solutions $(Mn,Fe)_7(PO_4)_6$ and $(Co,Fe)_7$-$(PO_4)_6$, results of which will be presented in a forthcoming publication.

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Structures of (I) Hexafluoroaluminic Acid Hexahydrate and (II) Pentafluoroaluminic Acid Pentahydrate*

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Abstract. (I) $H_3AlF_6.6H_2O$, $M_r = 252\cdot08$, hexagonal, $R\bar{3}c$, $a = 9\cdot861$ (5), $c = 17\cdot497$ (2) Å, $V = 1473\cdot4$ Å^3, $Z = 6$, $D_x = 1\cdot71$ Mg m^{-3}, $\lambda(Mo\,K\bar{\alpha}) = 0\cdot71073$ Å, $\mu = 0\cdot292$ mm^{-1}, $F(000) = 780$, $T = 183$ K, $R = 0\cdot036$ for 471 unique observed reflections. (II) $H_2AlF_5.5H_2O$, $M_r = 214\cdot06$. Previously reported [Trunov, Efremov, Konstantinova, Velikodnyi & Golota (1980). Sov. Phys. Dokl. 25, 508–509] structural data [monoclinic, Pc, $a = 7\cdot926$ (2), $b = 3\cdot651$ (2), $c = 13\cdot776$ (5) Å, $\beta = 108\cdot27$ (3)°, $Z = 2$] are newly interpreted in the centrosymmetric supergroup P2/c with the crystallographic axes unchanged. The crystalline compounds are oxonium salts, $(H_5O_2)_3AlF_6$ and $(H_5O_2)_2$-