damental layers and also on interstitial sites approximately ± one layer apart from each middle layer.

The structure of synthetic perryite is closely related to that of $Ni_{31}Si_{12}$ ($P321$, $a = 6.67$ and $c = 12.28$ Å; Frank & Schubert, 1971). The c-axis length of $Ni_{31}Si_{12}$ is approximately one third that of synthetic perryite, and the atomic arrangements in the unit cell of $Ni_{31}Si_{12}$ are similar to those in one third of the unit cell of synthetic perryite (Fig. 2), which contains 32 Ni(Fe) atoms and 12 Si(P) Atoms. The interstitial Ni(Fe) atom marked with an asterisk in layer 4 of Fig. 2 is absent in $Ni_{31}Si_{12}$ with significant displacements of the surrounding atoms.

In a similar way, the structure of synthetic perryite is also related to that of Pd_5Sb_2 ($P6_3cm$, $a = 7.606$ and $c = 13.863$ Å; El-Boragy, Bhan & Schubert, 1970). In this case, the unit-cell content is $Pd_{30}Sb_{12}$, and the two interstitial Ni(Fe) atoms marked with double asterisks in layers 2 and 7 of Fig. 2 are absent with significant displacements of the surrounding atoms. Thus, the structure of synthetic perryite $(Ni,Fe)_8(Si,P)_3$, which is isomorphous with that of

Pd_8Sb_3, is a stacking variant of $Ni_{31}Si_{12}$ and Pd_5Sb_2 structures.

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CoAPO-21, a Cobalt-Doped Aluminophosphate Related to AlPO4-21

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Abstract. $Co_{0.12}Al_{5.88}P_6O_{24}(OH)_2 \cdot C_2H_{10}N_2 \cdot 2H_2O$, $M_r = 867.7$, monoclinic, $P2_1/n$, $a = 8.992$ (3), $b = 17.760$ (8), $c = 8.359$ (4) Å, $\beta = 105.39$ (4)°, $U = 1287.0$ Å^3, $Z = 2$, $D_x = 2.24$ g cm^{-3}, $\lambda = 0.895$ (5) Å, $\mu = 14.7$ cm^{-1}, $F(000) = 871.4$, $R = 0.061$ for 1163 observed reflections, recorded with an area-detector diffractometer. The framework structure is similar to that of AlPO4-21 [Parise & Day (1985). *Acta Cryst.* C41, 515–520], with 4-, 5- and 6-coordinate aluminium atoms; Co^{2+} replaces tetrahedral Al^{3+} ions, and the 6-coordinate Al^{3+} has one water molecule as ligand (in addition to 5 framework O atoms). In the channels, the C and N atoms of the ethylenediamine molecule were located; the molecules are disordered, and occupy two mutually exclusive positions related by an inversion centre.

Introduction. A new group of microporous materials based on the aluminophosphate lattice has recently been the subject of intense investigation. These materials are characterized by a pronounced structural diversification: more than two dozen structure types have been reported (Bennet, Dytrych, Pluth, Richardson & Smith, 1986). Although there are indications (Pyke, Whitney & Houghton, 1985) that their range of microporosities make them useful for catalytic and absorption applications, the data for their structural characterization are still scarce. One of the reasons is probably that large single crystals are difficult to obtain. Structures of these materials, designated AlPO-n, where n denotes a specific structure type are named on the basis of similarity to known zeolite structures. Some structures, however, are completely new and have no zeolite analogs. The substitution of metallic elements such as cobalt or iron (Flanigen, Lok, Patton & Wilson, 1986) into the neutral aluminium–phosphorus framework during synthesis gives rise to novel acidic and catalytic properties, the previously ᵥuncharged frameworks being unable to function as solid acid catalysts. In summary, their remarkable diversity in crystal structure and crystal chemistry offers a nearly unlimited number of design parameters to tailor adsorptive and catalytic properties. In this paper we report the crystal structure of CoAPO-21 from single-crystal synchrotron X-ray data. This is the first metal-substituted $AlPO_4$ with the structure type 21.

Experimental. Synthesis used a reaction gel of molar composition 0·4 $Co(ac)_2$: 0·8 Al_2O_3: 1·0 P_2O_5: 1·0 en 50 H_2O (ac = acetate ion, en = ethylenediamine), and followed the procedure of Wilson & Flanigen (1986). Crystallization, in a teflon-lined autoclave under static conditions at 468 K over 4 d yielded royal blue needle-shaped crystals, which were designated CoAPO-21 on the basis of the similarity of their X-ray powder pattern and crystal morphology to $AlPO_4$-21; one of the largest crystals, 150 × 40 × 30 μm, was used here. Bulk chemical analysis gave $(Co_{0.08}Al_{0.42}P_{0.50})O_2*0.09en*0.10H_2O$, an IR spectrum of this material exhibiting a medium band at 1520 cm^{-1}, indicating that en molecules are present as protonated species.

Unit-cell determination and intensity measurement followed the procedure described by Rizkallah, Maginn & Harding (1990) using synchrotron radiation (SRS, Daresbury Laboratory, Warrington, England), the Enraf–Nonius FAST area-detector diffractometer, and $MADNES$ software (Messerschmidt & Pflugrath, 1987), except that the implementation of $MADNES$ included an amended polarization correction (Papiz, 1989). SRS running at 2 GeV, 200 mA, collimator 0·2 mm, φ range 185°, 1° frames accumulated for 10 s each, detector tilt −28°, crystal

detector distance 40 mm, thus minimum accessible d $(= \lambda/2\sin\theta_{max}) = 0.85$ Å, effective mosaic spread 4·2°. $-9 \le h \le 8$, $0 \le k \le 18$, $0 \le l \le 8$. 2532 reflection intensities measured, yielding 1675 unique intensities ($R_{merge} = 0.063$) of which 1165 were considered observed ($MADNES$ flag = 0, R_{merge} for these alone = 0·032). The structure was solved by direct methods ($SHELXS$86; Sheldrick, 1986).

The atoms of the ethylenediamine molecule, disordered, on two overlapping sites, were identified in an electron density difference map. In refinement (on F) ($SHELX$76; Sheldrick, 1976), the C—C and C—N distances were restrained to 1·54 (2) and 1·47 (2) Å, C and N were assigned site occupancy 0·5 and isotropic vibration parameters, H atoms were ignored, anisotropic vibration parameters were used for all other atoms, weights $w = 1/[\sigma^2(F) + 0.0001F^2]$, and scattering factors as in $SHELX$76, 198 parameters in all. After some refinement (with equal fixed U values for Al) occupancy factors for the three Al sites of 1·07 (1), 1·00 (1) and 0·98 (1) suggested that the first was the site where Co replaced Al; subsequently Al(1) was treated as a site occupied by pCo + (1−p) Al atoms and p was refined. This converged to $R = 0.061$, $wR = 0.062$, $S = 1.65$, for 1163 observations; the maximum and minimum electron density in the final difference map was 1·10 and -0.55 e Å^{-3}, mainly around the en template molecule; $(\Delta/\sigma)_{max} = 0.12$, except for the template atoms.

Discussion. Table 1 gives atom parameters,* Table 2 selected bond lengths and angles, and Fig. 1 illustrates the structure.

The zeolite-like framework of Al, P and O atoms except O(14) corresponds to the $AlPO_4$-21 framework described by Parise & Day (1985) and by Bennet, Cohen, Artioli, Pluth & Smith (1985) with a close similarity to the Al—O and P—O bond distances in both of these.

Following Bennett et al. (1985) we assume that O(9) represents a hydroxyl group which forms the bridge Al(2)—OH—Al(3). Al(1) is 4 coordinate, tetrahedral, and it is at this site that the cobalt substitution appears to take place, consistent with the blue colour of the crystals. Al(2) is 5-coordinate, approximately trigonal bipyramidal, while Al(3) has 5 framework O atoms as neighbours, at 1·813 (7)– 1·906 (7) Å, and one additional O atom, O(14), at 2·185 (7) Å. We identify O(14) as a water molecule; its presence is consistent with the chemical analysis

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$$

	x	y	z	U_{eq}
Al(1)/Co*	0·3060 (3)	0·8205 (2)	−0·0171 (3)	0·0098 (16)
Al(2)	0·7079 (3)	0·7061 (2)	−0·0749 (3)	0·0091 (16)
Al(3)	0·8246 (4)	0·8946 (2)	−0·1224 (3)	0·0119 (16)
P(1)	0·5223 (3)	0·7099 (1)	0·2075 (3)	0·0117 (15)
P(2)	0·5029 (3)	0·8287 (1)	−0·2740 (3)	0·0125 (15)
P(3)	0·8629 (3)	1·0712 (1)	−0·1588 (3)	0·0101 (14)
O(1)	0·5830 (8)	0·6943 (4)	0·0581 (7)	0·0176 (39)
O(2)	0·4049 (8)	0·7743 (3)	0·1663 (8)	0·0184 (40)
O(3)	0·4463 (8)	0·6395 (3)	0·2478 (7)	0·0161 (39)
O(4)	0·6535 (8)	0·7335 (3)	0·3567 (7)	0·0149 (38)
O(5)	0·4299 (8)	0·8494 (4)	−0·1315 (7)	0·0224 (41)
O(6)	0·5605 (7)	0·7477 (3)	−0·2513 (7)	0·0128 (37)
O(7)	0·3844 (8)	0·8378 (3)	−0·4387 (7)	0·0174 (40)
O(8)	0·6344 (8)	0·8835 (4)	−0·2693 (8)	0·0173 (38)
O(9)	0·8020 (8)	0·7986 (3)	−0·0294 (7)	0·0153 (38)
O(10)	0·8161 (8)	1·1177 (3)	−0·3171 (7)	0·0176 (38)
O(11)	0·8297 (7)	0·9903 (3)	−0·2066 (7)	0·0101 (36)
O(12)	1·0327 (8)	1·0834 (3)	−0·0708 (7)	0·0162 (38)
O(13)	0·2626 (8)	0·4056 (3)	0·4584 (8)	0·0196 (40)
O(14)	0·1770 (12)	0·5565 (6)	0·5214 (13)	0·0793 (79)
N(1)†	0·470 (3)	0·008 (2)	0·531 (3)	0·0689 (62)
N(2)†	0·136 (3)	−0·013 (1)	0·603 (3)	0·0537 (62)
C(1)†	0·237 (3)	0·057 (1)	0·610 (4)	0·0647 (86)
C(2)†	0·417 (3)	0·053 (2)	0·655 (3)	0·0613 (82)

* Site occupancy refined to 0·06 (1) for Co, 0·94 (1) for Al(1).
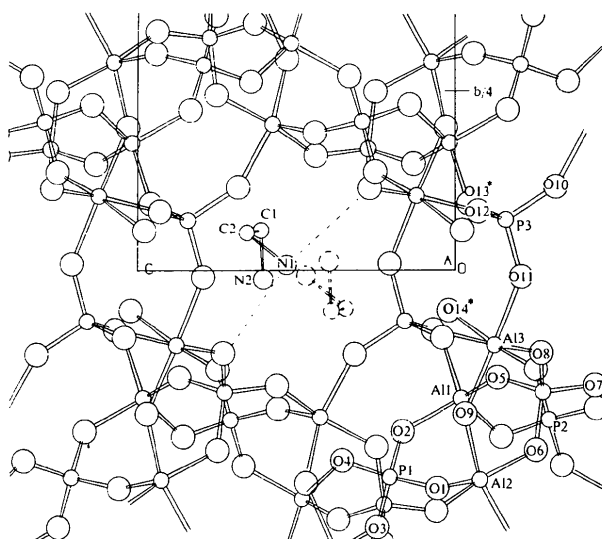† Site occupancy 0·5.

Fig. 1. *a*-axis projection showing alternative positions of the ethylenediamine molecule (one of them in dashed lines, H atoms omitted) in the channel. The two good hydrogen bonds to one N(1) are shown. O(13)* and O(14)* are related to O(13) and O(14) by $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

and its other contacts are with an O(5) at 2·79 Å and an O(13) at 2·87 Å, appropriate for two hydrogen bonds. Parise & Day (1985) identify this peak as the N atom of a disordered ethylenediamine molecule, while Bennett *et al.* (1985) do not find an atom at this position at all.

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Al(1)—O(2)ⁱ	1·756 (7)	P(1)—O(1)ⁱ	1·512 (7)
Al(1)—O(4)ⁱᵛ	1·766 (7)	P(1)—O(2)ⁱ	1·527 (7)
Al(1)—O(5)ⁱ	1·721 (7)	P(1)—O(3)ⁱ	1·502 (7)
Al(1)—O(13)ⁱⁱ	1·749 (7)	P(1)—O(4)ⁱ	1·525 (7)
Al(2)—O(1)ⁱ	1·784 (7)	P(2)—O(5)ⁱ	1·545 (7)
Al(2)—O(6)ⁱ	1·849 (7)	P(2)—O(6)ⁱ	1·523 (7)
Al(2)—O(7)ⁱᵛ	1·852 (6)	P(2)—O(7)ⁱ	1·506 (7)
Al(2)—O(9)ⁱ	1·838 (7)	P(2)—O(8)ⁱ	1·517 (7)
Al(2)—O(10)ⁱⁱ	1·795 (6)	P(3)—O(10)ⁱ	1·522 (7)
Al(3)—O(3)ⁱᵛ	1·831 (7)	P(3)—O(11)ⁱ	1·499 (6)
Al(3)—O(8)ⁱ	1·822 (7)	P(3)—O(12)ⁱ	1·514 (7)
Al(3)—O(9)ⁱ	1·906 (7)	P(3)—O(13)ᵛ	1·547 (6)
Al(3)—O(11)ⁱ	1·846 (7)		
Al(3)—O(12)ⁱⁱⁱ	1·813 (7)		
Al(3)—O(14)ⁱᵛ	2·185 (7)		

Al(2)—O(1)—P(1)	155·9 (5)	Al(2)—O(9)—Al(3)	143·8 (4)
Al(1)—O(2)—P(1)	134·7 (5)	Al(2)—O(10)—P(3)	151·7 (4)
Al(3)—O(3)—P(1)	141·5 (4)	Al(3)—O(11)—P(3)	143·5 (4)
Al(1)—O(4)—P(1)	129·8 (4)	Al(3)—O(12)—P(3)	145·6 (4)
Al(1)—O(5)—P(2)	145·3 (5)	Al(1)—O(13)—Al(3)	135·5 (4)
Al(2)—O(6)—P(2)	128·4 (4)		
Al(2)—O(7)—P(2)	142·5 (4)		
Al(3)—O(8)—P(2)	131·5 (4)		

Symmetry transformation of oxygen coordinates: (i) x, y, z; (ii) $\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$; (iii) $-x$, $-y$, $-z$; (iv) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$; (v) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $-\frac{1}{2} + z$.

N(1) is 0·44 (3) Å from an inversion centre; the ethylenediamine molecule must be disordered between two sets of positions, each 50% occupied. N(1) can form two hydrogen bonds to framework O atoms, N(1)—H···O(8) (at x, y, $z + 1$) 2·92 Å, and N(1)—H···O(8) (at $-x$, $-y$, $-z$) 2·88 Å; around each N atom there are a further three framework oxygens at distances between 3·1 and 3·3 Å. Two doubly charged ions, $H_3N^+.CH_2.CH_2.NH^+_3$, per unit cell (or four halves) would have the correct charge to balance the framework of composition equivalent to $4[Al_3P_3O_{12}(OH)^-]$. Our interpretation of the template atom positions is different from that of Parise & Day (1985), but fits the electron density in the channel.

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$$Co_{0\cdot12}Al_{5\cdot88}P_6O_{24}(OH)_2.C_2H_{10}N_2.2H_2O$$

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Crystal Chemistry of cyclo-Hexaphosphates. XVII. Structure of Chromium cyclo-Hexaphosphate Henicosahydrate

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Abstract. $Cr_2[P_6O_{18}].21H_2O$, $M_r = 956\cdot13$, cubic, $P\bar{4}3n$, $a = 19\cdot052$ (10) Å, $V = 6915$ (11) Å^3, $Z = 8$, $D_x = 1\cdot837$ Mg m^{-3}, $\lambda(Mo\ K\bar{\alpha}) = 0\cdot71073$ Å, $\mu = 1\cdot062$ mm^{-1}, $F(000) = 3936$, room temperature, final $R = 0\cdot053$ for 1655 independent reflections. The atomic arrangement of $Cr_2P_6O_{18}.21H_2O$ is a stacking of P_6O_{18} ring anions, $Cr(H_2O)_6$ octahedra and non-bonded water molecules interconnected by hydrogen bonds only. The phosphoric ring anion has a three-fold internal symmetry. One of the water molecules building the coordination polyhedron of Cr(1) is disordered.

Introduction. Crystal structure of anhydrous chromium cyclo-hexaphosphate, $Cr_2P_6O_{18}$, was determined some years ago (Bagieu-Beucher & Guitel, 1977). Up to now, no mention of the existence of possible hydrates of this salt has been reported in the chemical literature. Recently one of us (Rzaigui, 1990) characterized the first hydrate of this phosphate: $Cr_2P_6O_{18}.21H_2O$. The present work is devoted to the determination of the crystal structure of this hydrate.

Experimental. The preparation of $Cr_2P_6O_{18}.21H_2O$ and its main chemical properties have been reported elsewhere (Rzaigui, 1990). Crystal size: $0\cdot32 \times 0\cdot32 \times 0\cdot27$ mm (a rhombic dodecahedron). Density not measured. Nicolet diffractometer, graphite monochromator. 25 reflections ($10\cdot75 < \theta < 12\cdot60°$) for refining unit-cell dimensions. ω scan, scan width $1\cdot40°$, scan speed $0\cdot01°$ s^{-1}, total background measuring time 14 s. 7359 measured reflections, h, k, l,

$h_{max} = k_{max} = l_{max} = 26$. Three intensity and orientation reference reflections (222, $\bar{2}\bar{2}2$, 411) measured every 500 reflections with no significant variations. The systematic absences, hhl ($l = 2n$), the symmetry of the intensities and the study of the Patterson function lead to the space group $P\bar{4}3n$. Lorentz and polarization corrections, no absorption correction. 1807 unique reflections ($R_{int} = 0\cdot02$). The crystal structure has been solved by classical methods: study of the three-dimensional Patterson function followed by successive Fourier syntheses. A problem occurred with the water molecule O($W1$); first refined in the special position 12(f), this molecule had a very high thermal factor with an abnormally short Cr(1)—O($W1$) distance. A careful examination of Fourier maps showed that this water molecule is in fact disordered and split into three fragments of approximately identical weight. Two of these fragments occupy the general position while the third one is located on the special position 12(f). These three fragments are denoted O($W1$), O($W11$) and O($W12$). Refinements of the occupancy rates of these three fragments led to $0\cdot186$, $0\cdot166$ and $0\cdot157$ respectively, whose sum ($0\cdot499$) is close to the expected value of $0\cdot500$. H atoms were located by difference Fourier syntheses with the exception of those corresponding to the disordered water molecule and to O($W9$), a non-bonded water molecule. Anisotropic full-matrix least-squares refinement (on F), isotropic for H atoms. Unit weights. Scattering factors for neutral atoms and f', f'' from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B). Enraf–Nonius *SDP* (1977) used for all calculations. Com-