modification. From rotation photographs it appears that this modification also has a stacked structure, with a repeat distance of 7·40 (5) Å along the stacks. This can be deduced from the typical sequence of strong even, and weak odd layer lines. Poor crystal quality prevents further investigations.

The Pt^{IV} in the starting material has been reduced to Pt^{II} despite the presence of molecular iodine in excess. By analogy with other MX_2(dioxime) complexes (M = Ni, Pd, Pt) it is assumed that H_2bqd is present as a neutral molecule in the title compound. The assignment of the oxidation state of +2 to Pt is also favoured by the square-planar coordination. The species oxidized in this redox process is most likely to be $TCNQ^-$.

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The Structure of Trialuminium Tris(orthophosphate) Hydrate, $AlPO_4$-21, with Clathrated Ethylenediamine, $Al_3(PO_4)_3.C_2H_8N_2.H_2O$, and Pyrrolidine, $Al_3(PO_4)_3.C_4H_9N.H_2O$

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Abstract. $AlPO_4$-21(en): $M_r = 444·0$, monoclinic, $P2_1/n$, $a = 8·472$ (3), $b = 17·751$ (6), $c = 9·062$ (3) Å, $\beta = 106·73$ (3)°, $U = 1305$ (1) Å^3, $Z = 4$, $D_x = 2·26$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 7·21$ cm^{-1}, $F(000) = 914$, room temperature, non-hydrogen atoms refined anisotropically to $R = 0·045$ for 2612 reflections with $I > 3\sigma(I)$. $AlPO_4$-21(py): $M_r = 455·0$, monoclinic, $P2_1/n$, $a = 8·668$ (1), $b = 17·558$ (2), $c = 9·186$ (2) Å, $\beta = 107·75$ (1)°, $U = 1333·7$ (5) Å^3, $Z = 4$, $D_x = 2·27$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 7·07$ cm^{-1}, $F(000) = 920$, room temperature, non-hydrogen atoms refined anisotropically and H positions calculated; $R = 0·071$ for 2112 reflections with $I > 0·0$. Al^V and P^{IV} form ribbons of edge-shared three- and five-membered rings along [101], which are joined along [010] *via* four-membered rings to form corrugated sheets of $[Al_2^VP_2^{IV}O_7.H_2O]$ or $[Al_2^VP_2^{IV}O_7.OH]$. These sheets are cross linked by crankshaft-shaped single chains of strictly alternating Al- and P-centred tetrahedra at $y \simeq \frac{1}{4}, \frac{3}{4}$ to form an open network of channels in (010) bounded by eight-membered-ring apertures. The framework topology suggests a model for $AlPO_4$-25, the molecular sieve produced upon calcination of $AlPO_4$-21.

Introduction. A new series of aluminophosphate framework structures (designated $AlPO_4$-n, where n denotes a specific structure type) has been synthesized (Wilson, Lok & Flanigen, 1982; Wilson, Lok, Messina, Cannan & Flanigen, 1982) using various amines as 'templating agents'. A structure-directing role is presumed for the agent added to the starting aluminophosphate gel, which is treated hydrothermally at between 423 and 523 K. Many of the compounds are

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associated with more than one amine and it is believed that the shape and size of the template dictates the pores and channels formed by the $AlPO_4$ framework (Wilson, Lok & Flanigen, 1982). Syntheses of a similar nature have been carried out for some time in the $(Al,Si)_2O_4$ system. In fact, at least two $AlPO_4$ frameworks ($AlPO_4$-17, $AlPO_4$-20) have analogues in the $(Al,Si)_2O_4$ system (erionite and sodalite, respectively; Wilson, Lok, Messina, Cannan & Flanigen, 1982).

The novel structure of the $AlPO_4$-21 member of the family has been determined. It has been synthesized using either pyrrolidine (Wilson, Lok & Flanigen, 1982) or ethylenediamine. Since these two amines appear to have considerably different shapes this afforded an opportunity to study the role of two 'templates' in the same aluminophosphate framework. Although the framework composition is not exactly $AlPO_4$, the designation is used in the patent literature (Wilson, Lok & Flanigen, 1982) and will also be adopted here.

Upon heating, $AlPO_4$-21 is converted to a molecular sieve (Wilson, Lok & Flanigen, 1982) designated $AlPO_4$-25. The possible framework topology of this phase will also be discussed.

Experimental. Both compounds synthesized by combining, with stirring, H_3PO_4 (85%), water, Catapal® (as alumina source) and either ethylenediamine (en) or pyrrolidine (py), to give gel of composition (0·5 en) or (1·0 py):Al_2O_3:P_2O_5:$40H_2O$. Charge sealed under vacuum in thick-walled Pyrex® tube, placed in water-jacketted stainless steel bomb with Teflon® seal, heated at 423 K for 93 h for $AlPO_4$-21(py) and at 473 K for 68 h for $AlPO_4$-21(en).

Weisenberg and precision photographs indicated monoclinic ($2/m$) symmetry, space group $P2_1/n$ (No. 14) with absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$ for both compounds.

$AlPO_4$-21(en): Irregular blade, max. dimension = 0·60 mm, min. dimension = 0·08 mm; cell parameters determined from 15 reflections with $2\theta > 15°$; Nicolet Autodiffractometer; graphite monochromator (TOA = 4°); intensities measured with ω scans, $3 < 2\theta < 60·4°$, scan rate 3° min^{-1} for data with $2\theta < 48·3$ and 2° min^{-1} for $2\theta < 60·4°$; background measured at 1° above and below calculated ω value for each reflection; ratio of background count time to peak-scan time = 0·5; 6 independent reflections monitored every 300 reflections showed no significant variation; 3870 reflections collected, 2612 intensities with $I > 3\sigma(I)$ used in refinement; $\sigma^2(I) = C_t + k^2B$, where C_t = total scan time, $k = 0·5$, B = total background count; no absorption correction, ψ scans for several intense reflections confirmed absence of variable absorption effects; structure solved using *SHELXTL* to find 25 non-hydrogen atoms; H atoms not located; atomic parameters refined assuming anisotropic thermal motion using cascade block-diagonal least squares; function minimized: $\sum w(F_o - F_c)^2$, $w = \sigma^2(F)$ where $\sigma(F) = [\sigma(F_o)^2 + 0·01(F_o)^2]^{1/2}$. The en molecule is disordered with 0·5 en bonded to a framework aluminium atom and the remainder in a pore, not directly bound to the framework; $(\Delta/\sigma)_{max} = 0·02$ for final cycle, no peaks above noise (0·56 e $Å^{-3}$) in final difference Fourier map.

$AlPO_4$-21(py): Prism, 0·14 × 0·08 × 0·05 mm; cell parameters from 12 reflections with $25 < 2\theta < 31°$ (on a Picker FACS-I diffractometer); Phillips PW 1100 diffractometer for intensity data collection; graphite monochromator (TOA = 3°); θ–2θ scans, $3 < 2\theta < 50°$, 2° min^{-1} scan rate, 10 s background on each side of peak, scan width (0·8 + 0·34 tanθ)° on each side of calculated peak position; 3 independent reflections monitored every 100 min showed no significant deviation in intensity; 2596 reflections measured, 363 with $F \le 0·0$ rejected; 2112 unique intensities (R_{int} = 0·024). All data with $I > 0$ used in refinement (*SHELX*76; Sheldrick, 1976); $Al_3(PO_4)_3.H_2O$ framework taken from $AlPO_4$-21(en) and used to phase difference Fourier synthesis revealing py ring; H atoms calculated; remainder refined anisotropically; function minimized: $\sum w(F_o - F_c)^2$, $w = \sigma^{-2}(F)$, σ based on counting statistics; $(\Delta/\sigma)_{max} = 0·001$ for final cycle and no peaks above background (0·80 e $Å^{-3}$) in final difference Fourier map. Distinction between N and C in the ring was made on the basis of bond lengths and refined isotropic thermal parameters. The assignment given is not unambiguous and it was not possible on the basis of this study to distinguish whether py or py^+ occupies the channels in the structure (see below). Hydrogen positions within the framework were not located but are assumed to be associated with O(1) – the bridging oxygen between two aluminium atoms.

Analytical expressions for scattering factors from *International Tables for X-ray Crystallography* (1974), corrected for anomalous dispersion; final discrepancy factors: for $I > 3\sigma(I)$, $R = 0·045$, $wR = 0·048$ for $AlPO_4$-21(en) and for $I > 0·0$, $R = 0·071$, $wR = 0·071$ for $AlPO_4$-21(py). Calculations on Data General S-200 computer using versions of the Nicolet *E-XTL* or *SHELXTL* software package as modified by Crystalytics Company ($AlPO_4$-21; en) and Univac 1100 using *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Atomic parameters are given in Table 1* and lists of selected bond lengths and angles are given in Tables 2 and 3 (see Fig. 1 for numbering).

* Lists of structure factors, anisotropic thermal parameters and calculated hydrogen positions for $AlPO_4$-21 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39904 (31 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* ($\times 10^4$) *for non-hydrogen atoms in* $AlPO_4$-21(*en*), *shown on the top line of each entry, and* $AlPO_4$-21(*py*)

B_{eq} calculated from Schomaker & Marsh (1983).

The numbers in parentheses are the e.s.d.'s in the last significant digit.

Atom type*	x	y	z	B_{eq}(Å^2 ×10)
Al(1)	719 (1)	2947 (1)	1928 (1)	8
	833 (2)	2973 (1)	2850 (2)	5
Al(2)	1273 (1)	1073 (1)	1695 (1)	11
	1427 (2)	1113 (1)	1551 (2)	7
Al(3)	5154 (1)	3229 (1)	1912 (1)	9
	5358 (2)	3236 (1)	1804 (2)	7
P(1)	3424 (1)	4285 (1)	3611 (1)	11
	3597 (2)	4258 (1)	3475 (2)	5
P(2)	2949 (1)	2095 (1)	−253 (1)	9
	3164 (2)	2056 (1)	−346 (2)	6
P(3)	2659 (1)	1693 (1)	4984 (1)	10
	2753 (2)	1695 (1)	4896 (2)	5
O(1)	334 (3)	2042 (2)	1892 (3)	14
	483 (5)	2066 (2)	1808 (5)	8
O(2)	1856 (3)	3815 (2)	3141 (4)	18
	2035 (5)	3807 (2)	2934 (5)	9
O(3)	2454 (3)	2507 (1)	4416 (3)	12
	2517 (5)	2526 (2)	4383 (4)	8
O(4)	−600 (3)	3067 (2)	4136 (3)	16
	−474 (5)	3131 (2)	4006 (5)	12
O(5)	−690 (3)	3411 (2)	1194 (3)	15
	−607 (5)	3423 (2)	1092 (4)	8
O(6)	4553 (4)	4059 (2)	2622 (4)	20
	4652 (5)	4053 (2)	2459 (5)	11
O(7)	3361 (3)	2764 (2)	881 (3)	14
	3646 (5)	2726 (2)	761 (5)	11
O(8)	6260 (4)	3519 (2)	684 (3)	17
	6414 (5)	3543 (3)	587 (5)	14
O(9)	6410 (3)	2687 (2)	3422 (3)	14
	6631 (5)	2726 (2)	3343 (4)	8
O(11)	2573 (4)	1139 (2)	3673 (3)	15
	2658 (5)	1163 (2)	3555 (4)	9
O(12)	−658 (3)	841 (2)	314 (4)	18
	−483 (5)	939 (2)	114 (5)	9
O(13)	2928 (3)	5099 (1)	3288 (3)	11
	3160 (5)	5090 (2)	3272 (4)	9
O(14)	2601 (3)	1395 (2)	563 (3)	14
	2795 (5)	1371 (2)	504 (5)	11
N(1)†(en)	−4619 (12)	94 (6)	4536 (12)	55
N‡(py)	395 (6)	4911 (3)	−1644 (6)	17
N(2)(en)	−3967 (11)	−123 (4)	1338 (11)	98
C(1)(py)	565 (9)	4922 (5)	−3214 (8)	24
N(3)†(en)	−421 (10)	595 (5)	3020 (11)	17
C(2)(py)	2965 (10)	4368 (6)	−1591 (10)	37
C(1)†(en)	−3317 (19)	538 (1)	4021 (17)	80
C(3)(py)	1836 (10)	4483 (5)	−623 (9)	32
C(2)(en)	−3730 (13)	550 (6)	2398 (16)	100
C(4)(py)	1915 (13)	4395 (8)	−3155 (11)	64
C(3)(en)	−2340 (23)	883 (13)	2559 (29)	80

* Atoms are labelled in agreement with Fig. 1.

† The ethylenediamine moiety appears to be disordered in the lattice with two statistical orientations [N(1), C(1) and N(3), C(3)].

‡ Those atoms determined from the structural refinement of $AlPO_4$-21(en) are designated by (en) after the atom type.

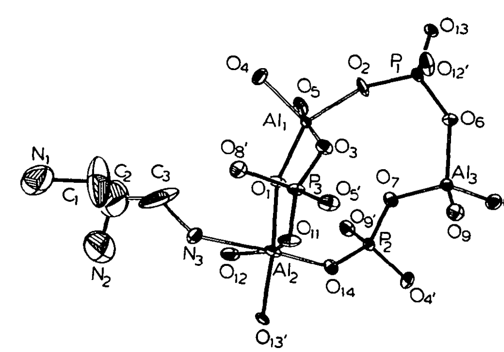


Fig. 1. Drawing of the structure of $AlPO_4$-21(en) for use with Tables 1–3. N(1), N(3), C(1), C(3) are only half occupied.

Table 2. *Bond lengths* (Å) *involving non-hydrogen atoms in* $AlPO_4$-21(*en*), *top line of each entry, and* $AlPO_4$-21(*py*)

The numbers in parentheses are the e.s.d.'s in the last significant digit.

Type*		Type*	
Al(1)–O(1)	1·838 (3)	P(1)–O(2)	1·522 (3)
	1·838 (4)		1·516 (4)
Al(1)–O(2)	1·798 (3)	P(1)–O(6)	1·541 (4)
	1·787 (4)		1·536 (4)
Al(1)–O(3)	1·861 (3)	P(2)–O(13)	1·511 (3)
	1·865 (4)		1·509 (4)
Al(1)–O(4)	1·796 (4)	P(1)–O(12')†	1·531 (3)
	1·795 (4)		1·514 (4)
Al(1)–O(5)	1·863 (3)	P(2)–O(7)	1·543 (3)
	1·887 (4)		1·529 (4)
Al(2)–O(1)	1·924 (3)	P(2)–O(4')†	1·514 (3)
	1·911 (4)		1·511 (4)
Al(2)–O(11)	1·817 (3)	P(2)–O(9')†	1·547 (3)
	1·827 (4)		1·545 (4)
Al(2)–O(12)	1·798 (3)	P(2)–O(14)	1·517 (3)
	1·802 (4)		1·523 (4)
Al(2)–N(3)	2·283 (10)	P(3)–O(3)	1·528 (3)
	—		1·530 (4)
Al(2)–O(13')†	1·858 (3)	P(3)–O(11)	1·527 (3)
	1·832 (4)		1·530 (4)
Al(2)–O(14)	1·820 (3)	P(3)–O(5')†	1·520 (2)
	1·798 (4)		1·523 (4)
Al(3)–O(6)	1·742 (3)	P(3)–O(8')†	1·543 (4)
	1·740 (4)		1·542 (4)
Al(3)–O(7)	1·745 (3)		
	1·748 (4)		
Al(3)–O(8)	1·727 (4)		
	1·733 (4)		
Al(3)–O(9)	1·758 (3)		
	1·752 (4)		
Ethylenediamine [$AlPO_4$-21(en)]			
N(1)–C(1)	1·53 (2)	C(1)–C(2)	1·41 (2)
N(2)–C(2)	1·51 (2)	C(2)–C(3)	1·29 (2)
N(3)–C(3)	1·64 (2)		
Pyrrolidine [$AlPO_4$-21(py)]			
N–C(1)	1·49 (1)	N(1)–C(3)	1·51 (1)
C(2)–C(3)	1·52 (1)	C(2)–C(4)	1·45 (1)
		C(1)–C(4)	1·48 (1)

* Atoms are labelled in agreement with Fig. 1.

† Atoms labelled with a prime(′) are related to non-primed atoms as follows, where the atomic coordinates (*x*,*y*,*z*) are given in Table 1: O(4′) $\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; O(5′) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; O(8′) $-\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; O(9′) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; O(12′) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; O(13′) $\frac{1}{2}-x, -\frac{1}{2}+y, \frac{1}{2}-z$.

Table 3. *Selected interatomic angles* (°) *for irregular polyhedra in* (*a*) $AlPO_4$-21(*en*) *and* (*b*) $AlPO_4$-21(*py*) (*see Fig.* 1)

	(*a*)*	(*b*)*		(*a*)*	(*b*)*
O(1)Al(1)O(2)	144·8	137·4	O(1)Al(2)O(11)	90·0	88·5
O(3)	89·5	89·6	O(12)	87·2	84·7
O(4)	111·4	114·2	N(3)	86·8	—
O(5)	89·1	87·5	O(13′)	172·5	158·4
O(2)Al(1)O(3)	89·5	90·1	O(14)	96·3	102·9
O(4)	103·7	108·2	O(11)Al(2)O(12)	150·8	150·5
O(5)	84·8	85·3	N(3)	78·5	—
O(3)Al(1)O(4)	95·9	96·2	O(13′)	86·1	85·4
O(5)	167·9	169·7	O(14)	103·8	104·4
O(4)Al(1)O(5)	95·8	94·0	O(12)Al(2)N(3)	72·4	—
			O(13′)	93·1	90·6
			O(14′)	105·4	105·1
			N(3)Al(2)O(13′)	86·2	—
			O(14)	176·1	—
			O(13′)Al(2)O(14)	90·8	98·7

* E.s.d.'s are 0·2°.

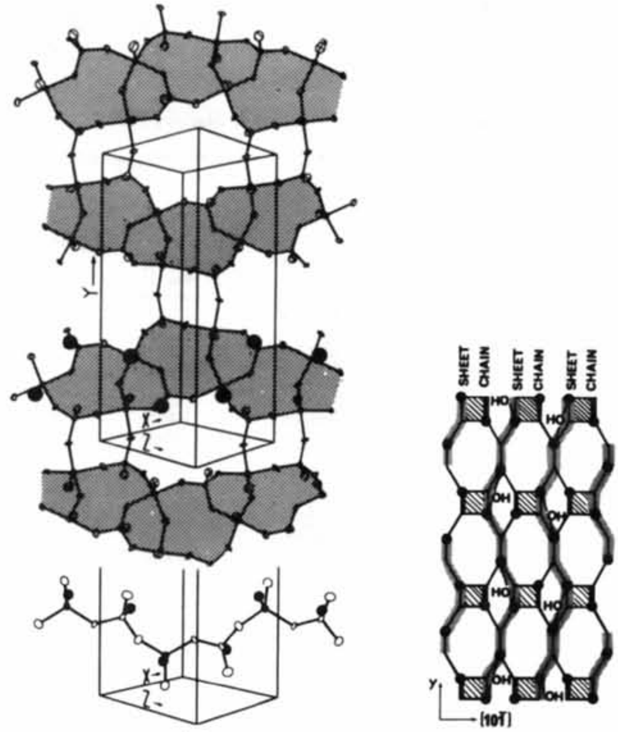
Discussion.

Polyhedral geometry. There are three types of metal-centred polyhedra in the structure; regular Al^{IV}- and P^{IV}-centred tetrahedra and irregular Al^{V} polyhedra [Al(1) and Al(2)] intermediate between trigonal bipyramids and tetragonal pyramids (Tables 2 and 3, Fig. 1). The greatest deviation from regular trigonal bipyramidal geometry is for Al(2) (about 14° on average if only bonds to oxygen are taken into account), which approaches a tetragonal pyramid [about 8° deviation on average using the ideal values given by Stephenson & Moore (1968) for grandidierite]. The only significant deviation in geometry in $AlPO_4$-21(py) compared with $AlPO_4$-21(en) is the O(1)–Al(2)–O(13) angle, which increases from 158 to 172° (Table 3, Fig. 1) owing to the approach of N(3) in $AlPO_4$-21(en). The way in which these polyhedra are connected to form the framework is the same in both compounds.

Framework. Two structural elements are common to a series of aluminophosphate networks (Parise, 1984*a,b,c*) containing Al^{V}. These elements are sheets or blocks of [Al^{V}, P^{IV}] polyhedra, which are connected *via* sheets or chains containing [Al^{IV}, P^{IV}] tetrahedra in strict alternation. In the case of $AlPO_4$-12 (Parise, 1984*b*) blocks of composition [$Al_2^{V}P_2^{IV}O_7(OH)$] alternate with sheets of [$Al^{IV}P^{IV}O_4(OH)$] while for $AlPO_2$-EN3 (Parise, 1984*b,c*) sheets of [$Al_4^{V}P_4O_{14}(OH)_4$] composed of edge-shared three- and five-membered rings are inter-connected by zig-zagging chains of [$Al_2^{IV}P_2^{IV}O_8$]. The strict separation of Al^{IV} from Al^{V} into distinct structural elements is seen in all $AlPO_4$-*n* family members containing Al^{V} studied so far.

The structure can most easily be visualized as being built from corrugated sheets stacked alongside one another in the [$\bar{1}01$] direction. These sheets are crosslinked to single crankshaft-shaped chains of $AlPO_4$ running between them (Fig. 2). Ribbons of edge-shared three- and five-membered rings run along [101] and are interconnected *via* four-membered rings to form the sheet (Fig. 2*a,b*). The edge between three- and five-membered rings is formed by Al(1)–O(1)–Al(2) and the undersaturated O(1) is likely to be either a hydroxyl group or a water molecule. Between the sheets, at about $y = \frac{1}{4}$ and $\frac{3}{4}$, chains of strictly alternating AlO_4 and PO_4 tetrahedra (Fig. 2*a*) run along [101]. These chains, crankshaft in shape, connect the sheets to form a three-dimensional network of channels bounded by eight-membered rings along [101] and [$\bar{1}01$] (Fig. 3).

Interestingly, if the –OH– group were removed, with the formation of a six-membered ring from the cleavage of the edge between the three-membered ring and the five-membered ring, there would be strict alternation of Al and P around the net formed. All metals would then be four coordinate (Fig. 2*b*). In fact, upon calcination both $AlPO_4$-21(en) and $AlPO_4$-21(py)



(*a*) (*b*)

Fig. 2. (*a*) The corrugated sheet in the (10$\bar{1}$) plane composed of ribbons of edge-shared three- and five-membered rings (shaded) connected *via* four-membered rings. These sheets are connected perpendicular to the plane of the paper by crankshaft-shaped $AlPO_4$ chains, shown exploded from the sheet at the bottom of the diagram. The trace of the chain across the top of the ribbon is emphasized by the large dots (representing oxygen). (*b*) A schematic drawing perpendicular to (*a*) with the corrugated sheets (shaded), and chains pointing out of the page. The orientation is similar to that of Fig. 3. The double crankshaft, pointing out of the page, is shown hatched and Al atoms are represented by dots. Oxygen is omitted.

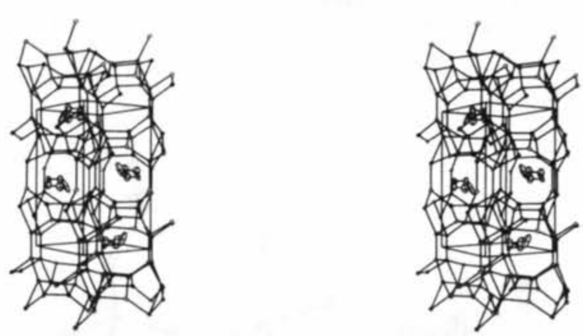


Fig. 3. The structure of the framework of $AlPO_4$-21 showing the pyrrolidine molecule at the intersection of two eight-membered-ring channel systems. The corrugated sheet, crankshaft chain and the straight eight-membered-ring channels (Fig. 1) are pointing out of the page. The origin of the cell is in the bottom back corner with **y** up, **x** to the right and **z** left. Al is represented by dots and oxygen, at the approximate mid-point of the straight-line segments, has been omitted for clarity.

are converted to the molecular sieve $AlPO_4$-25. Single-crystal data are being collected on $AlPO_4$-25 as well as the dehydration product of $AlPO_4$-EN3 (Parise, 1984*c*). Distance least squares (*DLS*76; Baerlocher, Hepp & Meier, 1977) is being used to construct models consistent with the observed orthorhombic cell parameters ($a = 8{\cdot}45$, $b = 18{\cdot}91$, $c = 15{\cdot}24$ Å). One such model is shown in Fig. 4. The straight eight-membered ring channel, found in $AlPO_4$-21 along [101], is maintained in $AlPO_4$-25 parallel to [100]. However, the presence of diffuse scattering perpendicular to [100] on single-crystal X-ray photographs suggests these channels may be partially blocked by faults, intergrowths or other short-range effects.

Templates. The en and py molecules occupy about the same position in the structure and seem to have similar space-filling requirements. Although the en molecule is statistically distributed with one half $C_2H_8N_2$ of one orientation per asymmetric unit, it has the same orientation in both cases with torsion angles N(1)—C(1)—C(2)—N(2) = 59 (2)° and N(2)—C(2)—C(3)—N(3) = −52 (3)°, Figs. 1 and 5. This arrangement is similar to that found for the en molecule in $AlPO_4$-12 (Parise, 1984*b*), where the torsion angle is 67 (3)°. This *gauche* configuration for en has been predicted to be the most stable form; its stability arising from the presence of intramolecular hydrogen bonding between N—H and the lone pair (—N:) on the second nitrogen (Radom, Lathan, Hehre & Pople, 1973). The configuration then approximates a five-membered ring (H—N—C—C—N:).

The statistical distribution of en is due to the close N(1)—N(1) distance [1·2 (2) Å], which precludes the full occupancy of this site. The C(1)—N(1) linkage is directed into the middle of an eight-membered ring, while C(3)—N(3) points to the top of a second eight-membered ring (Figs. 1 and 5*a*). The bulk of the molecule is in the cavity formed between the sheets and chains of Al^{V}, Al^{IV} and P^{IV} polyhedra (see above and Fig. 3). The aspect of en, and its consistent shape, suggests it may be responsible for the framework geometry, although this is by no means certain. Ethylenediamine has been used in the synthesis of four distinct aluminophosphate frameworks (Parise, 1984*c*). In each case the conformation of en is different.

The py molecule in $AlPO_4$-21(py) appears to be well ordered (Fig. 5*b*) with one py per asymmetric unit. It is positioned in the eight-membered ring channels with N once again pointing into another eight-membered ring (Figs. 3 and 5*b*). En and py are seen to occupy roughly equivalent positions and space within the framework.

$AlPO_4$-21 is a unique framework related to the other Al^{V}-containing $AlPO_4$-*n* family members by the separation of Al^{V} and Al^{IV} into discrete structural elements. It consists of sheets of $[Al_2^{V}P_2^{IV}O_8.H_2O]$ or $[Al_2^{V}P_2^{IV}O_8.OH]^-$ cross linked along $[\bar{1}01]$ by $[AlPO_4]$ chains of strictly alternating AlO_4 and PO_4 tetrahedra. These linkages (Fig. 3) form channels bounded by eight-membered rings along [101] and $[\bar{1}01]$. Upon calcination $AlPO_4$-21 is converted to $AlPO_4$-25. A comparison of measured and calculated cell volumes suggests the cleavage of Al(1)—O(1)—Al(2) connections to form a framework with an orthorhombic cell with flat four-, six- and eight-membered rings, through the dehydration of the O(1) site, which is the edge between three- and five-membered-ring units in $AlPO_4$-21. Within the channels en or py molecules are arranged in a fashion to suggest their structure-directing roles during synthesis.

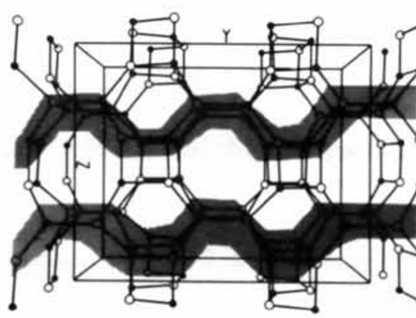


Fig. 4. A model for the structure of $AlPO_4$-25 calculated using *DLS*-76 (Baerlocher, Hepp & Meier, 1977) and the observed orthorhombic cell. Although the symmetry used ($B2_1/a$, an alternative setting of $P2_1/c$) is inconsistent with weak $0kl$, $l = 2n + 1$, reflections observed on single-crystal photographs, the connectivity of the framework is essentially correct. Oxygens are omitted and Al is represented by dots.

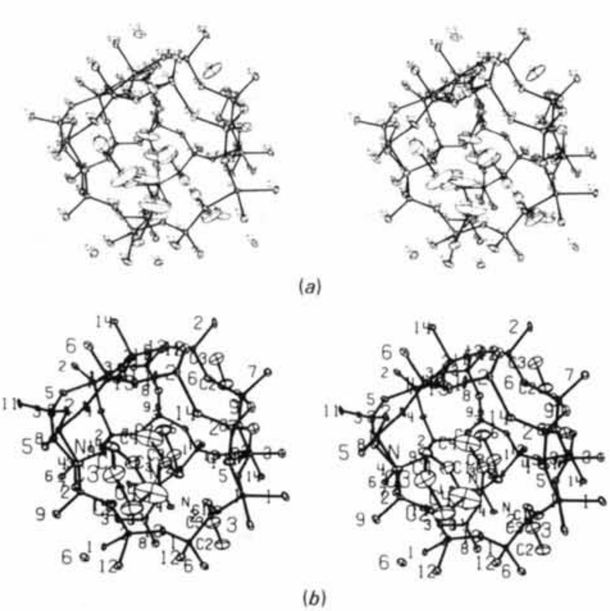


Fig. 5. The environment around (*a*) ethylenediamine and (*b*) pyrrolidine in the structure of $AlPO_4$-21. Aluminium atoms are represented by dots. Numbers are as per Tables 1 and 2.

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Structure of Iodobis(1-pyrrolidinecarbodithioato)antimony(III), $[SbI(C_5H_8NS_2)_2]$

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Abstract. $M_r = 541·5$, triclinic, $P\bar{1}$, $a = 5·993$ (1), $b = 16·981$ (6), $c = 8·595$ (2) Å, $\alpha = 93·55$ (3), $\beta = 100·16$ (2), $\gamma = 99·44$ (2)°, $V = 845·6$ (4) Å^3, $Z = 2$, $D_x = 2·13$, $D_m = 2·14$ (2) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 3·9$ mm^{-1}, $F(000) = 516$, $T = 295$ K, $R = 0·056$ for 1985 observed reflections. The complex consists of an infinite polymeric chain of $Sb[S_2CN(CH_2)_4]_2$ units linked by iodine bridges. Antimony and iodine alternate along the *a* axis. Besides two I atoms at 3·523 (1) and 3·365 (1) Å, the Sb atom is coordinated by four S atoms at 2·502 (3)–2·697 (4) Å forming a distorted polyhedron of an irregular geometrical shape.

Introduction. Complexes of dithiocarbamates (dtc's) with many different central metal ions have been extensively studied. However, only a limited amount of information on the bonding and structural properties is available for non-transition-metal complexes, especially for the $M(dtc)_2X$ type with the central atoms as As, Sb or Bi. Although a significant number of $M(dtc)_2X$ complexes have been prepared recently (Manoussakis, Tsipis & Hadjikostas, 1975; Tsipis & Manoussakis, 1976; Preti, Tosi & Zannini, 1979), to date only a few crystal structures of mixed-ligand halide dithiocarbamate complexes have been investigated. For antimony analogues the structures of $[Sb(S_2CN\textit{n}\text{-}Bu_2)_2]_2[Cd_2I_6]$ (van de Leemput, Cras & Willemse, 1977), $[SbI(S_2CNEt_2)_2].CHCl_3$ and $[SbI(S_2CNEt_2)_2]$-$(0·5I_2)_x$, $x \le 1$ (McKie, Raston, Rowbottom & White, 1981) have been determined. The type of structure in the Et_2dtc analogues is a polymeric chain of the form $-Sb(S_2CNEt_2)_2-I-Sb(S_2CNEt_2)_2-$; unlike the *n*-$Bu_2$dtc analogue, the description of the crystal structure has been made without consideration of the Sb···I contacts. The type of amine group ($-NR_2$) in the complexes mentioned above was ($-NEt_2$) or ($-NBu_2$), whereas a cyclic amine $[-N(CH_2)_4]$ has been used in the present work.

Experimental. Air-stable dark-orange needle-like crystals prepared as described previously for bromo

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