2b) remains practically unaffected by M-atom substitution. Thus this particular matrix element could also be of importance for the Mo_6-cluster geometry.

Further structural features which change significantly upon M-atom substitution are the amplitudes of thermal vibrations of the M and axial chalcogen [S(2)] atoms. They show strong anisotropy (see $U_\perp$ and $U_{\parallel}$ values in Table 2). The vibrations of the M atoms are up to three times larger parallel to than perpendicular to the ternary axis. As expected from the topology of the structure those of the axial S(2) atom ligands follow these vibrations. Those perpendicular to the ternary axis [$U_\perp = 0{\cdot}01744$ (Eu), 0·0166 (Sr), 0·01401 Å^2 (Ba)] correlate with the lattice transformation temperatures, $T_t = 109$ (Eu), 139 (Sr), 171 K (Ba).

Note added in proof: Structure parameters were recently reported for $EuMo_6S_8$ (Peña, Horyn, Geantet, Gougeon, Padiou & Sergent, 1986). They do not differ significantly from those reported above. Their precision is lower by a factor of two, on the average.

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Structure of an Ammonium Lead Polyphosphate

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Abstract. $NH_4Pb(PO_3)_3$, $M_r = 462{\cdot}2$, monoclinic, $P2_1/c$, $a = 7{\cdot}214\,(2)$, $b = 17{\cdot}062\,(3)$, $c = 14{\cdot}157\,(2)$ Å, $\beta = 105{\cdot}30\,(2)^\circ$, $V = 1680{\cdot}8$ Å^3, $Z = 8$, D_m not measured (insufficient material), $D_x = 3{\cdot}65$ Mg m^{-3}, λ(Mo $K\bar{\alpha}$) = 0·7107 Å, $\mu = 207{\cdot}5$ mm^{-1}, $F(000) = 1680$, $T = 293$ K, final $R = 0{\cdot}066$ for 3446 counter-measured reflections. The structure consists of infinite contorted $(PO_3)_n$ chains containing six unique phosphorus–oxygen tetrahedra separated by lead–oxygen polyhedra, one seven and one eight coordinate, and ammonium ions. The mean P—O and Pb—O distances are 1·544 and 2·655 Å respectively.

Introduction. Following from an interest in compounds containing chains or polyanions of the type $E_4O_{13}^{n-}$, the structure of $Ba_3V_4O_{13}$ was recently determined (Gatehouse, Guddat & Roth, 1987). The unit-cell dimensions of this compound and of low- and high-temperature $Ba_3P_4O_{13}$ were reported recently (Millet, Parker & Roth, 1986), as was a method of preparation of $Pb_3P_4O_{13}$ (Averbuch-Pouchot & Durif, 1986). During attempts to prepare single crystals of the latter compound, crystals of another material, that proved to be $NH_4Pb(PO_3)_3$, were obtained. The structure of this compound is reported here.

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Experimental. A suitable tabular crystal 0·21 × 0·09 × 0·02 mm was selected from a preparation in which 1 g of $Pb_3P_4O_{13}$ powdered material was heated with 3 g of $(NH_4)_2HPO_4$ for 3 days at 573 K, followed by slow cooling to room temperature.

Space group $P2_1/c$ from systematic absences $0k0$ k odd and $h0l$ l odd; cell parameters determined from 25 reflections ($6° < \theta < 12°$) with a Philips PW 1100 automatic four-circle diffractometer equipped with a graphite monochromator as described previously (Canty, Chaichit & Gatehouse, 1980). Three standard reflections measured at 4 h intervals. No decomposition occurred. Data collected using ω-scan technique with a symmetric scan width of ±0·700° in ω from the calculated Bragg angle, with an allowance for dispersion, at a scan rate of 0·05° s^{-1}. No reflection was sufficiently intense to warrant the insertion of an attenuation filter. Data processed using a program written specifically for the PW 1100 diffractometer (Hornstra & Stubbe, 1972). Values of I and $\sigma(I)$ corrected for Lorentz and polarization effects. Absorption correction applied based on indexed crystal faces, max. and min. transmission factors 0·5827 and 0·0769 respectively. 5410 reflections measured to $2\theta = 60°$, 3446 unique reflections [$I \geq 3\sigma(I)$] used in analysis; index range h −10/9, k 0/23, l 0/19. Pb-atom parameters found from Patterson synthesis and all non-H atoms located in subsequent difference Fourier syntheses. Function minimized in full-matrix least-squares refinement $\sum w(|F_o| - |F_c|)^2$, where w is the weight $\{[\sigma^2(F_o)]^{-1}\}$. Pb atoms refined anisotropically, other atoms refined isotropically (H atoms not located); 123 variable parameters, final $R = 0·066$ and $wR = 0·055$ (for observed reflections); max. Δ/σ in final cycle 0·006. Final difference Fourier synthesis had $\Delta\rho$ within 3·1 and $-3·4$ e Å^{-3}, both in the vicinity of Pb atoms. Scattering factors for neutral atoms and corrections for anomalous dispersion from *International Tables for X-ray Crystallography* (1974). All calculations performed on the Monash University VAX 11/780 computer system. Major programs used: *SHELX*76 (Sheldrick, 1976), *ORFFE* (Busing, Martin & Levy, 1964) and *ORTEP* (Johnson, 1965).

Discussion. Final fractional coordinates and thermal parameters are given in Table 1,* interatomic distances and selected angles are given in Table 2. The numbering scheme used in the tables and in Fig. 1 follows that of Averbuch-Pouchot, Durif & Guitel (1976) where O(*Lij*) denotes the O atom that links P*i* with P*j* and O(*Eij*) denotes the *j*th O atom exterior to the chain and bonded to phosphorus P*i*.

Table 1. *Final parameters* (× 10^5 *for* Pb, × 10^3 *for* O, × 10^4 *for other atoms*) *with their e.s.d.'s in parentheses*

	x	y	z	U (Å^2)
Pb(1)	20323 (8)	6853 (3)	11813 (4)	133 (2)†
Pb(2)	32988 (8)	−7666 (3)	36978 (4)	127 (2)†
N(1)	1611 (19)	1688 (7)	5040 (9)	182 (26)
N(2)	6177 (20)	1610 (7)	9505 (10)	231 (29)
P(1)	−147 (6)	−3624 (2)	6412 (3)	119 (7)
P(2)	361 (5)	−2514 (2)	8039 (3)	114 (7)
P(3)	4389 (5)	−2210 (2)	8132 (3)	119 (7)
P(4)	4572 (5)	−1235 (2)	6428 (3)	112 (7)
P(5)	1563 (6)	−103 (2)	6501 (3)	124 (7)
P(6)	2764 (6)	119 (2)	8641 (3)	135 (7)
O(*E*11)	−264 (15)	−3467 (5)	5365 (8)	18 (2)
O(*E*12)	1477 (15)	−4116 (5)	6961 (8)	17 (2)
O(*L*12)	−123 (15)	−2780 (6)	6917 (8)	18 (2)
O(*E*21)	897 (15)	−3211 (6)	8684 (8)	19 (2)
O(*E*22)	−1164 (15)	−1974 (5)	8172 (8)	18 (2)
O(*L*23)	2221 (15)	−1988 (5)	8115 (8)	17 (2)
O(*E*31)	5562 (15)	−1659 (5)	8878 (7)	16 (2)
O(*E*32)	4786 (15)	−3071 (5)	8286 (8)	18 (2)
O(*L*34)	4462 (16)	−2020 (5)	7040 (8)	19 (2)
O(*E*41)	5967 (14)	−674 (5)	7047 (7)	17 (2)
O(*E*42)	4863 (17)	−1497 (6)	5490 (9)	26 (3)
O(*L*45)	2413 (15)	−926 (5)	6203 (8)	16 (2)
O(*E*51)	−526 (17)	−104 (6)	6009 (8)	22 (2)
O(*E*52)	2858 (15)	538 (5)	6376 (8)	18 (2)
O(*L*56)	1716 (15)	−275 (5)	7637 (8)	19 (2)
O(*E*61)	1840 (16)	−204 (6)	9375 (8)	20 (2)
O(*E*62)	4860 (16)	125 (6)	8797 (8)	24 (3)
O(*L*61)	2124 (16)	1037 (5)	8470 (8)	19 (2)

† $U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

Anisotropic thermal parameters for Pb(1) and Pb(2) (× 10^4) are of the type $\exp[-2\pi^2(U_{11}h^2a^{*2} + \cdots + 2U_{12}hka^*b^*\cdots)]$.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb(1)	119 (3)	118 (2)	153 (3)	−24 (2)	20 (2)	10 (2)
Pb(2)	140 (3)	88 (2)	138 (3)	0 (2)	9 (2)	−10 (2)

The crystal structure of $NH_4Pb(PO_3)_3$ consists of infinite contorted chains of PO_4 tetrahedra sharing corners and repeating after six tetrahedra (Fig. 1). The P—O distances may be divided into the linking or bridging P—O distances that range from 1·467 to 1·501 Å, and the exterior P—O distances that range from 1·574 to 1·632 Å. A very similar distribution of P—O bond lengths was reported earlier for $Li_2NH_4(PO_3)_3$ (Averbuch-Pouchot, Durif & Guitel, 1976), with linking P—O distances 1·480–1·485 Å and exterior P—O distances 1·593–1·604 Å. The three unique PO_4 tetrahedra in $Li_2NH_4(PO_3)_3$ are repeated by a screw axis giving a period of six tetrahedra in the **b** direction of the unit cell. The unit-cell volume of $Li_2NH_4(PO_3)_3$ (1677·07 Å^3) is very similar to that of the compound reported here, $NH_4Pb(PO_3)_3$, which is 1680·8 Å^3.

The Pb-atom coordination polyhedra are shown in Fig. 2 where it can be seen that the irregular eight-coordinate Pb(1) atom shares an edge [O(*E*12) and O(*E*40)] with the seven-coordinate Pb(2) atom. A description of the polyhedra in terms of regular solids has not been attempted.

Contacts between O atoms and the N atoms of the ammonium ion, out to a limiting distance of 3·10 Å, are listed in Table 2. In the absence of resolution of the H atoms, no attempt has been made to describe any hydrogen bonding.

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* Lists of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43985 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 2. *Interatomic distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses for* $NH_4Pb(PO_3)_3$

P—O distances are underlined and O—P—O angles are given in the upper right triangles of the listing for each P.

P(1)	O($L61$)	O($E11$)	O($E12$)	O($L12$)
O($L61^{\rm i}$)	1·588 (12)	110·7 (6)	110·3 (6)	100·6 (6)
O($E11^{\rm i}$)	2·53 (2)	1·487 (12)	116·9 (7)	105·8 (6)
O($E12^{\rm i}$)	2·52 (1)	2·53 (1)	1·483 (9)	111·1 (5)
O($L12^{\rm i}$)	2·46 (1)	2·47 (2)	2·55 (1)	1·606 (10)

P(2)	O($L12$)	O($E21$)	O($E22$)	O($L23$)
O($L12$)	1·599 (11)	109·6 (6)	109·1 (6)	100·7 (6)
O($E21$)	2·52 (2)	1·487 (10)	120·0 (7)	109·3 (6)
O($E22$)	2·51 (2)	2·57 (1)	1·484 (12)	106·3 (6)
O($L23$)	2·46 (1)	2·51 (2)	2·47 (2)	1·595 (11)

P(3)	O($L23$)	O($E31$)	O($E32$)	O($L34$)
O($L23$)	1·603 (12)	103·3 (6)	112·5 (6)	102·7 (6)
O($E31$)	2·43 (1)	1·498 (10)	117·5 (5)	113·5 (6)
O($E32$)	2·58 (1)	2·56 (1)	1·501 (10)	106·6 (6)
O($L34$)	2·50 (2)	2·59 (1)	2·48 (1)	1·594 (12)

P(4)	O($L34$)	O($E41$)	O($E42$)	O($L45$)
O($L34$)	1·608 (10)	109·8 (5)	105·9 (6)	101·5 (6)
O($E41$)	2·54 (1)	1·494 (10)	119·4 (7)	112·0 (6)
O($E42$)	2·46 (2)	2·56 (2)	1·467 (14)	106·6 (6)
O($L45$)	2·48 (1)	2·56 (1)	2·46 (2)	1·600 (11)

P(5)	O($L45$)	O($E51$)	O($E52$)	O($L56$)
O($L45$)	1·631 (11)	106·4 (6)	108·3 (6)	99·8 (5)
O($E51$)	2·50 (2)	1·484 (11)	122·7 (6)	105·2 (7)
O($E52$)	2·52 (1)	2·60 (2)	1·478 (11)	112·0 (6)
O($L56$)	2·48 (2)	2·46 (1)	2·56 (2)	1·611 (12)

P(6)	O($L56$)	O($E61$)	O($E62$)	O($L61$)
O($L56$)	1·574 (10)	106·1 (6)	111·6 (7)	103·1 (5)
O($E61$)	2·44 (2)	1·481 (13)	122·2 (6)	107·4 (6)
O($E62$)	2·52 (1)	2·58 (2)	1·469 (12)	104·8 (6)
O($L61$)	2·51 (1)	2·51 (2)	2·46 (2)	1·632 (10)

Intertetrahedra angles

P(1)—O($L12$)—P(2)	132·1 (6)	P(4)—O($L45$)—P(5)	130·3 (6)
P(2)—O($L23$)—P(3)	131·9 (6)	P(5)—O($L56$)—P(6)	135·6 (7)
P(3)—O($L34$)—P(4)	135·3 (7)	P(6)—O($L61$)—P(1)	124·1 (7)

Lead—oxygen distances

Pb(1)—O($E31^{\rm ii}$)	2·420 (10)	Pb(2)—O($E32^{\rm v}$)	2·399 (10)
O($E22^{\rm iii}$)	2·524 (10)	O($E21^{\rm v}$)	2·455 (10)
O($E41^{\rm ii}$)	2·542 (9)	O($E12^{\rm v}$)	2·472 (9)
O($E62^{\rm ii}$)	2·627 (12)	O($E51^{\rm iii}$)	2·612 (12)
O($E11$)	2·653 (10)	O($E41^{\rm ii}$)	2·780 (10)
O($E61^{\rm iii}$)	2·817 (11)	O($E42$)	2·784 (11)
O($E61^{\rm iv}$)	2·945 (11)	O($E52^{\rm ii}$)	2·829 (11)
O($E12^{\rm v}$)	2·964 (9)		

Phosphorus—phosphorus distances		Lead—lead distances	
P(1)—P(2)	2·929 (5)	Pb(1)—Pb(2)	4·236 (1)
P(2)—P(3)	2·920 (6)	Pb(1)—Pb(1)	4·481 (1)
P(3)—P(4)	2·962 (5)	Pb(2)—Pb($2^{\rm ii}$)	4·657 (1)
P(4)—P(5)	2·928 (5)		
P(5)—P(6)	2·949 (5)		
P(6)—P($1^{\rm vii}$)	2·844 (5)		

Nitrogen—oxygen distances

N(1)—O($E52$)	2·71 (2)	N(2)—O($E62$)	2·80 (2)
O($E42^{\rm ii}$)	2·85 (2)	O($E31^{\rm ix}$)	2·89 (2)
O($E21^{\rm vii}$)	2·88 (2)	O($E11^{\rm viii}$)	2·91 (2)
O($E32^{\rm viii}$)	3·05 (2)	O($E61^{\rm ix}$)	3·02 (2)
O($E51^{\rm v}$)	3·08 (2)	O($L61$)	3·06 (2)

Symmetry code: (i) $-x, y-\frac{1}{2}, 1\frac{1}{2}-z$; (ii) $1-x, -y, 1-z$; (iii) $-x, -y, 1-z$; (iv) $x, y, z-1$; (v) $x, -\frac{1}{2}-y, z-\frac{1}{2}$; (vi) $1+x, y, z$; (vii) $-x, \frac{1}{2}+y, 1\frac{1}{2}-z$; (viii) $1-x, \frac{1}{2}+y, 1\frac{1}{2}-z$; (ix) $1-x, -y, 2-z$.

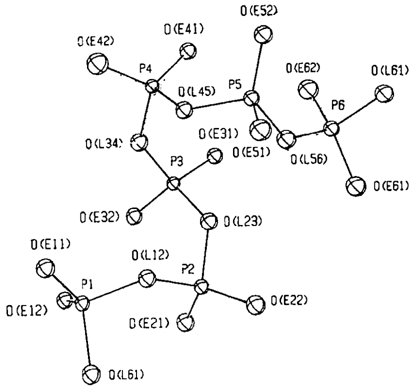

Fig. 1. The phosphorus–oxygen corner-linked tetrahedra in $NH_4Pb(PO_3)_3$ are shown together with the numbering scheme used.

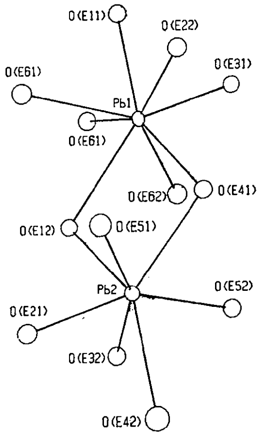

Fig. 2. The linked Pb(1) and Pb(2) polyhedra in $NH_4Pb(PO_3)_3$.

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