

Structure of $\text{NH}_4\text{Al}_2(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$, the Ammonium–Aluminum Analog of $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$ and Leucophosphate

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Abstract. $M_r = 315$, monoclinic, $P2_1/n$, $a = 9.6167$ (3), $b = 9.5720$ (4), $c = 9.5563$ (3) Å, $\beta = 103.589$ (2)°, $V = 855.0$ Å³, $Z = 4$, $D_x = 2.45$ g cm⁻³, $\lambda(\text{Mo K}\alpha) = 0.70926$ Å, $\mu = 7.6$ cm⁻¹, $F(000) = 640$, $T \sim 295$ K, $R = 0.031$ for 6674 reflections. The crystal, synthesized using 1,4-diaminobutane as trial template, contains a tetramer of edge-sharing $\text{AlO}_4(\text{OH})_2$ and vertex-sharing $\text{AlO}_4(\text{OH})(\text{H}_2\text{O})$ octahedra, which share vertices with PO_4 tetrahedra to form a framework three-connected at OH and two-connected at O. The NH_4^+ ion is hydrogen-bonded to four O atoms, and a water molecule is removable without framework collapse.

Introduction. Aluminum and iron phosphates containing ammonium and potassium are produced by the interaction of fertilizers with soils (Haseman, Lehr & Smith, 1951; Smith & Brown, 1959; Lehr, Brown, Frazier, Smith & Thrasher, 1967). Synthetic product *I*, $\text{KFe}_2(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ (Smith & Brown, 1959), is known to mineralogists as leucophosphate (Moore, 1972). Its crystal structure contains a tetramer of Fe-centered octahedra cross-linked by PO_4 tetrahedra into a three-dimensional (3D) framework (Moore, 1972) whose cavities contain K and one of the water molecules. Product *J* (Smith & Brown, 1959) has similar cell dimensions, with NH_4 and Al replacing K and Fe^{III} respectively. Heating of the NH_4 -Al analog (Boldog, Golub & Kalininichenko, 1976) resulted in sequential loss of the first H_2O , and then NH_3 and H_2O to yield amorphous AlPO_4 and ultimately the cristobalite variety; thermal decomposition of the K-Al and Rb-Al analogs was also reported. The NH_4 -Al analog was synthesized during exploration of a new family of aluminophosphate framework structures (Wilson, Lok, Messina, Cannan & Flanigen, 1982, 1983), and was labeled $\text{AlPO}_4\text{-15}$. We report the crystal structure of $\text{AlPO}_4\text{-15}$, for which the H positions were found by X-ray diffraction. Upon completion of the structure determination, it was found that leucophosphate and $\text{AlPO}_4\text{-15}$ are structurally related to $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$ (Mooney-Slater, 1966) for which an O

atom (perhaps part of a hydroxonium ion) had been placed in the position assigned to K in leucophosphate [$\text{H}_3\text{OGa}_2(\text{OH})(\text{H}_2\text{O})(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$].

Experimental. Crystals of $\text{AlPO}_4\text{-15}$ up to $0.5 \times 0.3 \times 0.3$ mm were synthesized using 1,4-diaminobutane as a trial template (Wilson *et al.*, 1982). D_m not determined. Tabular crystal $0.1 \times 0.2 \times 0.2$ mm. Automatic Picker four-circle diffractometer with Krisel automation. Refinement of 20 diffractions ($47 < 2\theta < 65^\circ$) yielded the cell dimensions. Total of 8554 intensities measured, 6674 unique [$I > 2\sigma(I)$], 1880 [$I < 2\sigma(I)$] unobserved. Max. $\sin\theta/\lambda = 1.08$ Å⁻¹. Data-collection range $h, k, \pm l$. Intensity variation of standard reflections 0.4%. Absorption correction, transmission factors 0.87 to 0.91. *MULTAN* (Germain, Main & Woolfson, 1971) yielded positions of all atoms except H, and difference-Fourier methods yielded H positions. Least-squares refinement used F with $w = \sigma^{-2}$. $R = 0.031$, $wR = 0.037$, $S = 1.4$, max. $\Delta/\sigma = 0.12$, max. and min. heights on final difference Fourier synthesis $\pm 0.5 \text{ e Å}^{-3}$. Neutral scattering factors (*International Tables for X-ray Crystallography*, 1974). Computer programs as in Pluth & Smith (1979).

Discussion. Final atomic coordinates and displacement parameters are given in Table 1 and interatomic distances and angles in Table 2.* To assist understanding of the *ORTEP* (Johnson, 1965) stereoplot (Fig. 1), the five structural units are shown separately in Fig. 2. The two Al atoms and two P atoms are respectively in octahedral and tetrahedral coordination. These four structural units share edges and vertices to give a 3D framework. Each Al(1) shares two hydroxyls O(9)-H(1) with another Al(1) related by a center of

* Lists of structure factors and anisotropic displacement parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39664 (41 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

symmetry (Fig. 1, body center; Fig. 2a). The octahedral coordination is completed by four O atoms, each of which is shared with a P atom [O(1) and O(3) with separate P(1) atoms; O(6) and O(7) with separate P(2) atoms]. In addition to being bonded to two Al(1), each hydroxyl O(9)—H(1) is also bonded to one Al(2). The octahedral coordination (Fig. 2b) of Al(2) is completed by one water molecule H(2)—O(10)—H(3) and four O atoms, each of which is shared with a P atom [O(2) and O(4) with separate P(1) atoms; O(5) and O(8) with separate P(2) atoms].

Table 1. Atomic positions and mean-square displacements (\AA^2) of $\text{AlPO}_4\cdot 15$

For non-hydrogen atoms $U_{eq}(\times 10^5) = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* (\mathbf{a}_i, \mathbf{a}_j)$; for H atoms $U_{iso}(\times 10^3)$.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} or U_{iso}
P(1)	0.34830 (2)	0.53183 (2)	0.69853 (2)	529 (4)
P(2)	0.13673 (2)	0.30797 (2)	0.29463 (2)	506 (4)
Al(1)	0.37209 (3)	0.53719 (3)	0.38618 (3)	573 (5)
Al(2)	0.31503 (3)	0.22896 (3)	0.60731 (3)	597 (5)
O(1)	0.29674 (6)	0.58593 (6)	0.54344 (6)	784 (11)
O(2)	0.19438 (7)	0.12742 (7)	0.69302 (7)	913 (13)
O(3)	0.48683 (6)	0.48033 (6)	0.26314 (6)	786 (11)
O(4)	0.28440 (7)	0.38569 (6)	0.70988 (7)	802 (12)
O(5)	0.16583 (7)	0.26782 (7)	0.45379 (6)	912 (12)
O(6)	0.20999 (6)	0.44859 (6)	0.27945 (6)	774 (12)
O(7)	0.30331 (7)	0.69867 (6)	0.29189 (7)	908 (12)
O(8)	0.47629 (6)	0.17560 (7)	0.73909 (7)	884 (12)
O(9)	0.44566 (6)	0.36468 (6)	0.50306 (6)	788 (12)
O(10)	0.35324 (8)	0.06688 (8)	0.49997 (8)	1402 (16)
O(11)	0.53720 (9)	0.14339 (9)	0.31701 (10)	1943 (20)
N	0.10388 (10)	0.80953 (11)	0.48671 (10)	1579 (13)
H(1)	0.4748 (18)	0.3109 (18)	0.4499 (18)	27 (4)
H(2)	0.3938 (18)	0.9970 (19)	0.5477 (19)	25 (4)
H(3)	0.3202 (19)	0.0438 (18)	0.4218 (20)	27 (5)
H(4)	0.6000 (23)	0.1442 (21)	0.2698 (21)	46 (6)
H(5)	0.4675 (23)	0.0928 (22)	0.2750 (23)	48 (6)
H(6)	0.0240 (24)	0.7849 (23)	0.4936 (23)	51 (6)
H(7)	0.0928 (21)	0.8565 (20)	0.4179 (22)	36 (5)
H(8)	0.1581 (22)	0.7310 (23)	0.4901 (21)	45 (6)
H(9)	0.1445 (20)	0.8500 (19)	0.5601 (20)	30 (5)

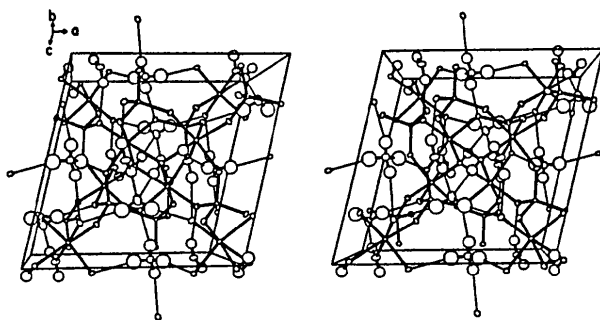


Fig. 1. Stereoplot of the $\text{AlPO}_4\cdot 15$ structure. Displacement figures are isotropic for H and anisotropic for all other atoms; 50% probability level. See Fig. 2 for drawings of the octahedral and tetrahedral subunits. There is a center of symmetry at the body center and each edge center, face center and corner of the unit cell. The diagonal glide planes $1n1$ lie at $y = \frac{1}{4}$ and $\frac{3}{4}$. A screw axis lies at each combination of $x = \frac{1}{4}$ or $\frac{3}{4}$ and $z = \frac{1}{4}$ or $\frac{3}{4}$. Hydrogen bonds are drawn as thin lines.

Each pair of Al(1) octahedra can be regarded as a dimer sharing an edge between two hydroxyls O(9)—H(1) (Fig. 3). Further sharing of each O(9) with an Al(2) produces an edge-vertex-sharing tetramer $\text{Al}_4\text{-}$

Table 2. Interatomic distances (\AA) and angles ($^\circ$) of $\text{AlPO}_4\cdot 15$

P(1)—O(1)	1.5379 (6)	P(2)—O(5)	1.5295 (6)
P(1)—O(2)	1.5098 (6)	P(2)—O(6)	1.5418 (6)
P(1)—O(3)	1.5455 (6)	P(2)—O(7)	1.5280 (7)
P(1)—O(4)	1.5419 (6)	P(2)—O(8)	1.5173 (6)
Mean	1.5338	Mean	1.5292
Al(1)—O(1)	1.8743 (7)	Al(2)—O(2)	1.8461 (7)
Al(1)—O(3)	1.8724 (7)	Al(2)—O(4)	1.8530 (6)
Al(1)—O(6)	1.8554 (7)	Al(2)—O(5)	1.8331 (7)
Al(1)—O(7)	1.8327 (7)	Al(2)—O(8)	1.8259 (7)
Al(1)—O(9)	2.0257 (7)	Al(2)—O(9)	2.2014 (7)
Al(1)—O(9)	2.0500 (7)	Al(2)—O(10)	1.9419 (8)
O(1)—P(1)—O(2)	112.29 (4)	O(5)—P(2)—O(6)	109.39 (4)
O(1)—P(1)—O(3)	109.53 (4)	O(5)—P(2)—O(7)	111.22 (4)
O(1)—P(1)—O(4)	109.25 (4)	O(5)—P(2)—O(8)	107.90 (4)
O(2)—P(1)—O(3)	108.19 (4)	O(6)—P(2)—O(7)	107.93 (4)
O(2)—P(1)—O(4)	108.93 (4)	O(6)—P(2)—O(8)	109.04 (4)
O(3)—P(1)—O(4)	108.58 (3)	O(7)—P(2)—O(8)	111.33 (3)
P(1)—O(1)—Al(1)	126.23 (4)	P(2)—O(5)—Al(2)	140.60 (4)
P(1)—O(2)—Al(2)	157.54 (4)	P(2)—O(6)—Al(1)	133.69 (4)
P(1)—O(3)—Al(1)	126.49 (4)	P(2)—O(7)—Al(1)	134.83 (4)
P(1)—O(4)—Al(2)	125.58 (4)	P(2)—O(8)—Al(2)	147.28 (4)
O(1)—Al(1)—O(3)	166.35 (3)	O(2)—Al(2)—O(4)	89.83 (3)
O(1)—Al(1)—O(6)	96.97 (3)	O(2)—Al(2)—O(5)	90.38 (3)
O(1)—Al(1)—O(7)	91.23 (3)	O(2)—Al(2)—O(8)	93.85 (3)
O(1)—Al(1)—O(9)	84.92 (3)	O(2)—Al(2)—O(9)	175.12 (3)
O(1)—Al(1)—O(9)	85.22 (3)	O(2)—Al(2)—O(10)	91.74 (3)
O(3)—Al(1)—O(6)	93.72 (3)	O(4)—Al(2)—O(5)	93.85 (3)
O(3)—Al(1)—O(7)	97.72 (3)	O(4)—Al(2)—O(8)	94.39 (3)
O(3)—Al(1)—O(9)	85.89 (3)	O(4)—Al(2)—O(9)	86.57 (3)
O(3)—Al(1)—O(9)	84.20 (3)	O(4)—Al(2)—O(10)	178.17 (3)
O(6)—Al(1)—O(7)	87.46 (3)	O(5)—Al(2)—O(8)	170.75 (3)
O(6)—Al(1)—O(9)	94.01 (3)	O(5)—Al(2)—O(9)	86.60 (3)
O(6)—Al(1)—O(9)	177.73 (3)	O(5)—Al(2)—O(10)	87.08 (3)
O(7)—Al(1)—O(9)	176.02 (3)	O(8)—Al(2)—O(9)	89.70 (3)
O(7)—Al(1)—O(9)	91.92 (3)	O(8)—Al(2)—O(10)	84.57 (3)
O(9)—Al(1)—O(9)	86.75 (3)	O(9)—Al(2)—O(10)	91.92 (3)
O(9)—H(1)	0.818 (17)	O(11)—H(4)	0.835 (21)
O(10)—H(2)	0.852 (18)	O(11)—H(5)	0.847 (22)
O(10)—H(3)	0.772 (18)		
Al(1)—O(9)—H(1)	107.3 (1.2)	Al(2)—O(10)—H(3)	130.8 (1.3)
Al(1)—O(9)—H(1)	103.5 (1.2)	Al(2)—O(10)—H(2)	117.7 (1.2)
Al(2)—O(9)—H(1)	103.0 (1.2)	H(4)—O(11)—H(5)	110.0 (1.8)
Al(1)—O(9)—Al(1)	93.25 (3)	H(4)—O(11)—H(2)	101.3 (1.5)
Al(1)—O(9)—Al(2)	124.62 (3)	H(4)—O(11)—H(1)	129.2 (1.5)
Al(1)—O(9)—Al(2)	123.11 (3)	H(5)—O(11)—H(2)	91.7 (1.5)
H(2)—O(10)—H(3)	109.1 (1.7)	H(5)—O(11)—H(1)	113.2 (1.4)
		H(2)—O(11)—H(1)	102.9 (0.7)
Ammonium ion			
N—H(6)	0.821 (23)	N—O(4)	2.9375 (12)
N—H(7)	0.783 (20)	N—O(5)	2.8795 (12)
N—H(8)	0.911 (22)	H(6)—O(5)	2.067 (23)
N—H(9)	0.816 (19)	H(7)—O(3)	2.089 (22)
N—O(1)	2.8004 (11)	H(8)—O(1)	1.909 (22)
N—O(3)	2.8558 (11)	H(9)—O(4)	2.170 (19)
H(6)—N—H(7)	106.7 (1.9)	O(5)—N—O(4)	90.37 (4)
H(6)—N—H(8)	107.4 (1.9)	O(3)—N—O(1)	131.12 (4)
H(6)—N—H(9)	109.6 (1.9)	O(3)—N—O(4)	130.71 (4)
H(7)—N—H(8)	117.9 (1.7)	O(1)—N—O(4)	85.79 (3)
H(7)—N—H(9)	113.1 (1.8)	N—H(6)—O(5)	170.6 (2.1)
H(8)—N—H(9)	101.9 (1.7)	N—H(7)—O(3)	166.6 (1.9)
O(5)—N—O(3)	101.53 (4)	N—H(8)—O(1)	165.3 (1.8)
O(5)—N—O(1)	110.58 (4)	N—H(9)—O(4)	156.7 (1.7)
Hydrogen bonds			
D—H...A	H...A	D...A	\angle D—H...A
O(9)—H(1)...O(11)	2.214 (17)	3.0263 (11)	172.4 (1.6)
O(10)—H(2)...O(11)	1.874 (19)	2.7117 (12)	167.6 (1.8)
O(10)—H(3)...O(6)	2.086 (19)	2.8318 (9)	162.4 (1.8)
O(11)—H(4)...O(4)	2.008 (22)	2.8144 (11)	162.3 (1.9)
O(11)—H(5)...O(6)	2.162 (22)	2.9913 (11)	166.1 (2.0)

$(\text{OH})_2(\text{H}_2\text{O})_2\text{O}_{16}$ like that idealized in Fig. 1 of Moore (1972). Each tetramer is distorted from the idealized shape in order to share each O with a P atom. The resulting 3D framework is two-connected at each such shared O, but three-connected at each hydroxyl. O(10) belongs to a water molecule, and is not connected directly to a P atom or to a second Al atom. However, the hydrogen bonds from H(2) and H(3) to O(11) and O(6) respectively must be important for the stability of the octahedral–tetrahedral framework (see Fig. 1 where hydrogen bonds are drawn as lines). From the topological viewpoint, the framework is characterized by three-rings of type Al(1)–Al(1)–P(1), Al(1)–Al(2)–P(1) and Al(1)–Al(2)–P(2), whose interrelations are shown at the center of Fig. 1. Most of the

octahedral and tetrahedral bonds lie in layers parallel to the (101) plane, and these layers are connected only through O(2).

The N atom has a similar position to that of K in leucophosphate and an O in $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$ (note that the y coordinate should be negative in Table 2 of Moore, 1972), but the hydrogen bonding changes the details of the linkage to the framework species. Whereas the K atom of leucophosphate is bonded to six O atoms at 2.8–3.03 Å (Fig. 5; Moore, 1972), the N atom of $\text{AlPO}_4 \cdot 15$ is surrounded by four H, each of which is hydrogen-bonded to one framework O (Fig. 2e). Five O atoms (1, 2, 3, 4, 5) remain at similar distances (2.80–3.04 Å) to those for K in leucophosphate, but the sixth O atom O(7) moves away to 3.15 Å. The remaining volume is occupied by a water molecule which is hydrogen bonded from H(4) and H(5) to framework O atoms O(4) and O(6) respectively, and from O(11) to both H(1) of a hydroxyl and H(2) of the other water molecule. Because the water molecule H(4)–O(11)–H(5) is not bonded directly to a framework cation, as is H(2)–O(10)–H(3), it must be the one lost during initial heating (Boldog *et al.*, 1976).

Returning to the framework, it is quite obvious from a study of Fig. 1 that the geometrical details depend in part on electrostatic repulsions. The positions of H(1), H(2) and H(3) allow large separations from each other and from the Al atoms. Water molecule H(2)–O(10)–H(3) is an essential component of the structure, as shown by collapse to an amorphous form when the second water molecule is removed (Boldog *et al.*, 1976). Furthermore, the hydrogen bond H(3)–O(6) is important in determining the shape of the octahedral–tetrahedral sheet. The other H atom H(2) is bonded to O(11) of the extraframework water molecule. Loss of this molecule during initial heating might result in a substantial change of shape of the framework so that H(2) could bond to a framework O, perhaps O(6).

All the distances in Table 2 can be interpreted semiquantitatively on an ionic model. Thus the Al bonds to O atoms of hydroxyl [O(9)] and water [O(10)] ligands are longer than those to O^{2-} ions. The shortest P–O and Al–O bonds are to O atoms not bonded to H. Each framework O^{2-} ion is linked to one P and one Al, and the Al–O–P angles range from 126 to 158°, with the largest angle at the O(2) bridge for which geometrical constraints are weakest. The O–P–O angles are near to ideal tetrahedral [107.9–112.3°] whereas the O–Al–O angles deviate rather more from the ideal 90° for a regular octahedron (84.2–97.7°). Although the H atoms are correctly located, it would be unwise to attempt detailed interpretation of the associated distances and angles. Let it suffice that all distances appear reasonable within the 3σ limit.

H positions were not located in the structures of $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$ and leucophosphate, but the proposed positions in Mooney-Slater (1966) and Moore (1972)

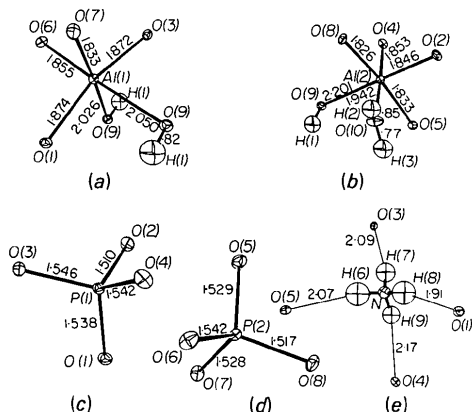


Fig. 2. Perspective drawings of the structural subunits showing displacement ellipsoids at 50% probability. Each subunit can be located in Fig. 1. (a) Octahedron around Al(1) at $x = 0.372$, $y = 0.537$, $z = 0.386$. (b) Octahedron around Al(2) at 0.685, 0.771, 0.393. (c) Tetrahedron around P(1) at 0.652, 0.468, 0.301. (d) Tetrahedron around P(2) at 0.363, 0.808, 0.205. (e) Hydrogen bonding around NH_4^+ ion at 0.604, 0.691, 0.987. Distances are in Å.

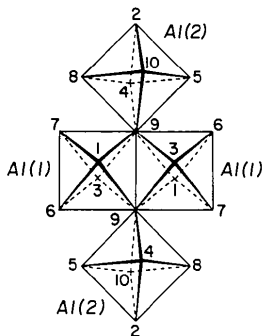


Fig. 3. Idealized polyhedral drawing of the octahedral tetramer. O(9) forms a hydroxyl with H(1), O(10) a water molecule with H(2) and H(3); all other numbers refer to O^{2-} ions. The tetramer is centrosymmetric, and an unidealized one occurs at the body center of Fig. 1.

appear plausible. Particularly interesting is the suggestion that a hydroxonium ion in $\text{GaPO}_4 \cdot 2\text{H}_2\text{O}$ occupies the position later found to be occupied by NH_4 in AlPO_4 -15 and K in leucophosphate.

Finally, the source of the NH_4 in AlPO_4 -15 is of interest with respect to the synthesis of aluminophosphate molecular sieves (Wilson *et al.*, 1982, 1983). For AlPO_4 -5, the tetrapropylammonium species apparently acted as a template for assembly of the aluminophosphate framework (Bennett, Cohen, Flanigen, Pluth & Smith, 1983). During synthesis of AlPO_4 -15, it is apparent that the attempt to use 1,4-diaminobutane as a template failed because of fragmentation into NH_4 and organic species.

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Tris(1,10-phenanthroline)potassium Tetrphenylborate, $[\text{K}(\text{C}_{12}\text{H}_8\text{N}_2)_3][\text{B}(\text{C}_6\text{H}_5)_4]$

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Abstract. $M_r = 898.6$, triclinic, $P\bar{1}$, $a = 10.455$ (2), $b = 14.435$ (5), $c = 18.209$ (6) Å, $\alpha = 103.5$ (1), $\beta = 103.7$ (1), $\gamma = 110.1$ (1)°, $U = 2353$ (3) Å³, $D_x = 1.26$ Mg m⁻³, $Z = 2$, $\lambda(\text{Mo K}\alpha) = 0.71069$ Å, $\mu = 0.156$ mm⁻¹, $F(000) = 940$, $T = 298$ K, final $R = 0.068$, $R_w = 0.074$ for 3408 reflections. The structure consists of BPh_4^- anions and $[\text{K}(\text{phen})_3]_2^{2+}$ centrosymmetric dimeric cationic species (phen = 1,10-phenanthroline) in which the K atoms are eight coordinated by the N atoms of the phen molecules in a square-antiprismatic geometry. The $\text{K}\cdots\text{K}'$ contact distance in the dimer is 3.813 (3) Å. The K–N bond distances range from 2.800 (6) to 2.893 (5) Å for the singly chelated phen molecules, while for the bridging phens these vary from 3.010 (5) and 3.167 (6) Å.

Introduction. The biological significance of Na and K has prompted the current interest in products of the interactions of alkali-metal ions with donor molecules.

Compounds with N donors are still little known, and the title complex is the result of recent work first showing that the interaction of K compounds with a bidentate N-donor ligand such as 1,10-phenanthroline (phen) could give products having a 1:3 stoichiometry (Grillone & Kedzia, 1977; Grillone & Nocilla, 1978).

The present crystal structure determination is part of our investigations on the coordination geometry of K in such compounds, as influenced also by the nature of the counter ion.

Experimental. The compound has been prepared according to the procedure of Grillone & Nocilla (1978). Prismatic crystal 0.15 × 0.10 × 0.15 mm. 20

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