appear plausible. Particularly interesting is the suggestion that a hydroxonium ion in $GaPO_4.2H_2O$ occupies the position later found to be occupied by NH_4 in $AlPO_4$-15 and K in leucophosphite.

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 Tetraphenylborate, [K(C12H8N2)3][B(C6H5)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, $Z = 2$, $\lambda(Mo K\alpha) = 0.71069$ 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 $[K(phen)_3]_2^{2+}$ 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 $K\cdots K'$ 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.

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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 $0.15 \times 0.10 \times 0.15$ mm. 20

reflections with $7 \le \theta \le 10°$ for measuring the unit-cell parameters. Three standard reflections measured every 120 min, no significant intensity variation. 4322 independent reflections collected. Siemens–Stoe four-circle diffractometer. $2\theta = 3–50°$, $-10 \le h \le 10$, $-15 \le k \le 15$, $0 \le l \le 20$, ω/θ scan mode. 3408 with $I \ge 2 \cdot 5\sigma(I)$. Lp correction, absorption ignored. Structure solved by Patterson and Fourier methods and because of the large number of parameters refined in blocks with the sequence: phen (1) + phen (3) + K; phen (2) + BPh$_4$ + K; phen (1) + phen (3) + K; phen (2) + BPh$_4$ + K; phen (1) + BPh$_4$ + K; phen (2) + phen (3) + K; H atoms introduced at calculated positions (C—H 0·95 Å) with isotropic $U - 0·06$ Å^2; anisotropic temperature factors assigned to the non-hydrogen atoms except for the C atoms of the B(C$_6$H$_5$)$_4$ moiety; phenyl rings refined as rigid groups (D_{6h} symmetry, C—C 1·395 Å, C—C—C 120°); $\sum w(|F_o| - |F_c|)^2$ minimized, with $w = 3·036 [\sigma^2(F_o) + 9·6 \times 10^{-4} (F_o)^2]^{-1}$ in the last refinement cycles; final $R = 0·068$ and $R_w = 0·074$. Atomic scattering factors (corrected for anomalous dispersion of K) from *International Tables for X-ray Crystallography* (1974). Final $(\Delta/\sigma)_{max} = 0·1$. Final $\Delta\rho$ excursions $\le 0·4$ e Å^{-3}. Computations carried out using the *SHELX76* system (Sheldrick, 1976) on an IBM 4331 computer.

Discussion. Final coordinates for non-hydrogen atoms are in Table 1.* Bond lengths and angles for the K coordination sphere and for the BPh$_4^-$ anion are in Table 2.

A view down **a** of the asymmetric [K(phen)$_3$]$^+$ and BPh$_4^-$ units is shown in Fig. 1.

Two phen molecules chelate to K *via* the N atoms, while the third bridges the two centrosymmetric K atoms of the dimer unit, each N being shared by the two K atoms.

The metal ion exhibits a coordination geometry conforming to a square antiprism [the twist angle between the opposite squares is 47·7 (1)°], a face of the antiprism being shared by the two centrosymmetric coordination polyhedra as shown in Fig. 2; the two BPh$_4^-$ units balance the charge of the dimer.

The ligand molecules are virtually planar, and the values of the bond distances and angles are comparable to those found in the structure of free phen (Nishigaki, Yoshioka & Nakatsu, 1978).

The K is displaced with respect to the molecular mean planes of the phen molecules: $-1·48$ (1) Å from

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* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, distances and angles for the phen molecules, and intermolecular contacts <3·65 Å have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39594 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

phen (1), $-1·07$ (1) Å from phen (2), 2·01 (1) Å from phen (3) and $-1·79$ (1) Å from phen (3').

No significant short contacts between cations and anions are present; the shorter C···C contact distances are of the order of 3·60 Å while the H···H contacts are about 2·5—2·6 Å.

Table 1. *Atomic coordinates for non-hydrogen atoms* $(\times 10^4)$, *and isotropic thermal parameters, with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq} or U_{iso}† (Å² × 10³)
K	6737 (1)	5155 (1)	9774 (1)	46·8 (8)
N(1)	8888 (6)	7300 (4)	10300 (3)	61 (4)
N(2)	9416 (5)	5916 (4)	11006 (3)	56 (4)
C(1)	9672 (7)	5268 (6)	11373 (5)	76 (5)
C(2)	10351 (7)	5563 (7)	12201 (5)	79 (5)
C(3)	10858 (7)	6577 (7)	12660 (4)	75 (5)
C(4)	10649 (6)	7305 (6)	12316 (4)	57 (4)
C(5)	11162 (7)	8398 (7)	12772 (4)	62 (5)
C(6)	10935 (8)	9062 (6)	12409 (5)	68 (5)
C(7)	10163 (7)	8732 (6)	11581 (4)	59 (5)
C(8)	9863 (8)	9407 (6)	11214 (6)	81 (6)
C(9)	9081 (9)	9034 (7)	10412 (6)	90 (6)
C(10)	8645 (8)	7978 (7)	9975 (4)	81 (6)
C(11)	9646 (6)	7669 (5)	11098 (4)	52 (5)
C(12)	9916 (6)	6939 (5)	11475 (4)	45 (4)
N(3)	6677 (5)	4675 (5)	8181 (3)	55 (3)
N(4)	6890 (5)	3255 (4)	8930 (3)	54 (3)
C(13)	6625 (7)	5336 (6)	7791 (4)	72 (5)
C(14)	6132 (8)	5057 (8)	6964 (5)	90 (6)
C(15)	5637 (8)	4054 (9)	6502 (4)	84 (6)
C(16)	5668 (7)	3298 (7)	6871 (4)	64 (5)
C(17)	5169 (8)	2215 (8)	6421 (4)	77 (6)
C(18)	5272 (8)	1527 (6)	6787 (5)	70 (6)
C(19)	5875 (7)	1854 (6)	7641 (4)	56 (4)
C(20)	6058 (8)	1154 (6)	8039 (5)	73 (5)
C(21)	6677 (9)	1543 (7)	8854 (5)	89 (6)
C(22)	7041 (8)	2570 (6)	9270 (4)	75 (5)
C(23)	6327 (6)	2907 (5)	8113 (3)	47 (4)
C(24)	6220 (6)	3652 (6)	7720 (3)	50 (4)
N(5)	4434 (6)	5916 (5)	9142 (4)	69 (4)
N(6)	3595 (5)	3803 (5)	8588 (3)	58 (4)
C(25)	4812 (9)	6946 (8)	9408 (5)	87 (6)
C(26)	4483 (11)	7502 (7)	8934 (7)	112 (8)
C(27)	3740 (10)	6982 (8)	8135 (7)	108 (7)
C(28)	3370 (7)	5919 (8)	7815 (5)	85 (6)
C(29)	2680 (9)	5338 (9)	6988 (5)	96 (7)
C(30)	2290 (8)	4286 (9)	6689 (4)	90 (6)
C(31)	2581 (7)	3750 (7)	7222 (4)	70 (5)
C(32)	2184 (8)	2672 (8)	6934 (5)	75 (6)
C(33)	2486 (8)	2176 (6)	7465 (6)	77 (6)
C(34)	3191 (7)	2777 (7)	8288 (5)	77 (6)
C(35)	3291 (6)	4290 (6)	8055 (3)	52 (5)
C(36)	3713 (6)	5401 (6)	8366 (4)	62 (5)
B	651 (7)	2286 (5)	3563 (4)	42 (4)
C(42)	2722 (3)	4114 (3)	4637 (2)	44 (1)†
C(43)	3264 (3)	5183 (3)	5075 (2)	51 (2)†
C(44)	2455 (3)	5744 (3)	4897 (2)	55 (2)†
C(45)	1104 (3)	5237 (3)	4280 (2)	55 (2)†
C(46)	562 (3)	4168 (3)	3842 (2)	50 (2)†
C(41)	1371 (3)	3606 (3)	4020 (2)	39 (1)†
C(52)	-891 (4)	2253 (2)	4536 (2)	55 (2)†
C(53)	-1767 (4)	1757 (2)	4924 (2)	64 (2)†
C(54)	2009 (4)	732 (2)	4886 (2)	61 (2)†
C(55)	-1373 (4)	202 (2)	4459 (2)	62 (2)†
C(56)	-496 (4)	698 (2)	4071 (2)	48 (2)†
C(51)	255 (4)	1723 (2)	4109 (2)	42 (1)†
C(62)	-1778 (4)	955 (3)	2320 (2)	57 (2)†
C(63)	-2667 (4)	573 (3)	1514 (2)	74 (2)†
C(64)	2306 (4)	1133 (3)	1009 (2)	74 (2)†
C(65)	1055 (4)	2075 (3)	1309 (2)	68 (2)†
C(66)	-166 (4)	2456 (3)	2116 (2)	57 (2)†
C(61)	-527 (4)	1896 (3)	2621 (2)	45 (2)†
C(72)	2766 (4)	1701 (3)	4136 (2)	51 (2)†
C(73)	3977 (4)	1508 (3)	4116 (2)	60 (2)†
C(74)	4472 (4)	1560 (3)	3472 (2)	64 (2)†
C(75)	3754 (4)	1805 (3)	2849 (2)	67 (2)†
C(76)	2543 (4)	1999 (3)	2869 (2)	54 (2)†
C(71)	2049 (4)	1947 (3)	3512 (2)	43 (1)†

Table 2. *Bond lengths* (Å) *and angles* (°) *involving* K *and* B *atoms*

Primed atoms are at $1 - x, 1 - y, 2 - z$.

K···K'	3·813 (3)	C(41)–B	1·693 (7)
K–N(1)	2·893 (5)	C(51)–B	1·685 (9)
K–N(2)	2·800 (5)	C(61)–B	1·688 (7)
K–N(3)	2·800 (6)	C(71)–B	1·710 (9)
K–N(4)	2·890 (6)		
K–N(5)	3·073 (5)		
K–N(6)	3·086 (6)		
K–N(5')	3·010 (5)		
K–N(6')	3·167 (6)		
N(2)–K–N(1)	57·9 (2)	C(51)–B–C(41)	107·9 (4)
N(3)–K–N(1)	94·6 (2)	C(61)–B–C(41)	111·5 (5)
N(3)–K–N(2)	118·1 (2)	C(61)–B–C(51)	108·5 (4)
N(4)–K–N(1)	128·0 (2)	C(71)–B–C(41)	107·7 (4)
N(4)–K–N(2)	94·6 (2)	C(71)–B–C(51)	112·4 (5)
N(4)–K–N(3)	57·9 (2)	C(71)–B–C(61)	108·9 (4)
N(5)–K–N(6)	52·4 (2)		
N(5')–K–N(6')	52·1 (2)		

The intermolecular contacts among the phen molecules are few, their distribution in this compound permitting only two phens to face each other partially: the N(3)–C(13)–C(14)–C(15)–C(16)–C(24) ring of one phen and the N(6)–C(31)–C(32)–C(33)–C(34)–C(35) ring of the adjacent phen. The contacts range from 3·331 (9) Å for N(3)···C(35) to 3·84 (1) Å for C(15)···C(32), indicating some interaction of the graphite type; the three phen molecules appear, however, to be almost parallel: phen (1) ∧ phen (2) 8·5 (2), phen (2) ∧ phen (3) 4·9 (2) and phen (1) ∧ phen (3) 4·3 (2)°.

Here crystal packing forces do not appear to favour any significant interaction among the molecules of the ligand. This is in contrast with what has been found in the crystal structure of $[K(phen)_3][Cr_2(CO)_{10}(\mu\text{–}H)]$ for which an unexpected cubic arrangment appears to be stabilized around the K atoms (Bombieri, Bruno, Grillone & Polizzotti, 1984); this is promoted by the layer disposition of the phen molecules with several short contacts (<3·6 Å) between them. The complex cation $[K(phen)_3]_2^{2+}$ is a centrosymmetric dimer in this case also, with the same coordination mode of the phen molecules but with different coordination geometry.

In fact, a comparison of the cubic geometry of the K⁺ ion in the above compound with the anitprismatic one of the present compound shows relevant differences in the two polyhedra:

(a) The K···K distance is 0·34 Å longer in the cubic derivative (A) with respect to that of the antiprismatic one (B).

(b) The K–N bond distance for the singly coordinate N is on average 2·95 (1) Å in (A) and 2·85 (3) Å in (B).

(c) The K–N bridging distances are rather symmetrical in (B) with three values close to 3·08 Å and one different [3·167 (6) Å] and unsymmetrical in (A) with values ranging from 2·91 (1) to 3·34 (1) Å.

From these observations it can be seen that the K–N bond distances are longer in (A) than those in (B) and

then the packing forces that promote a parallel disposition of the three phen in (A) with strong graphite-type interactions are in favour of a cubic coordination geometry around the K, which is otherwise unfavourable. Here the intermolecular phen interactions are weakened and then the more energetically favoured square-antiprismatic polyhedron is found.
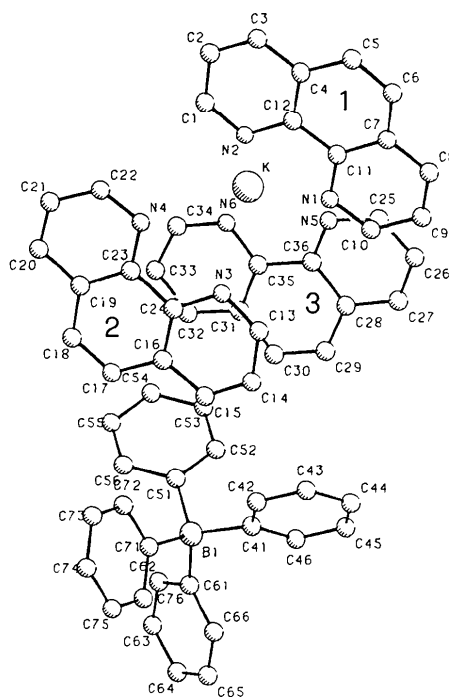

Fig. 1. View down a of the asymmetric units K(phen)₃ and BPh₄ (the numbers 1, 2 and 3 show the different phen units) (*PLUTO*78; Motherwell & Clegg, 1978).
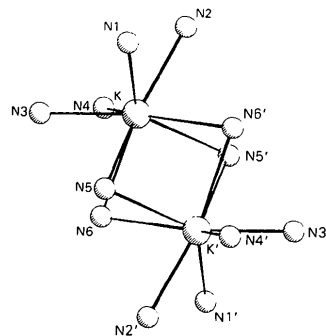

Fig. 2. Potassium coordination polyhedra (the primed atoms are centrosymmetrically related to the unprimed) (*PLUTO*78; Motherwell & Clegg, 1978).

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{2,16-Dimethyl-3,15,21-triaza-6,9,12-trithiabicyclo[15.3.1]henicosa-1(21),2,15,17,19-pentaene}silver(I) Tetraphenylborate, [Ag(C₁₇H₂₅N₃S₃)][B(C₆H₅)₄]

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Abstract. $M_r = 794.7$, triclinic, $P\bar{1}$, $a = 13.863$ (9), $b = 10.965$ (11), $c = 14.990$ (12) Å, $\alpha = 109.0$ (1), $\beta = 99.2$ (1), $\gamma = 65.0$ (1)°, $U = 1957.1$ Å³, $Z = 2$, D_m(flotation) = 1.35 (2), $D_x = 1.35$ g cm⁻³, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 6.90$ cm⁻¹, $F(000) = 824$, room temperature (space group established from the successful structure determination). 3966 independent reflections; $R = 0.063$. The structure consists of discrete [AgL^1] cations (L^1 represents the macrocycle) and [BPh₄] anions. The Ag atoms are six-coordinate, being bonded to three N atoms [2.613 (9), 2.422 (9), 2.399 (7) Å] and three S atoms [2.670 (3), 2.655 (3), 2.949 (4) Å]. The geometry of the coordination sphere is irregular.

Introduction. We are investigating the relationship between macrocycle conformation and 'hole' size and the effect upon metal complexation. 18-membered macrocycles of type L are particularly interesting as in a planar conformation they produce a hole size only suitable for the larger metal ions, such as Pb²⁺, Ca²⁺, Sr²⁺.
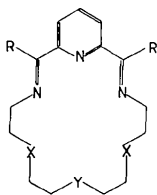
L^1 $X = Y = S, R = $ Me
L^2 $X = Y = O, R = $ H
L^3 $X = S, Y = O, R = $ Me

Several structures have been determined for macrocycle complexes of L, viz [CaL^2(NCS)₂], [SrL^2(NCS)₂] (Fenton, Cook, Nowell & Walker, 1978), [PbL^2(NCS)₂] (Nowell, 1979), [PbL^3(NCS)₂]

(Richards, 1978) and [PbL^3(OH₂)(ClO₄)] (Silong, 1983). In these structures the metal atom is 8- or 9-coordinate being bonded to the six donor atoms of the macrocycle and two (or three) anionic ligands. In [CaL^2(NCS)₂], the Ca atom occupies a distorted hexagonal bipyramid with the macrocycle providing the planar girdle and the two thiocyanates in axial positions. This suggests that the ion fits satisfactorily into the planar macrocycle 'hole'. With the larger Pb and Sr atoms, the macrocycle is less planar.

The title compound [AgL^1][BPh₄] is a particularly interesting member of this series because it is certain to have a different structure. The tetraphenylborate anion is non-coordinating and also the silver ion is smaller than those atoms in the analogous macrocycle complexes and therefore the conformation of L^1 must be radically different from that of L^2 or L^3 in the complexes if it is to be 6-coordinate and accommodate the silver ion.

Experimental. The title compound (I) was prepared by adding a solution of 2,6-diacetylpyridine (3·26 g, 0·02 mol) in methanol (50 cm³) to a methanolic solution of silver nitrate (3·39 g, 0·02 mol in 450 cm³). The solution was rapidly stirred and warmed. Then followed the dropwise addition of a solution of 1,11-diamino-3,6,9-trithiaundecane (prepared following Drew, Rice & Richards, 1980) (4·81 g, 0·02 mol) in methanol (50 cm³). The reaction mixture was allowed to reflux for 20 h. Sodium perchlorate (8 g) in ethanol (50 cm³) was added and the reaction mixture allowed to stand for 1 d. A yellow crystalline product [AgL^1][ClO₄] was obtained in 74% yield, which was then reacted in (1:1) ratio with NaBPh₄ in methanol to give [AgL^1][BPh₄] (I) in 77% yield. (I) was recrystallized from an acetonitrile/methanol mixture.