

this replacement leads to an increase of the average metal-sulphur distances [$\bar{d}(\text{K-S}) = 3.30 \text{ \AA}$] and hence to a greater separation of the $\infty^2\text{Cu}_3\text{S}_2$ sheets along *c*, but there exists a particular metal-sulphur distance (marked by a broken line in Fig. 1) which is 0.09 Å shorter in the Tl than in the K compound. As a consequence the $\infty^1\text{Cu}_4\text{S}_4$ tubes are deformed in the *c* direction such that the S(2)-S(2) distances (marked by a dotted line in Fig. 1) are 0.2 Å longer in TlCu_3S_2 than in KCu_3S_2 . Since the anionic $\infty^2\text{Cu}_3\text{S}_2$ network has a tendency to maintain the length of its Cu-S bonds [$\bar{d}(\text{Cu-S}) = 2.32$ (TlCu_3S_2), 2.33 Å (KCu_3S_2)] it will tend to compensate the expansion along *c* by a contraction along *a* and *b* mainly through a change of the S-Cu-S bond angles of the $\infty^1\text{Cu}_4\text{S}_4$ units (Table 2).

There exist several other thiocuprates which contain $\infty^1\text{Cu}_4\text{S}_4$ units as structural elements. These units may be isolated as in $\text{Na}_3\text{Cu}_4\text{S}_4$ (Burschka, 1979*a*) or connected with each other by additional atoms (Cu,S) and thus take part in the formation of a more complex thioanion as in the title compound, in $\text{NH}_4\text{Cu}_7\text{S}_8$, which may be written as $\text{NH}_4[\infty^3\text{Cu}_3\infty^1(\text{Cu}_4\text{S}_4)]$ (Gattow, 1957), and in $\text{K}_3\text{Cu}_8\text{S}_6 - \text{K}_3[\infty^2\text{Cu}_2^3\text{Cu}_2^4\text{S}_2\infty^1(\text{Cu}_4\text{S}_4)]$ (Burschka, 1979*b*). On the other hand the complex anion $[\infty^2(\text{Cu}_4\text{S}_3)]^{2-}$ in $\beta\text{-BaCu}_4\text{S}_3$ (Iglesias, Pachali & Steinfink, 1972) is built up by $\infty^1\text{Cu}_4\text{S}_4$ units which share S atoms. A comparison of all these compounds shows that the $\infty^1\text{Cu}_4\text{S}_4$ units cannot be considered as rigid structural elements since their shape varies strongly as a function of the packing and connexion type. Thus it may for certain purposes be useful to describe the thiocuprates differently, for instance in terms of layer structure compounds (Bronger, Eyck & Schils, 1978).

Finally it is worth pointing out that the powder diffraction diagram of the mineral chalcocite,

TlCu_3S_2 (Semenov, Sorenson, Bessmertnaja & Novorossova, 1967), shows no similarity to that of the present compound.

This work was supported in part by the Swiss National Science Foundation under contract No. 2.250-0.79.

References

- BRONGER, W., EYCK, J. & SCHILS, H. (1978). *J. Less Common Met.* **60**, P5-P13.
- BURSCHKA, C. (1979*a*). *Z. Naturforsch. Teil B*, **34**, 396-397.
- BURSCHKA, C. (1979*b*). *Z. Naturforsch. Teil B*, **34**, 675-677.
- BURSCHKA, C. & BRONGER, W. (1977*a*). *Z. Anorg. Allg. Chem.* **430**, 61-65.
- BURSCHKA, C. & BRONGER, W. (1977*b*). *Z. Naturforsch. Teil B*, **32**, 11-14.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
- GATTOW, G. (1957). *Acta Cryst.* **10**, 549-553.
- IGLESIAS, J. E., PACHALI, K. E. & STEINFINK, H. (1972). *Mater. Res. Bull.* **7**, 1247-1258.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KLEPP, K. & BOLLER, H. (1978). *Monatsh. Chem.* **109**, 1049-1057.
- KLEPP, K., BOLLER, H. & VÖLLENKLE, H. (1980). *Monatsh. Chem.* **111**, 727-733.
- PARTHÉ, E. (1980). *Acta Cryst.* **B36**, 1-7.
- SEME NOV, E. I., SORENSON, H., BESSMERTNAJA, M. S. & NOVOROSSOVA, L. E. (1967). *Medd. Groenl.* **181**, 21-26 (from *JCPDS Powder Diffraction File* 20-370).
- XRAY system (1976). Tech. Rep. TR-446. Computer Science Center, Univ. of Maryland, College Park, Maryland.

Acta Cryst. (1980). **B36**, 2391-2393

Structure of Potassium Phosphoramidate

BY T. STANLEY CAMERON, CHRISTINE CHAN AND WALTER J. CHUTE

Department of Chemistry, Dalhousie University, Halifax, Nova Scotia, Canada B3H 4J3

(Received 22 January 1980; accepted 27 May 1980)

Abstract. $\text{K}[\text{H}_2\text{NO}_2\text{P}]$, monoclinic, $P2_1/n$, $a = 6.143$ (2), $b = 6.872$ (1), $c = 10.288$ (1) Å, $\beta = 89.25$ (2)°, $Z = 4$, $D_c = 2.066 \text{ Mg m}^{-3}$, $\mu(\text{Mo } K\alpha_1) = 1.346 \text{ mm}^{-1}$, $\lambda = 0.70926 \text{ \AA}$ (graphite monochromator). The structure was solved by an application of the tangent formula, and refined by full-matrix least squares to $R = 0.027$. The anion contains an 'ideal' P-N single bond with a length of 1.800 (4) Å.

Introduction. There are many factors that influence the length of a nominal P-N single bond (Bullen & Dann, 1973). It has been shown, for example, that the P-N distance is significantly shortened when the N atom is sp^2 rather than sp^3 hybridized (Cameron, Cordes & Jackman, 1979) and particularly for the sp^2 -hybridized N atom the P-N bond lengths further vary according to the extent of the overlap of the P atomic orbitals and

the lone-pair electrons of the N (Cameron, 1978; Cameron & Owen, 1979). It is valuable, therefore, to know the length of an 'ideal' P–N single bond where the N atom is sp^3 with no lone pair of electrons.

The phosphoramidate salts are normally considered to have such an ideal single bond and the refined structure of the sodium salt $\text{Na}[\text{H}_3\text{NO}_3\text{P}]$ was reported by Cruickshank (1964); the recorded P–N bond length is 1.769 Å but the e.s.d. is ± 0.019 Å, and a more reliable value was required (Cameron, Cordes & Jackman, 1979). An attempt was made to re-prepare the sodium salt but suitable crystals could not be obtained. Stokes (1893) reported the preparation of the analogous potassium salt and Klement & Becht (1947) showed that it was anhydrous. The preparation of potassium phosphoramidate has been repeated; crystals suitable for X-ray analysis were prepared and the structure is reported here. The crystal system and approximate cell dimensions were determined from equi-inclination Weissenberg photographs. The systematic extinction $h0l, h + l \neq 2n; 0k0 k \neq 2n$ uniquely indicated space group $P2_1/n$ [equivalent positions $\pm(x, y, z; \frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z)$]. The cell dimensions were refined on a CAD-4 diffractometer from the circle angles of 25 general reflections with Bragg angle θ between $14\text{--}15^\circ$, and with θ maximum 25° ; 1271 unique reflections were collected, and of these, 545 had $I > 3\sigma(I)$. The data were reduced to a standard scale by routine procedure (Cameron & Cordes, 1979) and were corrected for Lorentz and polarization factors; no corrections were made for extinction or absorption.

The structure was solved by application of the tangent formula with the Sheldrick (1976) system. All but H atoms were located from the resultant E map and the structure with isotropic temperature factors was refined by a full-matrix least-squares procedure, minimizing $\sum w(\Delta F)^2$. It converged at $R = 0.04$ with weights $w = (\sigma^2 |F_o| + 0.0026F_o^2)^{-1}$, where σ is the individual e.s.d. for each reflection calculated from the diffractometer counting statistics. H atom positions were determined from a difference synthesis and refinement was continued with anisotropic temperature factors on all but these H atoms. A final refinement on all the atoms converged with $R = 0.027$ and $R_w = 0.026$.

The atomic scattering factors were those recorded in *International Tables for X-ray Crystallography* (1974), and were corrected for the real part of the anomalous-dispersion effect.

The final atomic parameters* are given in Table 1

* Lists of structure factors, thermal parameters and an extended table of distances and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35309 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

and the interatomic distances and bond angles are given in Table 2. Figs. 1 and 2 show two projections of the unit cell along axes b and c .

Discussion. The structure is constructed from K^+ and $[\text{H}_3\text{N}-\text{PO}_3]^-$ ions only. Each H atom in the anion forms a hydrogen bond to an O atom in an adjacent ion, but the structure determination clearly shows that each H atom is firmly bonded to the N rather than an O atom. Thus the anion should contain an 'ideal' P–N single bond.

Table 1. Atomic parameters ($\times 10^4$, except $\times 10^3$ for hydrogen)

	x	y	z	Mod (U) (Å ²)
K	2490 (1)	9883 (1)	−2089 (1)	191
P	2506 (2)	3405 (1)	892 (1)	132
O(11)	802 (5)	2841 (4)	1890 (3)	205
O(2)	4820 (4)	2944 (4)	1254 (3)	189
O(3)	1915 (5)	2946 (4)	−496 (3)	193
N(1)	2451 (6)	6024 (5)	897 (4)	147
H(1)	298 (9)	657 (8)	159 (5)	
H(2)	335 (9)	643 (8)	19 (5)	
H(3)	147 (26)	674 (22)	102 (13)	

Table 2. Interatomic distances (Å) and interbond angles ($^\circ$)

P–O(1)	1.505 (3)	O(1)–P–O(2)	115.1 (2)
P–O(2)	1.509 (3)	O(1)–P–O(3)	114.5 (2)
P–O(3)	1.512 (3)	O(1)–P–N(1)	104.0 (2)
P–N(1)	1.800 (4)	O(2)–P–O(3)	115.6 (2)
		O(2)–P–N(1)	103.1 (2)
		O(3)–P–N(1)	101.9 (2)

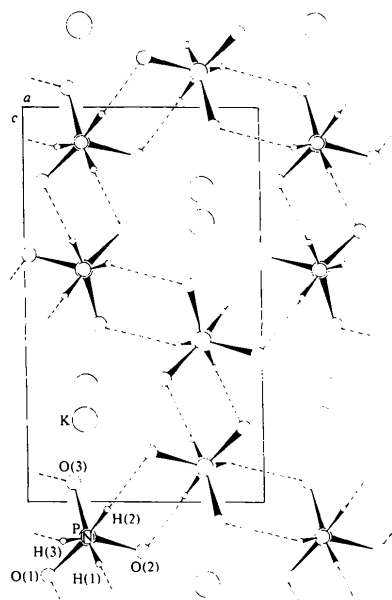


Fig. 1. The structure projected along b .

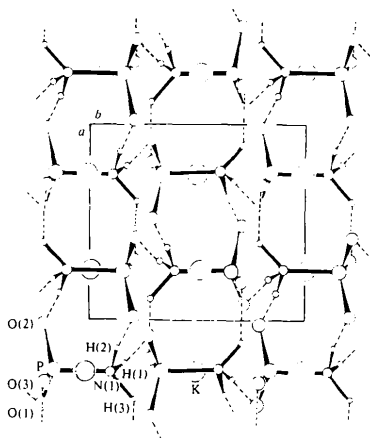


Fig. 2. The structure projected along *c*.

The P–N bond length is 1.800 (4) Å, which is longer than the 1.769 (19) Å recorded by Cruickshank (1964) for the corresponding sodium salt, but the two lengths are not significantly different. The P–N single-bond length reported here is probably the longest recorded in recent years but the length is not unexpected. Apart from confirming the earlier work, a P–N single-bond length of 1.77 (1) Å was proposed from the variation in exocyclic P–N bond lengths in hexakis(methylamino)-bicyclopentaphosphazene (Cameron, Cordes & Jackman, 1979). This bicyclopentaphosphazene actually contains a P–N bond length of 1.723 (6) Å where the sum of the interbond angles at the N atom is 337.5°. [VSEPR considerations (Gillespie, 1963) suggest that the sum of the angles should be 360° for sp^2 and less than 328.5° for sp^3 N.] The P–C(aliphatic) bond lengths are regularly in the range 1.80–1.86 Å (Brown, Brown & Hawthorne, 1978). The aliphatic C atoms, like the N atom of this present compound, are unable to donate any non-bonding electrons to empty P orbitals. Thus from covalent-radius considerations, the observed P–N bond length is not unreasonable.

The three P–O bond lengths are 1.505 (3), 1.509 (3) and 1.512 (3) Å; these are not significantly different and they compare with lengths in the range 1.504–1.517 (5) Å in a sodium salt of *N*-phosphoryl-creatinine (Na[RNH₂.PO₃]) (Herriott & Love, 1968). Each O atom forms one hydrogen bond with a H of the NH₃ group in an adjacent ion. The anions pack in layers perpendicular to *b*; two of the hydrogen bonds are formed with adjacent anions within the layer, the third with an anion in the next layer (Fig. 2). However, since each anion contains both an NH₃ and a PO₃ group, the hydrogen bonds extend to form a three-dimensional net (Fig. 1). The N...O contact distances are 2.825 (5), 2.843 (5) and 2.811 (5) Å for O(1), O(2) and O(3) respectively and the corresponding N–H...O angles are 179 (5), 176 (5), 139 (8)°. The N...O contact distances are consistent with an

N–H...O hydrogen bond and the bent N–H(3)...O(3) bond is not unusual (Olovsson & Jönsson, 1976). The positions of the H atoms themselves were refined; the subsequent N–H bond lengths for H(1), H(2) and H(3) are 0.87 (6), 0.95 (6) and 0.79 (16) Å. These are all short, but none differ significantly from the expected values of 1.01, 1.02 and 0.99 Å (Olovsson & Jönsson, 1976). A refinement was also calculated in which the H atoms were constrained (Waser, 1963) to be the expected distances from the N atom; this produced no significant improvement in the *R* factor or the e.s.d.'s. Since it is important in this structure to establish the positions of the H atoms without prejudice, only the result of the unconstrained refinement is reported here.

The K⁺ ion is surrounded by six O atoms, each from different anions. The oxygens are arranged on the corners of a slightly distorted octahedron with K⁺...O contact distances in the range 2.687 (3)–2.815 (3) Å. Adjacent octahedra share a common face and so form connected columns in the zone of the *b* axis (Fig. 1). A full list of contact distances and angles has been deposited.*

We thank the Canadian Natural Sciences and Engineering Research Council for a grant in aid of research to TSC.

* See previous footnote.

References

- BROWN, I. D., BROWN, M. C. & HAWTHORNE, F. C. (1978). *Bond Index to the Determinations of Inorganic Crystal Structures*, pp. 41–44. Institute for Materials Research, McMaster Univ., Hamilton, Ontario, Canada.
- BULLEN, G. J. & DANN, P. E. (1973). *Acta Cryst.* **B29**, 331–337.
- CAMERON, T. S. (1978). *Z. Naturforsch. Teil B*, **33**, 728–730.
- CAMERON, T. S. & CORDES, R. S. (1979). *Acta Cryst.* **B35**, 748–750.
- CAMERON, T. S., CORDES, R. E. & JACKMAN, F. A. (1979). *Acta Cryst.* **B35**, 980–982.
- CAMERON, T. S. & OWEN, G. (1979). *Second Can. Crystallogr. Conf. Proc.* p. 1. Canadian Crystallography Group.
- CRUICKSHANK, D. W. J. (1964). *Acta Cryst.* **17**, 671–672.
- GILLESPIE, R. J. (1963). *J. Chem. Educ.* **40**, 295–301.
- HERRIOTT, J. R. & LOVE, W. E. (1968). *Acta Cryst.* **B24**, 1014–1027.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- KLEMENT, R. & BECHT, K.-R. (1947). *Z. Anorg. Chem.* **254**, 217–220.
- OLOVSSON, I. & JÖNSSON, P.-B. (1976). *The Hydrogen Bond*, edited by P. SCHUSTER, G. ZUNDEL & C. SANDORFY, pp. 407–412. Amsterdam: North-Holland.
- SHELDRIK, G. M. (1976). Personal communication.
- STOKES, N. H. (1893). *Am. Chem. J.* **15**, 198–214.
- WASER, J. (1963). *Acta Cryst.* **16**, 1091–1094.