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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N. VII. $(RbPO_3)_\infty$

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The crystallographic data given by Corbridge (1956) have been used in a structure refinement. The revised dimensions average P – O(linked) = 1·616 ± 0·010, P – O(unlinked) = 1·488 ± 0·010 Å and ∠P – O – P = 129°.

The crystal structure of rubidium metaphosphate $(RbPO_3)_\infty$ was determined by Corbridge (1956) by three-dimensional Fourier methods with back-shift corrections. In view of the importance of the dimensions of the metaphosphate chain, and as an extensive set of three-dimensional data was available, it seemed worth while attempting further refinement of the structure by least squares.

The space group is $P2_1/n$, with cell dimensions $a = 12{\cdot}123$, $b = 4{\cdot}228$, $c = 6{\cdot}479$ Å and $\beta = 96°\ 19'$. The structure consists of Rb^+ cations and $(PO_3)_n^{n-}$ chain anions. Each chain has 2_1 symmetry and has a PO_3^- group as its asymmetric unit.

The data used in the refinement were the 621 non-zero $|F_o|$ given by Corbridge. Five cycles of least-squares refinement were carried out, the last two with anisotropic vibrations for all atoms. The maximum coordinate shift was 0·04 Å for the x coordinate of O(3). The residual R dropped from the 14·5% given by Corbridge to a final 11·4%. The revised atomic coordinates are given in Table 1 and the vibration parameters in Table 2. The $|F_o|$ scale factor determined by the least-squares process was 0·928 ± 0·014. The weighting scheme used was

$$w = 1/(4 + |F_o| + |F_o|^2/74{\cdot}5)\,,$$

without the factor 0·928 applied to the $|F_o|$.

Table 1. *Atomic coordinates*

	x	y	z
Rb	1·112 Å	0·567 Å	5·030 Å
P	2·174	2·086	2·059
O(1)	2·652	3·159	0·992
O(2)	0·946	1·438	1·377
O(3)	2·146	2·702	3·401

Table 2. *Mean square vibration amplitudes* (Å²)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Rb	0·023	0·021	0·021	0·000	0·000	0·004
P	0·013	0·010	0·014	0·002	0·000	0·003
O(1)	0·022	0·015	0·009	0·006	−0·002	0·002
O(2)	0·017	0·009	0·026	0·001	−0·002	0·003
O(3)	0·036	0·012	0·015	0·006	−0·003	0·006

The coordinate e.s.d.'s given by the least-squares process are 0·002 Å for Rb, 0·004 Å for P and 0·013 Å for O. These are about one-third the values estimated by Corbridge, so that his data have yielded much better results than he would have expected. The e.s.d.'s of the U_{ij} are approximately 0·001 Å² for Rb, 0·002 Å² for P and 0·005–0·006 Å² for O.

The vibrations of the Rb^+ cation are somewhat greater than those of the P and O(1) atoms which constitute the backbone of the metaphosphate chain. The U_{22} vibrations of P, O(1), O(2) and O(3) are all relatively small; they may be regarded as equal to 0·011 Å² within experimental error. The external atoms O(2) and O(3) show greater U_{11} and U_{33} vibrations than P, probably as a consequence of some type of angular oscillation. From the magnitudes of the differences, the external P–O bond lengths should be increased by very roughly 0·005 Å to allow for angular oscillation effects as compared with the lengths calculated directly from Table 1.

Table 3. *Interatomic distances and angles in rubidium metaphosphate*

P–O(1)	1·622 Å	P–O(1)–P	128° 58′
P–O(1′)	1·611 Å	O(1)–P–O(1′)	103° 5′
P–O(2)	1·491 Å	O(2)–P–O(3)	120° 3′
P–O(3)	1·485 Å	O(1)–P–O(3)	110° 56′
		O(1′)–P–O(3)	104° 4′
		O(1)–P–O(2)	106° 0′
		O(1′)–P–O(2)	110° 52′

The bond lengths and angles within the metaphosphate chain are listed in Table 3; the lengths of P–O(2) and P–O(3) include the rotational correction of 0·005 Å. The e.s.d.'s of the P–O lengths are about 0·014 Å. The P–O(chain) lengths are close to the values given by Corbridge, but the external P–O(2) and P–O(3) lengths have increased by 0·017 and 0·047 Å to 1·491 and 1·485 Å and are now close to the values found in the similarly linked tetrahedra in the triphosphate (Cruickshank, 1964*a*) and tetrametaphosphate (Cruickshank, 1964*b*) ions. The angles around P listed in Table 3 are somewhat different from those given by Corbridge owing to errors in some of his calculations (private communication).

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The small shifts in the oxygen atomic coordinates found in this refinement do not affect the description of the Rb^+ anion coordination polyhedron given by Corbridge. No Rb–O distance changes by more than 0·02 Å. Each Rb^+ is coordinated to seven oxygen atoms, six of them (three O(2) and three O(3)) in a distorted octahedral arrangement with a mean Rb–O length of 2·95 Å, while the seventh (O(1)) is slightly further away at 3·19 Å.

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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N. VIII. $KHSO_4$ (Mercallite)

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The crystallographic data given by Loopstra & MacGillavry (1958) have been used in a structure refinement. The oxygen atoms to which hydrogen atoms are attached have been identified. The average dimensions are S – O(H) = 1·56 and S – O = 1·47 Å, both ± 0·015 Å.

The crystal structure of $KHSO_4$ (mercallite) was determined by Loopstra & MacGillavry (1958) from the 0*kl* and *h*0*l* projections. There are two distinct HSO_4^- groups in the asymmetric unit and these are differently linked by hydrogen bonds: one group forms dimers across a symmetry centre, the other is linked into infinite chains along a glide plane. The reported lengths (1·51–1·53 Å) of the eight independent S–O bonds in two groups were practically all equal, so that there was no indication of a difference between S–O(H) and S–O bonds. This is a little surprising as in the $H_2PO_4^-$ ion in the ordered low-temperature form (Bacon & Pease, 1955) of KH_2PO_4, the P–O(H) bond at 1·58 Å is 0·07 Å longer than the P–O bond, while in phosphoric acid (Furberg, 1955) the three P–O(H) bonds at 1·57 Å are 0·05 Å longer than the P–O bond. Further in $KC_2H_5SO_4$ (Truter, 1958) the S–O(R) bond at 1·60 Å is distinctly larger than the three S–O bonds at 1·46 Å. Accordingly it seemed worthwhile refining $KHSO_4$ to see if it conformed to the general pattern.

The space group is *Pbca*, with cell dimensions $a = 8·40$, $b = 9·79$, $c = 18·93$ Å. Both K atoms and both HSO_4 groups are in general positions, but S(1) is virtually at $x = \frac{1}{4}$ and its *x* coordinate cannot be located with precision from the available 0*kl* and *h*0*l* data.

The data used in the refinement were the 325 non-zero $|F_o|$ given by Loopstra & MacGillavry (the 14,0,4 and 063 reflexions were omitted as their phases were persistently uncertain). Seven cycles of least-squares refinement were carried out. These produced shifts of less than 0·005 Å for K, 0·02 Å for S and 0·11 Å for O. The residual *R* dropped from an initial 15% to a final 8·8%. In particular for the weak 0*kl* reflexions with *l* odd *R* dropped from the 29·2% of Loopstra & MacGillavry to 11·7%, and for the weak *h*0*l* reflexions with $h + l$ odd from 21·4% to 10·7%. The final coordinates and e.s.d.'s are given in Table 1 and the vibration parameters in Table 2. Anisotropic vibrations were allowed for K and S but not for O. The vibration e.s.d.'s are about 0·001 Å² for K and S, and 0·003 Å² for O. If the $|F_o|$ listed by Loopstra & MacGillavry are for $\frac{1}{8}$th of the cell contents, the $|F_o|$ scale determined by the least-squares process was 0·986 ± 0·012. The weighting scheme used was

$$w = 1/(30 + |F_o| + |F_o|^2/178)\,,$$

with $|F_o|$ appropriate to whole cell, but without the factor 0·986.

With the available reflexions the *x* coordinate of S(1) cannot be precisely determined, because its contributions to the structure factors are very insensi-

Table 1. *Atomic coordinates and e.s.d.'s*

Atom	*x*	*y*	*z*
K(1)	3·212 ± 0·005 Å	1·760 ± 0·005 Å	2·369 ± 0·003 Å
K(2)	− 1·031 ± 0·005	3·144 ± 0·004	2·245 ± 0·003
S(1)	2·100 ± 0·02(?)	4·139 ± 0·005	0·059 ± 0·003
S(2)	− 0·171 ± 0·005	0·180 ± 0·005	3·901 ± 0·004
O(11)	2·408 ± 0·018	5·669 ± 0·016	0·041 ± 0·012
O(12)	3·457 ± 0·018	3·478 ± 0·016	0·054 ± 0·012
O(13)	1·375 ± 0·020	3·888 ± 0·019	− 1·163 ± 0·013
O(14)	1·367 ± 0·018	3·908 ± 0·018	1·272 ± 0·013
O(21)	0·502 ± 0·019	− 0·059 ± 0·017	5·199 ± 0·013
O(22)	− 1·357 ± 0·018	1·111 ± 0·017	4·247 ± 0·012
O(23)	− 0·673 ± 0·025	− 1·089 ± 0·023	3·354 ± 0·016
O(24)	0·679 ± 0·016	0·912 ± 0·015	2·981 ± 0·011

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