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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N. III. $Na_5P_3O_{10}$, Phase II

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The crystallographic data given by Davies & Corbridge (1958) have been used in a structure refinement. The dimensions are close to those reported by Davies & Corbridge.

The crystal structure of sodium triphosphate, $Na_5P_3O_{10}$, phase II, was determined by Davies & Corbridge (1958) by difference syntheses for the three principal projections, which were refined to residuals R of 13·8%, 11·8% and 13·4%. As all atoms were assumed to have the same common isotropic vibration parameter by Davies & Corbridge, it appeared worth while attempting to refine the structure. In the event there is little evidence of any substantial anisotropic vibration, and the coordinates obtained in the present refinement are close to those given by Davies & Corbridge, though they are probably slightly more accurate.

The space group is $C2/c$, with cell dimensions $a=16{\cdot}00$, $b=5{\cdot}24$, $c=11{\cdot}25$ Å and $\beta=93{\cdot}0°$. The structure consists of sodium cations and $P_3O_{10}^{5-}$ anions, which lie on twofold axes.

The data used in the refinement were the 166 non-zero $|F_o|$ listed by Davies & Corbridge. Four cycles of least-squares refinement were carried out. The largest shift was 0·08 Å for the y coordinate of Na(2); the oxygen shifts were in general much smaller. The residual R dropped to 10·6%. The revised atomic coordinates are given in Table 1 and the vibration parameters in Table 2. Because of the relatively small number of reflexions and because there is little evidence of substantial anisotropy from the phosphorus U_{ij} or from the variation of the oxygen isotropic U, anisotropic vibrations were not calculated for the oxygen atoms. The $|F_o|$ scale factor determined by the least-squares process was $1{\cdot}09 \pm 0{\cdot}02$. The weighting scheme used was

$$w = 1/(15+|F_o|+|F_o|^2/122)$$

without the factor of 1·09 applied to the $|F_o|$.

Table 1. *Atomic coordinates*

	x	y	z
P(1)	0·000 Å	1·600 Å	2·813 Å $(\frac{1}{4}c)$
P(2)	2·333	1·026	4·505
O(1)	0·603	2·385	1·731
O(2)	1·073	0·554	3·450
O(3)	2·405	2·511	4·439
O(4)	3·474	0·269	3·923
O(5)	1·921	0·468	5·826
Na(1)	4·000 $(\frac{1}{4}c)$	3·930 $(\frac{3}{4}b)$	5·625 $(\frac{1}{2}c)$
Na(2)	0·632	3·876	5·189
Na(3)	2·577	3·840	2·331

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

	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
P(1)	0·034	0·028	0·031	0·000	0·000	0·004
P(2)	0·035	0·028	0·031	−0·003	0·001	0·000

	U		U
O(1)	0·042	Na(1)	0·052
O(2)	0·035	Na(2)	0·038
O(3)	0·032	Na(3)	0·036
O(4)	0·037		
O(5)	0·044		

With some allowance for the effects of overlapping the coordinate e.s.d.'s given by the least-squares process are about 0·008 Å for phosphorus, 0·012 Å for sodium, 0·02 Å for oxygen in the x and z directions and about 0·03 Å in the y direction. The e.s.d.'s of the anisotropic U_{ij} for phosphorus are about 0·004 Å², though rather greater in the y direction. The oxygen and sodium isotropic U have e.s.d.'s of about 0·005 Å². From the variation in the vibration parameters, there is evidence of small angular oscillations which may imply rotational corrections of 0·003–0·008 Å. These have however been neglected since they are small in comparison with the e.s.d.'s of about 0·02 Å in the P–O bond lengths.

The revised molecular dimensions are shown in Table 3 and are not significantly different from those

Table 3. *Molecular dimensions*

P(1)–O(1) = 1·488 Å
P(1)–O(2) = 1·606
P(2)–O(2) = 1·669

P(2)–O(3) = 1·488 Å
P(2)–O(4) = 1·510
P(2)–O(5) = 1·511

P(1) –O(2)–P(2) = 122·2°
O(1) –P(1)–O(1′) = 116·4
O(1) –P(1)–O(2) = 110·1
O(1′)–P(1)–O(2) = 110·0
O(2′)–P(1)–O(2) = 98·7

O(2)–P(2)–O(3) = 106·9°
O(2)–P(2)–O(5) = 102·5
O(2)–P(2)–O(4) = 100·1
O(3)–P(2)–O(4) = 116·4
O(3)–P(2)–O(5) = 115·0
O(4)–P(2)–O(5) = 113·4

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given by Davies & Corbridge. The greatest change is an increase of 0·020 Å in the length of P(2)–O(4). Fig. 1 shows the dimensions when the values of the three similar bonds in the P(2) tetrahedron are averaged.

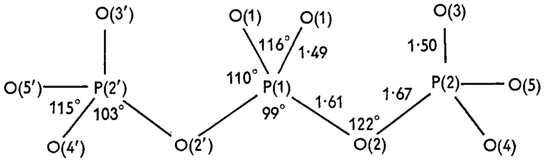

Fig. 1. Dimensions of the triphosphate ion.

Davies & Corbridge found a difference in length of the two long bonds P(2)–O(2) = 1·68 and P(1)–O(2) = 1·61 Å which they considered probably significant. This refinement confirms the dimensions as 1·67 Å and 1·61 Å. As it is an empirical rule (Cruickshank, 1961) that the average of the four bonds in a tetrahedron is roughly constant, the difference is consistent with the fact that the two short bonds in the P(1) tetrahedron are nearly equal to the three short bonds in the P(2) tetrahedron. The P(1)–O(2)–P(2) angle of 122° is the smallest known for linked phosphate tetrahedra.

The crystal structure of $Na_5P_3O_{10}$, phase I, has been determined by Corbridge (1960) from difference syntheses in two zones. Within the rather larger experimental error, the bond lengths are the same in the two P_3O_{10} ions, but some of the angles, particularly in the terminal phosphate tetrahedra, are rather different.

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Refinements of Structures Containing Bonds between Si, P, S or Cl and O or N.

IV. $(NH_4)_4P_4O_{12}$

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The crystallographic data given by Romers, Ketelaar, & MacGillavry (1951) have been used in a structure refinement. In the tetrametaphosphate ion the two types of ring bond have P–O = 1·65 and 1·58 Å, both ± 0·03 Å. The exocyclic P–O bonds are 1·47 – 1·52 Å.

The crystal structure of ammonium tetrametaphosphate (ATMP), $(NH_4)_4P_4O_{12}$, was determined by Romers, Ketelaar & MacGillavry (1951) from three electron-density projections along [100] [110] and [010]. As no back-shift corrections seem to have been applied, it appeared worthwhile refining the structure by least squares.

The space group is *Cmca*, with cell dimensions $a = 10{\cdot}42$, $b = 10{\cdot}82$, $c = 12{\cdot}78$ Å. The structure consists of tetramer anions $P_4O_{12}^{4-}$ and NH_4^+ cations. There are four P_4O_{12} groups in the cell clustered around the 4(*a*) positions. Each tetramer has point-group symmetry $2/m$ as shown in Fig. 1. There are eight $(NH_4)_I$ at the 8(*c*) positions and eight $(NH_4)_{II}$ at the 8(*f*) positions.

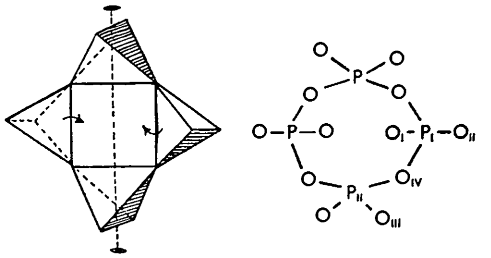

Fig. 1. Position of the P_4O_{12} group with respect to symmetry elements 2 and *m* of the space group *Cmca*.

The data used in the refinement were the 224 nonzero $|F_o|$ for the three zones given by Romers, Ketelaar & MacGillavry (1951) (the listed 003 and 0,6,14 reflexions were omitted because of suspected misprints). Four cycles of least-squares refinement were carried out. These produced coordinate shifts not exceeding 0·02 Å for either phosphorus atom or 0·06 Å for any oxygen or nitrogen atom. The residual *R* dropped from an initial 19·7% to a final 14·7% (hydrogen atoms were not included). The revised atomic coordinates are given in Table 1 and the

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