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Crystallographic data on some hypophosphates and pyrophosphates.

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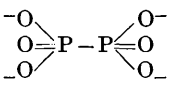
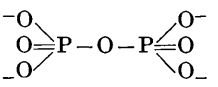
As part of an investigation into the structure of the hypophosphate (I) and pyrophosphate (II) ions, unit cell and space-group data have been obtained for the salts shown in Table 1.



I



II

The cell dimensions were measured from rotation photographs, and the space-group extinctions were obtained from zero- and first-layer Weissenberg photographs taken about all the principal axes. Small crystals of β-calcium pyrophosphate were obtained by slow cooling of the melt, and crystals of the remaining salts were grown from aqueous solution. Strong pyroelectric effects were found in β-calcium pyrophosphate and in trisodium hydrogen hypophosphate.

The isomorphism of the first two hypophosphate and pyrophosphate salt pairs (Table 1) is in accordance with indications from early optical data (Groth, 1908). A relationship between the crystal structures of the disodium and the tetrasodium salts is also suggested by the similarities in cell constants (Table 1).

Space-group data on ammonium hypophosphate (Raistrick & Hobbs, 1949) indicate either a centrosymmetric or a twofold axially symmetric hypophosphate ion (I), while a centrosymmetric pyrophosphate ion (II) has been established in zirconium pyrophosphate (Levi & Peyronel, 1935). Non-linear P–O–P linkages have been found in other phosphates so far studied, e.g. long-chain rubidium metaphosphate (Corbridge, 1956), ammonium tetrametaphosphate (Romers, Ketelaar & MacGillavry, 1951), phosphorus pentoxide (Hampson & Stosick, 1938).

Detailed structural work is proceeding on the isomorphous acid salts $Na_2H_2P_2O_6.6H_2O$ and $Na_2H_2P_2O_7.6H_2O$. Preliminary (*b* axis) projection studies on the latter salt indicate a linear P–O–P bond lying parallel to (010), with the central oxygen situated on the twofold axis (or at a centre of symmetry). A similar orientation of the P–P bond in the hypophosphate has also been found.

References

CORBRIDGE, D. E. C. (1956). *Acta Cryst.* **9**, 308.
GROTH, P. (1908). *Chemische Krystallographie*, vol. 2, pp. 780–98. Leipzig: Engelmann.
HAMPSON, G. C. & STOSICK, A. J. (1938). *J. Amer. Chem. Soc.* **60**, 1814.
LEVI, G. R. & PEYRONEL, G. (1935). *Z. Kristallogr.* **92**, 190.
RAISTRICK, B. & HOBBS, E. (1949). *Nature, Lond.* **164**, 113.
RANBY, P. W., MASH, D. H. & HENDERSON, S. T. (1955). *Brit. J. Appl. Phys.*, supplement No. 4, 18.
RAO, R. V. G. S. & NAMPOOTHIRI, N. S. (1955). *Acta Cryst.* **8**, 850.
ROMERS, C., KETELAAR, J. A. A. & MACGILLAVRY, C. H. (1951). *Acta Cryst.* **4**, 114.

Table 1. *Crystallographic data*

	a (Å)	*b* (Å)	*c* (Å)	β (°)	*n*	ϱ_o (g.cm.$^{-3}$)	ϱ_c (g.cm.$^{-3}$)	Space group
Tetrasodium pyrophosphate, $Na_4P_2O_7.10H_2O$†	16·95	6·94	14·81	112	4	1·83	1·83	$C2/c$
Tetrasodium hypophosphate, $Na_4P_2O_6.10H_2O$	16·97	6·97	14·50	116	4	1·84	1·85	$C2/c$
Disodium dihydrogen pyrophosphate, $Na_2H_2P_2O_7.6H_2O$	14·11	7·03	13·50	117·6	4	1·85	1·85	$C2/c$
Disodium dihydrogen hypophosphate, $Na_2H_2P_2O_6.6H_2O$	14·12	7·00	12·71	115·4	4	1·85	1·84	$C2/c$
Trisodium hydrogen pyrophosphate, $Na_3HP_2O_7.9H_2O$	8·59	31·65	6·13	113·7	4	1·78	1·77	$P2_1/a$
Trisodium hydrogen hypophosphate, $Na_3HP_2O_6.9H_2O$	26·96	6·00	9·26	110	4	1·73	1·75	Pn
Dipotassium dihydrogen pyrophosphate, $K_2H_2P_2O_7.\frac{1}{2}H_2O$	17·92	7·01	14·27	120·7	8	2·27	2·27	$C2/c$
Zinc pyrophosphate, $Zn_2P_2O_7.4H_2O$	9·07	25·27	8·32	—	8	2·64	2·63	$Pnma$
β-Calcium pyrophosphate, $Ca_2P_2O_7$‡	6·66	—	23·86	—	8	~3·1	3·19	$P4_1$

† Data for this salt have also been given by Rao & Nampoothiri (1955).
‡ Data for the α orthorhombic form have been given (Ranby, Mash & Henderson, 1955).