tions perpendiculaires à l'axe de la molécule confère à l'atome Hg^{II} une coordination 6 (=2+4) (Zvonkova & Zhdanov, 1952; Beauchamp & Goutier, 1972). Il faut signaler également qu'en présence de Hg^{II} les groupements $(SCN)^-$ ont tendance à s'unir au mercure plutôt qu'à s'insérer dans le réseau sous forme d'ions. C'est ainsi que $K_2Hg(SCN)_4$ ne contient pas de molécule digonale mais des ions complexes $Hg(SCN)_4^{2-}$ tétraédriques (Zvonkova & Zhdanov, 1952). Toutefois, il existe certains sels qui contiennent à la fois des groupements $(SCN)^-$ liés et ioniques; c'est le cas de $KHg(SCN)_3$ et $NH_4Hg(SCN)_3$ où Hg a plutôt tendance à former des entités digonales que trigonales et de ce fait un $(SCN)^-$ se trouve logé dans le réseau sous forme d'ion. Ceci a été confirmé par spectrométrie vibrationnelle (Larbot & Beauchamp, 1973).

Ces quelques considérations montrent combien il est difficile de dégager des règles bien précises sur la cristallochimie du Hg.

En ce qui concerne la structure d'un autre sel, $NH_4Hg(SCN)_2Cl$ actuellement en cours d'étude, on peut cependant émettre l'hypothèse que celle-ci serait formée de chaînes renfermant cette fois des unités moléculaires $Hg(SCN)_2$ reliées entre elles par des atomes Cl, comme dans la structure étudiée dans le présent travail. L'absence d'ion $(SCN)^-$ isolé dans le réseau a d'ailleurs été mise en évidence par l'étude Raman du composé. On trouve en effet une seule fréquence de vibration correspondant au mode d'élongation de valence —C≡N située à 2117 cm^{-1}. Cette valeur de fréquence est caractéristique de groupements $(SCN)^-$ liés; lorsque ceux-ci sont isolés dans le réseau, ils vibrent à une fréquence légèrement plus basse (~2050 cm^{-1}).

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Structure of Potassium Dihydrogenphosphite, KH_2PO_3

By Bohumil Kratochvíl and Jana Podlahová

Department of Inorganic Chemistry, Charles University, Albertov 2030, 128 40 *Praha* 2, *Czechoslovakia*

and Jindřich Hašek

Institute of Macromolecular Chemistry, Czechoslovak Academy of Sciences, 162 06 *Praha* 6, *Czechoslovakia*

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Abstract. $M_r = 120{\cdot}09$, $P2_1/c$, $a = 7{\cdot}341\,(1)$, $b = 8{\cdot}579\,(2)$, $c = 11{\cdot}975\,(3)$ Å, $\beta = 101{\cdot}98\,(2)^\circ$, $V = 737{\cdot}8\,(2)$ Å^3, $Z = 8$, $D_m = 2{\cdot}14\,(1)$, $D_x = 2{\cdot}16\,(2)$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu(\text{Mo } K\alpha) = 1{\cdot}66$ mm^{-1}, $F(000) = 480$, $R = 0{\cdot}038$ for 2161 unique reflections. HPO_3 tetrahedra are connected through hydrogen bonds so that infinite chains of composition $[HPO_3H]_n^{n-}$ are formed in the structure parallel to the [201] direction. The chains are held together by the K^+ ions.

Introduction. The preparation of KH_2PO_3 has been described by Amat (1891), and Ebert & Muck (1963) found the exact conditions for its crystallization from

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the solubility diagram of the K_2HPO_3–H_3PO_3–H_2O system at 298 K. The cell dimensions and the space group were determined by Norbert, Brun, Maurin & Barnoyer (1971). A crystal structure study of KH_2PO_3 was undertaken as part of an investigation of hydrogenphosphites.

Experimental. Spherical crystal, $r = 0{\cdot}3$ mm, Syntex $P2_1$ diffractometer, absorption correction, $\mu r = 0{\cdot}498$, transmission factors $0{\cdot}48-0{\cdot}49$, 2307 reflections measured, $0° < 2\theta < 60°$, three standard reflections, 2161 unique reflections, 95 unobserved reflections $[I < 1{\cdot}96\sigma_1(I)]$, direct methods, F magnitudes used in full-matrix least-squares refinement; scale factor, positions and anisotropic temperature factors of non-H atoms refined; H-atom positions from ΔF synthesis, H(1) and H(2) positions refined, H(11) and H(21) positions fixed, H atoms assigned the isotropic temperature factors of the atoms to which they are bonded, $R = 0{\cdot}038$,* $wR = 0{\cdot}061$, $w = 1/\sigma^2(F_o)$ derived from $\sigma(F_o)/|F_o| = (1/2)[\sigma_2(I)/I]$ and $\sigma_2(I) = [\sigma_1^2(I) + (0{\cdot}04I)^2]^{1/2}$, maximum height in final ΔF map 0·3 e $Å^{-3}$, isotropic extinction correction $g = 1{\cdot}9 \times 10^{-9}$, scattering factors for neutral atoms from *International Tables for X-ray Crystallography* (1974), ICL 4-72 computer, programs *SHELX* 76 (Sheldrick, 1976) and *TLS* (Sklenář & Petříček, 1981).

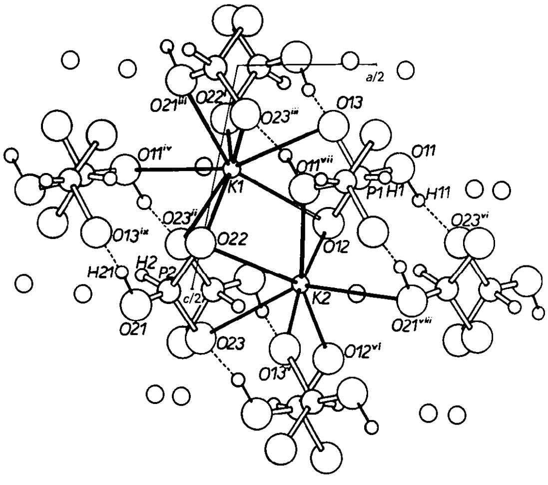

Fig. 1. The structure viewed along the *Y* direction. The broken lines between atoms represent hydrogen bonding.

Table 1. *Atomic coordinates* ($\times 10^4$, *for* H $\times 10^3$)

B_{eq} corresponds to non-H atoms, B to H atoms. $B_{eq} = \frac{4}{3}\sum_i\sum_j B_{ij}(a_i a_j)$.

	x	y	z	$B_{eq}, B(Å^2)$
K(1)	502·7 (8)	194·0 (7)	2295·1 (5)	2·04 (1)
K(2)	3950·4 (9)	2318·4 (7)	4886·3 (5)	2·03 (1)
P(1)	5223·0 (9)	113·0 (7)	2435·6 (5)	1·53 (1)
P(2)	−731·8 (9)	2147·3 (8)	5000·4 (5)	1·57 (1)
O(11)	6643 (3)	−1212 (3)	2278 (2)	2·47 (4)
O(12)	4477 (3)	−110 (2)	3488 (2)	2·45 (5)
O(13)	3827 (3)	217 (2)	1325 (2)	2·27 (4)
O(21)	−1986 (3)	3542 (3)	5251 (2)	3·12 (5)
O(22)	11 (3)	2387 (2)	3949 (2)	2·53 (4)
O(23)	639 (3)	1866 (3)	6093 (2)	2·81 (4)
H(1)	614 (5)	130 (5)	246 (3)	1·63
H(2)	−189 (5)	98 (5)	479 (3)	1·65
H(11)	760	−150	300	2·51
H(21)	−260	413	460	2·94

Table 2. *Bond distances* (Å) *and angles* (°)

Symmetry code
(i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$
(ii) $-x, -y, 1-z$
(iii) $x, \frac{1}{2}-y, z-\frac{1}{2}$
(iv) $x-1, y, z$
(v) $x, \frac{1}{2}-y, \frac{1}{2}+z$
(vi) $1-x, -y, 1-z$
(vii) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$
(viii) $1+x, y, z$
(ix) $-x, \frac{1}{2}+y, \frac{1}{2}-z$

P(1)—O(11)	1·579 (3)	O(11)—P(1)—O(12)	112·2 (1)
—O(12)	1·487 (2)	O(11)—P(1)—O(13)	106·4 (1)
—O(13)	1·504 (2)	O(11)—P(1)—H(1)	103 (2)
—H(1)	1·22 (4)	O(12)—P(1)—O(13)	117·0 (1)
		O(12)—P(1)—H(1)	113 (2)
		O(13)—P(1)—H(1)	104 (2)
P(2)—O(21)	1·576 (3)	O(21)—P(2)—O(22)	112·8 (1)
—O(22)	1·487 (2)	O(21)—P(2)—O(23)	105·6 (1)
—O(23)	1·495 (2)	O(21)—P(2)—H(2)	104 (2)
—H(2)	1·30 (4)	O(22)—P(2)—O(23)	117·7 (1)
		O(22)—P(2)—H(2)	106 (2)
		O(23)—P(2)—H(2)	110 (2)
K(1)—O(12)	2·982 (2)	K(2)—O(12)	2·749 (2)
—O(13)	2·912 (2)	—O(23)	3·099 (2)
—O(22)	2·809 (2)	—O(22)	2·877 (2)
—O(11ⁱᵛ)	3·075 (2)	—O(11ᵛⁱⁱ)	2·833 (3)
—O(21ⁱⁱⁱ)	2·941 (2)	—O(12ᵛⁱ)	2·789 (2)
—O(22ⁱ)	2·815 (2)	—O(13ᵛ)	2·741 (2)
—O(23ⁱⁱ)	2·869 (3)	—O(21ᵛⁱⁱⁱ)	3·107 (2)
—O(23ⁱⁱⁱ)	2·916 (3)		

O···O distances in the indicated hydrogen bonds

O(11)···O(23ᵛⁱ)	2·547 (3)	O(21)···O(13ⁱˣ)	2·529 (3)

Discussion. The structure is depicted in Fig. 1. Atomic parameters are given in Table 1 and the interatomic distances and angles in Table 2. The P atoms are tetrahedrally coordinated by one H and three O atoms. HPO_3 tetrahedra are connected through hydrogen bonds so that infinite chains of composition $[HPO_3H]_n^{n-}$ are formed in the structure parallel to the [201] direction. Two P—P distances of 4·676 (1) and 4·938 (1) Å alternate in the chains. A similar structural motif of infinite hydrogenphosphite chains was also found in LiH_2PO_3 where the P—P distance is 4·197 Å from X-ray data (Philippot & Lindqvist, 1970) and 4·196 Å from neutron data (Johansson & Lindqvist, 1976). The hydrogen bonds in KH_2PO_3 are fairly strong and are present only within the chains. The O atoms can act as H donors [O(11),O(21)] or as H acceptors [O(13),O(23)] or do not take part in hydrogen bonding [O(12),O(22)]. This partition of the O atoms is in agreement with the P—O bond-length differences. The P—OH (H-donor) bond is by far the

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38261 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

longest, followed by the P—O···H (H-acceptor) bond; the P—O bond without contact with H is the shortest, owing to the partly multiple character of the terminal bonds. A comparison of the P—O bond distances in the related compounds $KH_2PO_3.HF$ (Altenburg & Mootz, 1971), $2KH_2PO_3.H_3PO_3$ (Loub & Paulus, 1981) and KH_2PO_3 shows no significant differences.

The hydrogenphosphite chains are held together by the K^+ ions. K(1) is surrounded by eight O atoms, and K(2) by seven O atoms, in both cases corresponding to six different HPO_3 tetrahedra. The distances to the next-nearest O atoms are: K(1)—O = 3·703 (2), K(2)—O = 3·454 (2) Å.

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