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Structure of Potassium Sodium Orthoperiodate(VII) Tetrahydrate

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Abstract. $K_2Na[H_2IO_6].4H_2O$, $M_r = 398{\cdot}17$, triclinic, $P\bar{1}$, $a = 6{\cdot}7201$ (5), $b = 7{\cdot}3601$ (4), $c = 10{\cdot}7671$ (6) Å, $\alpha = 97{\cdot}607$ (5), $\beta = 108{\cdot}002$ (5), $\gamma = 93{\cdot}935$ (6)°, $V = 498{\cdot}62$ Å^3, $Z = 2$, $D_m = 2{\cdot}70$, $D_x = 2{\cdot}652$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 40{\cdot}838$ cm^{-1}, $F(000) = 384$, $T = 295$ K, $R = 0{\cdot}0184$ for 5751 observed unique reflections. The $[H_2IO_6]^{3-}$ anion has octahedral geometry, the OH groups are next to each other and the I—OH bonds are on average 0·14 (1) Å longer than the I—O bonds. The structure consists of $(H_2O)_4Na[\mu\text{-}(OH)_2]IO_4$ double octahedra, which are linked by hydrogen bonds of medium strength, and two independent potassium ions. The coordination polyhedra of the potassium ions are trigonal prismatic and very irregular with coordination numbers 6 and 9, respectively.

Introduction. Although a large variety of compounds in the alkali metal–water–orthoperiodic acid systems have been reported [see, for example, Siebert (1967) and the references cited therein], the number of those which are structurally well characterized is rather limited.

The orthoperiodate anion is known to exist in different degrees of protonation. In the solid state, monomeric $[IO_6]^{5-}$ anions have been observed for $K_4Li[IO_6]$ (Hoppe & Schneider, 1988) and $K_9Li_3O[IO_6]_2$ (Untenecker & Hoppe, 1987). The $[HIO_6]^{4-}$ anion probably occurs in $Cu_2[HIO_6].2H_2O$ (Adelsköld, Werner, Sundberg & Uggla, 1981), although the structural parameters deduced from X-ray powder data are of limited accuracy, and as a ligand in the copper(III) complex salt $KNa_4[Cu(HIO_6)_2].12H_2O$ (Adelsköld, Eriksson, Wang & Werner, 1988). The $[H_3IO_6]^{2-}$ anion is found in '$NaIO_4.3H_2O$' = $Na(H_3O)[H_3IO_6]$ (Abrahams & Bernstein, 1978) and $Na_2[H_3IO_6]$ (Jansen & Rehr, 1988). Additionally, the structures of some compounds containing binuclear anions have been reported, *e.g.* $[I_2O_9]^{4-}$ (Brehler, Jacobi & Siebert, 1968) and $[H_2I_2O_{10}]^{4-}$ (Mikhail, 1977; Ferrari, Braibanti & Tiripicchio, 1965; Tobias & Jansen, 1987).

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The chemical composition of the title compound suggested the existence of $[H_2IO_6]^{3-}$ anions which have hitherto not been characterized. A structure determination seemed, therefore, to be desirable.

Experimental. Crystals of $K_2Na[H_2IO_6].4H_2O$ were grown by slow evaporation of a concentrated alkaline solution (5*M* KOH) of KIO_4 and $NaIO_4$, total molar ratio K:Na ≃ 10:1, at room temperature. Density was measured pycnometrically under degassed toluene. Crystal selected for data collection was a slightly irregularly shaped platelet with max. dimensions 0·32 × 0·29 × 0·11 mm. The triclinic crystal system and approximate lattice constants were obtained from precession photographs. The specimen was mounted in an arbitrary orientation in a sealed glass capillary tube on an Enraf–Nonius CAD-4 diffractometer. Lattice parameters were refined from 25 well centred reflections with $32 < 2\theta < 62°$. 7773 reflections were measured in the ω–2θ scan mode with a scan width of $\Delta\omega = (1{\cdot}0 + 0{\cdot}35\sin\theta)°$ and a maximum scan time of 90 s up to $2\theta = 70°$, $[(\sin\theta)/\lambda]_{max} = 0{\cdot}8036$ Å^{-1}, range of hkl: $-1 \le h \le 10$, $-11 \le k \le 11$, $-17 \le l \le 17$. Five monitor reflections were measured every 3 h and exhibited an average total intensity decrease of 1·8% for the 102 h of data collection. Therefore, a linear decay correction was applied to the data. Absorption effects were corrected empirically (North, Phillips & Mathews, 1968) from the ψ-scan intensities of seven reflections, max./min. correction 0·999/0·778. Merging of symmetry equivalent reflections gave 6072 unique reflections ($R_{int} = 0{\cdot}011$ based on I).

The centrosymmetric space group $P\bar{1}$ was suggested by intensity statistics and confirmed by the structure determination. The I, K, Na and O coordinates were determined from Patterson and subsequent Fourier syntheses. After refinement of positional and anisotropic displacement parameters ($R = 0{\cdot}022$), the H-atom positions were revealed from several difference Fourier syntheses and included in the refinement. Although the isotropic temperature factors of the H atoms refined to reasonable values between $0{\cdot}8 < B_{iso}(H) < 3{\cdot}9$ Å^2, the R factors and the goodness-of-fit were not improved and therefore they were kept constant at 2·5 Å^2 in

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Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters B_{eq}(Å^2) with e.s.d.'s given in parentheses*

$$B_{eq} = (4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + (2ab\cos\gamma)\beta_{12} + (2ac\cos\beta)\beta_{13} + (2bc\cos\alpha)\beta_{23}].$$

	x	y	z	B_{eq}
I	0·13927 (1)	0·18159 (1)	0·24671 (1)	0·943 (1)
K1	0·37746 (8)	0·65452 (6)	0·37756 (4)	2·393 (7)
K2	0·43226 (6)	0·68775 (6)	0·85359 (4)	2·159 (6)
Na	0·22080 (11)	0·18658 (10)	0·76637 (7)	1·79 (1)
O1	−0·1460 (2)	0·0718 (2)	0·1335 (1)	1·50 (2)
O2	0·1386 (2)	−0·0470 (2)	0·3257 (1)	1·47 (2)
O3	0·0005 (2)	0·2778 (2)	0·3606 (1)	1·60 (2)
O4	0·2402 (2)	0·0531 (2)	0·1250 (1)	1·45 (2)
O5	0·1227 (2)	0·3865 (2)	0·1652 (1)	1·83 (2)
O6	0·4019 (2)	0·2650 (2)	0·3640 (1)	1·56 (2)
O7	0·4129 (2)	0·7421 (2)	0·1376 (2)	2·16 (2)
O8	0·1871 (3)	0·4074 (2)	0·6241 (1)	2·42 (3)
O9	0·2919 (2)	0·9638 (2)	0·5992 (1)	2·01 (2)
O10	0·1861 (2)	0·4169 (2)	0·9332 (1)	2·19 (2)
H11	−0·142 (5)	0·026 (5)	0·053 (3)	2·5*
H21	0·191 (5)	−0·003 (5)	0·405 (3)	2·5*
H71	0·357 (5)	0·834 (5)	0·135 (3)	2·5*
H72	0·346 (5)	0·663 (5)	0·098 (3)	2·5*
H81	0·122 (5)	0·494 (5)	0·624 (3)	2·5*
H82	0·144 (5)	0·360 (5)	0·542 (3)	2·5*
H91	0·396 (5)	0·899 (5)	0·614 (3)	2·5*
H92	0·212 (5)	0·897 (5)	0·607 (3)	2·5*
H101	0·076 (5)	0·469 (5)	0·888 (3)	2·5*
H102	0·156 (5)	0·377 (5)	0·998 (3)	2·5*

* B_{iso} fixed at the given value.

the final cycles. Full-matrix least-squares refinement with the *SDP* program (B. A. Frenz & Associates, Inc., 1988) of 158 parameters based on F magnitudes of 5751 reflections with $F \geq 2\sigma_F$ converged at $R = 0{\cdot}0184$, $wR = 0{\cdot}0221$(unit weights, including unobserved reflections), $S = 0{\cdot}598$. An isotropic extinction coefficient refined to $2{\cdot}00\,(1) \times 10^{-6}$. The ratio of max. least-squares shift to e.s.d. was less than 0·001, max. peak heights in a final difference Fourier synthesis corresponded to $1{\cdot}4/-1{\cdot}3$ e Å^{-3} within 1 Å from the I-atom position. Complex atomic scattering factors for neutral atoms were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Cell standardization was performed according to Gelato & Parthé (1987) with the exception that all atoms (O1 to O6) belong to one $[H_2IO_6]^{3-}$ unit. The final atomic coordinates and equivalent isotropic temperature factors are given in Table 1.*

Discussion. All atoms occupy the general position 2(*i*). Selected bond distances and angles are given in Table 2. In contrast to most previous studies on similar compounds, the H atoms could be located.

The composition of $K_2Na[H_2IO_6].4H_2O$ can be derived formally from $K_4[H_2I_2O_{10}].8H_2O$ by addition of two equivalents of NaOH, and since the latter compound also crystallizes in the triclinic system with similar lattice parameters (Ferrari, Braibanti & Tiripicchio, 1965; Mikhail 1977), it was first supposed to be identical with the compound under study.

$K_2Na[H_2IO_6].4H_2O$ is shown to be the first compound with dihydrogenorthoperiodate $[H_2IO_6]^{3-}$ anions. However, these are not isolated, but share both OH groups with an adjacent sodium ion resulting in two edge-sharing octahedra which are additionally connected by one hydrogen bond, see Fig. 1. The orthoperiodate part of these double octahedra is only slightly distorted: the bonds to the OH oxygen atoms are on average (combined e.s.d.'s) 0·14 (1) Å

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53779 (63 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected interatomic distances (Å) and angles (°) with e.s.d.'s given in parentheses*

H_2IO_6 octahedron

I—O1	1·974 (1)	I—O4	1·839 (1)
I—O2	1·984 (1)	I—O5	1.836 (1)
I—O3	1·855 (1)	I—O6	1·832 (1)
O1—I—O2	83·66 (5)	O2—I—O6	90·20 (5)
O1—I—O3	83·98 (5)	O3—I—O5	92·97 (6)
O1—I—O4	87·46 (5)	O3—I—O6	93·91 (5)
O1—I—O5	92·48 (5)	O4—I—O5	92·33 (6)
O2—I—O3	87·07 (5)	O4—I—O6	94·08 (5)
O2—I—O4	87·08 (5)	O5—I—O6	93·68 (5)

$Na(H_2O)_4(OH)_2$ octahedron

Na—O1^{i}	2·403 (2)	Na—O8	2·352 (2)
Na—O2^{i}	2·404 (1)	Na—O9^{iii}	2·452 (2)
Na—O7^{ii}	2·348 (1)	Na—O10	2·380 (2)
O1^{i}—Na—O2^{i}	66·60 (4)	O2^{i}—Na—O10	99·64 (5)
O1^{i}—Na—O7^{ii}	102·86 (5)	O7^{ii}—Na—O8	94·50 (6)
O1^{i}—Na—O9^{iii}	87·22 (5)	O7^{ii}—Na—O9^{iii}	87·22 (5)
O1^{i}—Na—O10	95·77 (6)	O7^{ii}—Na—O10	87·46 (5)
O2^{i}—Na—O8	95·65 (5)	O8—Na—O9^{iii}	89·41 (6)
O2^{i}—Na—O9^{iii}	85·91 (5)	O8—Na—O10	89·16 (6)

K coordination

K1—O2^{iv}	2·823 (1)	K2—O1^{v}	2·724 (1)
K1—O5	2·824 (1)	K2—O3^{v}	3·154 (1)
K1—O6	2·870 (1)	K2—O4^{ii}	2·744 (1)
K1—O6^{ii}	2·680 (1)	K2—O5^{ii}	3·138 (2)
K1—O7	2·891 (2)	K2—O6^{ii}	2·938 (2)
K1—O8^{ii}	2·998 (2)	K2—O7^{vi}	3·075 (2)
		K2—O8	2·957 (1)
		K2—O10	2·885 (2)
		K2—O10^{vii}	3·089 (1)

Hydrogen bonding

O—H···X	O—H	O···X	H···X	O—H···X
O1—H11···O4^{viii}	0·90 (4)	2·673 (2)	1·82 (3)	158 (3)
O2—H21···O9^{iii}	0·83 (3)	2·791 (2)	2·04 (4)	151 (4)
O7—H71···O4^{iv}	0·79 (4)	2·637 (2)	1·84 (4)	176 (4)
O7—H72···O10^{ix}	0·71 (3)	2·987 (2)	2·30 (3)	164 (4)
O8—H81···O3^{v}	0·80 (4)	2·723 (2)	1·93 (4)	172 (3)
O8—H82···O3	0·85 (3)	2·731 (2)	1·89 (3)	169 (4)
O9—H91···O6^{ii}	0·86 (4)	2·716 (2)	1·86 (4)	174 (3)
O9—H92···O3^{v}	0·74 (4)	2·732 (2)	2·00 (4)	177 (3)
O10—H101···O5^{v}	0·89 (3)	2·643 (2)	1·77 (4)	166 (3)
O10—H102···O5^{vi}	0·86 (4)	2·695 (2)	1·87 (4)	158 (3)

Symmetry operations: (i) $-x, -y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $x, y-1, z$; (iv) $x, y+1, z$; (v) $-x, 1-y, 1-z$; (vi) $x, y, z+1$; (vii) $1-x, 1-y, 2-z$; (viii) $-x, -y, -z$; (ix) $x, y, z-1$.

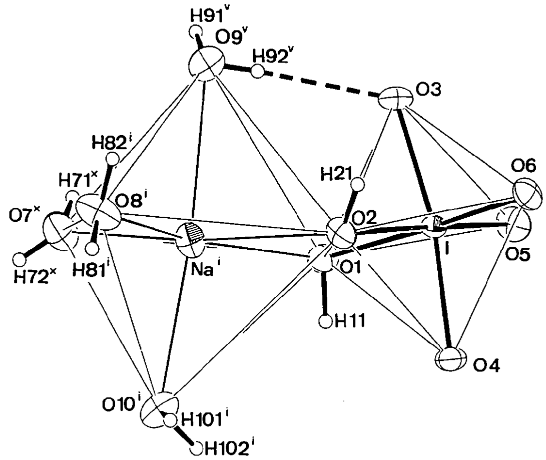

Fig. 1. $(H_2O)_4Na[\mu\text{-}(OH)_2]IO_4$ double octahedron. Vibrational ellipsoids (Johnson, 1976) are drawn at the 50% level, H atoms are given arbitrary radii. The dashed line represents a hydrogen bond.

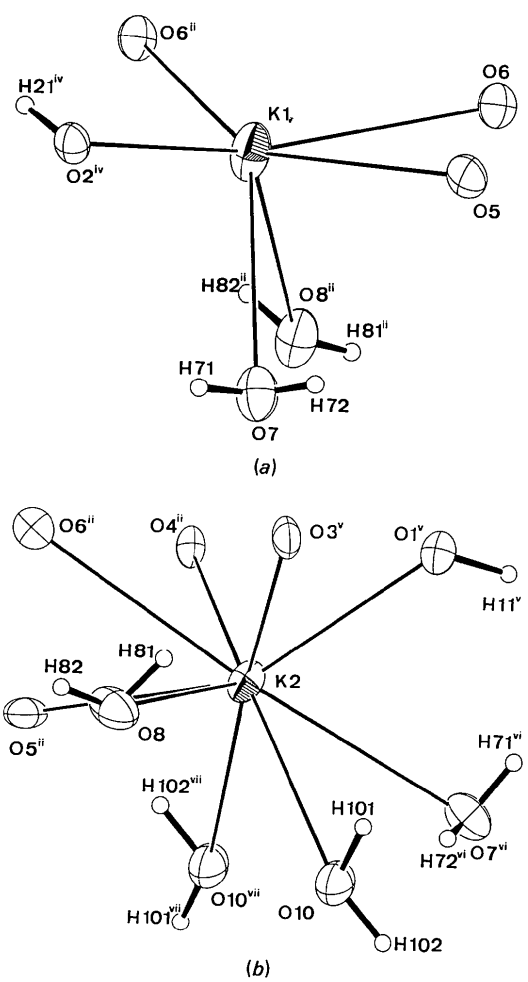

Fig. 2. Environment of (*a*) K1 and (*b*) K2. For further explanations see Fig. 1.

longer than the remaining ones and all bond angles are close to 90°, see Table 2. A similar significant difference between I—O and I—OH bonds has also been found for $Na(H_3O)[H_3IO_6]$, *i.e.* 0·076 (4) Å (Abrahams & Bernstein, 1978), which is in accordance with the findings of Ferraris & Ivaldi (1984) that these differences become smaller with an increase of the degree of protonation of such oxoanions. Surprisingly, in $Na_2[H_3IO_6]$ no such difference is observed (Jansen & Rehr, 1988) although that compound exhibits a similar structural element, *i.e.* chains of common-edged octahedra. Moreover, for $KNa_4[Cu(HIO_6)_2].12H_2O$ (Adelsköld, Eriksson, Wang & Werner, 1988) and for $K_2[H_2I_2O_{10}].4H_2O$ (Mikhail, 1977), the OH groups have been assigned to the *shorter* I—O bonds.

The $Na(H_2O)_4(OH)_2$ octahedron is significantly more distorted than the $[H_2IO_6]^{3-}$ anion. This is mainly shown from the respective bond angles (see Table 2). The short O1···O2 distance of 2·640 (2) Å and the small O1···Na···O2 angle are obviously caused by the geometry constraints of the $[H_2IO_6]^{3-}$

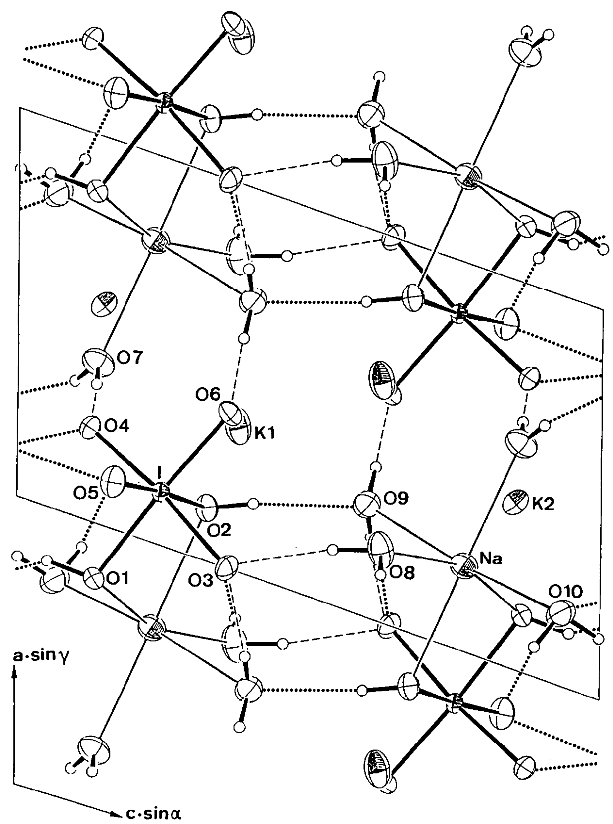

Fig. 3. Structure of $K_2Na[H_2IO_6].4H_2O$, parallel projection along **b**. I, K, and Na are represented as shaded ellipsoids, H atoms as open circles. Dashed lines represent hydrogen bonds between the depicted atoms, dotted lines indicate those to symmetry-related ones ($y + 1$ or $y - 1$, respectively).

anion. All remaining O···O distances in the Na coordination polyhedron are larger than 3·25 Å.

The coordination of the potassium ions by water molecules and orthoperiodate O atoms is very unequal, see Fig. 2. Whereas the coordination is quite well defined for K1, *i.e.* trigonal prismatic with K1 being moved off-centre, this is not the case for K2, which has a very irregular coordination sphere. Only those oxygen neighbours with distances <3·2 Å are included in Table 2 and Fig. 2.

The potassium ions and the extensive hydrogen-bond network link the $(H_2O)_4Na[\mu\text{-}(OH)]_2IO_4$ double octahedra as shown in Fig. 3. Three water molecules are each donor for two hydrogen bonds of similar medium strength with O_W···O distances in the range 2·643 (2)–2·791 (2) Å, see Table 2. A noticeably different behaviour is found for H_2O (O7), which shows simultaneously the shortest [2·637 (2) Å] and the longest [2·987 (2) Å] hydrogen-bond distance. It is therefore likely that the OH stretching vibrations of this water molecule are decoupled owing to this asymmetry in hydrogen bonding, a feature which has sometimes been observed for solid hydrates (Lutz, 1988; Lutz, Kellersohn & Beckenkamp, 1991). With this assumption, the occurrence of a relatively sharp, high-wavenumbered (3516 cm^{-1}) OH stretching band in the IR spectra (95 K) can be explained. The remaining water bands are found as broad features between 3400 and 2700 cm^{-1}, the O—H vibrations of the $[H_2IO_6]^{3-}$ anion are assigned to the lower frequency bands of the given range. Thus, it is qualitatively shown that $[H_2IO_6]^{3-}$ anions are stronger hydrogen-bond acceptors than IO_4^- and IO_3^- anions and they are expected to be comparably strong as H_2O (for a detailed list see the survey given by Lutz, 1988). The I—OH deformation frequencies are observed at 1178 and 1153 cm^{-1}, thus confirming the existence of two independent I—OH groups.

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Structure of β-$TlMo_2P_3O_{13}$

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Abstract. Thallium molybdenum triphosphate, $TlMo_2P_3O_{13}$, $M_r = 697{\cdot}16$, monoclinic, $P2_1/c$, $a = 9{\cdot}7536$ (3), $b = 19{\cdot}0640$ (16), $c = 6{\cdot}3945$ (7) Å, $\beta = 107{\cdot}099$ (7)°, $V = 1136$ (2) Å^3, $Z = 4$, D_m not measured, $D_x = 4{\cdot}08$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 16{\cdot}90$ mm^{-1}, $F(000) = 314$, $T = 293$ K, 951 reflections, $R = 0{\cdot}047$, $wR = 0{\cdot}047$. The lattice is built up from MoO_6, PO_4 and P_2O_7 groups delimiting tunnels where the Tl^+ ions are located. The title compound is isotypic with β-$KMo_2P_3O_{13}$.

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