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 = 697·16, monoclinic, $P2_1/c$, a = 9·7536 (3), b = 19·0640 (16), c = 6·3945 (7) Å, β = 107·099 (7)°, V = 1136 (2) Å^3, Z = 4, D_m not measured, D_x = 4·08 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 16·90 mm^{-1}, $F(000)$ = 314, T = 293 K, 951 reflections, R = 0·047, wR = 0·047. 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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Table 1. *Positional and thermal parameters with e.s.d.'s in parentheses*

	x	y	z	B(Å^2)
Mo(1)	0·0643 (2)	0·16279 (9)	0·3898 (3)	0·57 (3)
Mo(2)	0·6174 (2)	0·37407 (9)	0·1872 (3)	0·50 (3)
P(1)	0·2939 (6)	0·5896 (3)	0·2658 (9)	0·8 (1)
P(2)	0·3050 (5)	0·4652 (3)	0·0077 (8)	0·5 (1)
P(3)	−0·0344 (5)	0·3246 (3)	0·3445 (8)	0·6 (1)
Tl(1)	0·0278 (4)	0·0001 (2)	−0·0143 (7)	5·72 (7)
Tl(2)	0·3576 (2)	0·1590 (1)	0·0415 (4)	3·51 (5)
O(1)	0·215 (1)	0·2098 (7)	0·456 (2)	1·1 (2)*
O(2)	0·061 (1)	0·1546 (8)	0·075 (2)	1·6 (3)*
O(3)	0·051 (1)	0·1520 (7)	0·695 (2)	0·9 (2)*
O(4)	0·154 (1)	0·0641 (7)	0·428 (2)	0·8 (2)*
O(5)	−0·069 (1)	0·2467 (7)	0·328 (2)	0·8 (2)*
O(6)	−0·136 (1)	0·1071 (7)	0·284 (2)	1·1 (3)*
O(7)	0·572 (1)	0·2900 (7)	0·187 (2)	1·2 (2)*
O(8)	0·626 (1)	0·3720 (8)	−0·130 (2)	1·4 (2)*
O(9)	0·621 (1)	0·3997 (7)	0·493 (2)	1·2 (3)*
O(10)	0·830 (1)	0·3674 (8)	0·290 (2)	1·4 (3)*
O(11)	0·411 (1)	0·4066 (7)	0·078 (2)	0·6 (2)*
O(12)	0·666 (1)	0·4840 (7)	0·150 (2)	1·1 (2)*
O(13)	0·306 (1)	0·5068 (7)	0·226 (2)	0·7 (2)*

Starred atoms were refined isotropically
Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Introduction. Among the molybdenophosphates, those of pentavalent molybdenum are remarkable for the great ability of the MoO_6 octahedra to form with the PO_4 tetrahedra various $[Mo_2P_3O_{13}]_\infty$ frameworks with different geometries. Six forms of oxides with the composition $AMo_2P_3O_{13}$ have been synthesized up to now, depending on the nature of the A cation and on the experimental conditions of synthesis: $K_4Mo_8P_{12}O_{52}$ (or α-$KMo_2P_3O_{13}$) (Leclaire, Monier & Raveau, 1983), α- and β-$CsMo_2P_3O_{13}$ (Lii & Haushalter, 1987), β-$RbMo_2P_3O_{13}$ (Riou & Gooreaud, 1989), β-$KMo_2P_3O_{13}$ (Leclaire, Borel, Grandin & Raveau, 1990*a*), γ-$CsMo_2P_3O_{13}$ (Chen, Lii & Wang, 1988), δ-$KMo_2P_3O_{13}$ (Leclaire, Borel, Grandin & Raveau, 1989) and $AMo_5P_8O_{33}$ (A = Li, Na, Ag) (Lii, Johnston, Goshorn & Haushalter, 1987), $Cs_2K_2Mo_8P_{12}O_{52}$ (Haushalter & Lai, 1989), ε-$NaMo_2P_3O_{13}$ (Leclaire, Borel, Grandin & Raveau, 1990*b*), ζ-$NaMo_2P_3O_{13}$ (Costentin, Borel, Grandin, Leclaire & Raveau, 1990).

The present work deals with the structure of $TlMo_2P_3O_{13}$, a β-$KMo_2P_3O_{13}$ isotypic compound.

Experimental. The preparation was performed in two steps; firstly, $H(NH_4)_2PO_4$, Tl_2CO_3 and MoO_3 were mixed in an agate mortar in the molecular ratios needed to obtain the composition '$TlMo_{1.67}P_3O_{13}$' and heated at 600 K to decompose the ammonium phosphate and the carbonate. The resulting mixture was then added to the required amount of molybdenum and placed in an evacuated silica ampoule. This mixture was heated for several days at 1200 K.

Yellow green crystal, 0·096 × 0·024 × 0·018 mm. $2/m$ symmetry with systematic absences $l = 2n + 1$ in $h0l$ and $k = 2n + 1$ in $0k0$. Space group $P2_1/c$. Enraf–Nonius CAD-4 diffractometer, Mo $K\alpha$ radiation. Unit cell: least squares on 25 reflections; $\pm 2\theta$: $36 < 2\theta < 48°$. Intensity: measurement by ω–θ scan of $(1·10 + 0·35 \tan\theta)°$ with a $(1 + \tan\theta)$mm counter slit; determined by a study of some reflections in the ω–θ plane. Scanning speed adjusted to obtain $\sigma(I)/I < 0·018$ or to approach it in a time limited to 60 s. Three standards: for count, every 3000 s, and for orientation every 600 reflections; no appreciable trends. 951 reflections ($h_{max} = 19$, $k_{max} = 37$, $l_{max} = 12$), $2 < \theta < 45°$ with $I/\sigma(I) > 3$ (9233 reflections) used to solve and refine the structure solved by heavy-atom method. Refinement by full-matrix least squares using F's. Atomic scattering factors of the neutral atoms from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The two independent positions of the thallium ions are half occupied. Calculation on a MicroVAX II with the *SDP* system (B. A. Frenz & Associates, Inc., 1982), $(\Delta/\sigma)_{max} = 0·57$, $\Delta\rho < 2·43$ e Å^{-3}, $R = 0·047$, $wR = 0·047$, $w = 1/\sigma^2(F)$. $S = 0·994$. Atomic parameters are given in Table 1.*

Discussion. The $TlMo_2P_3O_{13}$ compound is isotypic with β-$KMo_2P_3O_{13}$ (Leclaire *et al.*, 1990*a*), β-$RbMo_2P_3O_{13}$ (Riou & Goreaud, 1989) and β-$CsMo_2P_3O_{13}$ (Lii *et al.*, 1987). Its structure (Fig. 1) consists of corner-sharing MoO_6 octahedra, PO_4 monophosphate groups and P_2O_7 diphosphate groups delimiting spacious tunnels where the thallium ions are located. Curiously, the thallium com-

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53782 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

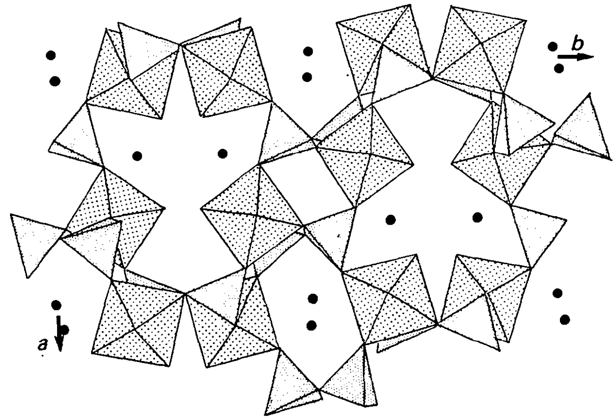

Fig. 1. Projection of the structure along **c**.

Table 2. *Distances* (Å) *and angles* (°) *in the* MoO_6 *and* PO_4 *polyhedra and main* Tl—O *distances*

The Mo—O^{i} or P—O^{i} distances are on the diagonal, above it are the O^{i}—O^{j} distances and under it are the O^{i}—Mo—O^{j} angles.

Mo(1)	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)
O(1)	1·66 (1)	2·68 (2)	2·74 (2)	2·83 (2)	2·74 (2)	3·81 (2)
O(2)	92·9 (7)	2·01 (2)	2·41 (2)	2·77 (2)	2·92 (2)	2·80 (2)
O(3)	96·3 (7)	168·8 (6)	2·00 (1)	2·78 (1)	2·92 (2)	2·86 (2)
O(4)	98·5 (6)	85·8 (6)	86·5 (5)	2·06 (1)	4·06 (2)	2·83 (2)
O(5)	95·2 (6)	92·7 (6)	92·9 (6)	166·2 (5)	2·02 (1)	2·74 (2)
O(6)	175·8 (6)	84·3 (6)	86·9 (6)	84·4 (6)	81·9 (6)	2·15 (2)

Mo(2)	O(7)	O(8)	O(9)	O(10)	O(11)	O(12)
O(7)	1·66 (1)	2·73 (2)	2·81 (2)	2·82 (2)	2·70 (2)	3·83 (2)
O(8)	93·9 (7)	2·05 (2)	2·46 (2)	2·84 (2)	2·87 (2)	2·74 (2)
O(9)	99·5 (7)	166·6 (7)	2·00 (2)	2·78 (2)	2·84 (2)	2·85 (2)
O(10)	100·8 (7)	89·2 (6)	88·5 (6)	1·99 (1)	3·99 (2)	2·73 (2)
O(11)	93·4 (6)	89·5 (6)	89·5 (6)	165·8 (6)	2·03 (1)	2·82 (2)
O(12)	174·0 (7)	80·7 (6)	86·0 (6)	81·7 (6)	84·1 (5)	2·18 (1)

P(1)	O(6^{i})	O(8^{ii})	O(9^{iii})	O(13)
O(6^{i})	1·52 (2)	2·57 (2)	2·55 (2)	2·52 (2)
O(8^{ii})	115·9 (9)	1·52 (2)	2·46 (2)	2·53 (2)
O(9^{iii})	113·3 (9)	107·1 (9)	1·54 (2)	2·48 (2)
O(13)	107·5 (8)	108·1 (9)	104·2 (8)	1·61 (1)

P(2)	O(4^{iv})	O(11)	O(12^{ii})	O(13)
O(6^{iv})	1·52 (1)	2·47 (2)	2·48 (2)	2·45 (2)
O(11)	109·9 (8)	1·50 (1)	2·53 (2)	2·48 (2)
O(12^{ii})	111·6 (8)	116·3 (9)	1·48 (2)	2·51 (2)
O(13)	103·5 (8)	106·2 (8)	108·5 (8)	1·60 (2)

P(3)	O(2^{v})	O(3^{iv})	O(5)	O(10^{vi})
O(2^{v})	1·54 (2)	2·41 (2)	2·54 (2)	2·48 (2)
O(3^{iv})	103·8 (8)	1·51 (2)	2·53 (2)	2·44 (2)
O(5)	111·9 (9)	113·3 (8)	1·52 (2)	2·49 (2)
O(10^{vi})	108·9 (9)	107·9 (9)	110·7 (8)	1·50 (2)

Tl(1)—O(2^{vii})	3·07 (2)	Tl(1)—O(13^{iv})	3·57 (2)
Tl(1)—O(2)	3·00 (2)	Tl(2)—O(1^{iv})	2·84 (1)
Tl(1)—O(3^{viii})	3·49 (2)	Tl(2)—O(2)	2·96 (2)
Tl(1)—O(4^{vii})	2·98 (2)	Tl(2)—O(3^{viii})	3·16 (1)
Tl(1)—O(4)	2·99 (2)	Tl(2)—O(7)	3·22 (2)
Tl(1)—O(6^{vii})	3·05 (2)	Tl(2)—O(8^{v})	2·89 (2)
Tl(1)—O(10^{ix})	3·20 (2)	Tl(2)—O(9^{iv})	2·90 (2)
Tl(1)—O(10^{x})	3·03 (2)	Tl(2)—O(11^{iv})	3·55 (2)
Tl(1)—O(12^{x})	3·21 (2)		

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

pound exhibits a more symmetrical space group ($P2_1/c$) identical to that of potassium, whereas the rubidium and caesium phases are characterized by the $P2_1$ group. This different behaviour of thallium compared to rubidium in spite of the similar size of these cations may be due to the presence of the $6s^2$ lone pair of Tl^+. Moreover, it is worth pointing out that one of the thallium ions [Tl(1)] is significantly displaced from the positions observed for potassium.

The Mo—O interatomic distances in the MoO_6 octahedra are characteristic of Mo^{V} with one abnormally short Mo—O bond, four intermediate Mo—O distances and a very long one (Table 2). The P(3)—O distances are close to those observed for a monophosphate, *i.e.* four almost equal distances. The P(1)—O and P(2)—O distances correspond to those observed in diphosphate groups, *i.e.* one long distance and three medium ones (Table 2). Tl(1) is surrounded by ten O atoms with Tl—O distances ranging from 2·98 (2) to 3·57 (2) Å and Tl(2) is linked to seven O atoms with 2·84 (1) < Tl—O < 3·55 (2) Å (Table 2).

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$KVPO_5$, an Intersecting Tunnel Structure Closely Related to the Hexagonal Tungsten Bronze

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Abstract. Potassium vanadium phosphate, M_r = 201·01, orthorhombic, $Pn2_1a$, a = 12·7640 (8), b = 10·5153 (9), c = 6·3648 (4) Å, V = 854·3 (2) $Å^3$, Z = 8, D_x = 3·13 Mg m^{-3}, λ/D(Mo $K\alpha$) = 0·71073 Å, μ = 2·94 mm^{-1}, $F(000)$ = 776, T = 294 K, R = 0·028, wR = 0·033 for 1321 independent reflections with I >

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