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$TlHP_2O_7$: structure determination from X-ray powder diffraction data

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The crystal structure of monoclinic thallium(III) hydrogendiphosphate, $TlHP_2O_7$, has been solved from laboratory X-ray powder diffraction data and refined by the Rietveld method. All atoms occupy general positions. The Tl^{III} ions have a distorted octahedral coordination environment of O atoms from four diphosphate groups. Adjacent TlO_6 octahedra form edge-shared Tl_2O_{10} dimers which share corners with PO_4 tetrahedra to build a three-dimensional polymeric structure.

Key indicators

Powder X-ray study
$T = 295$ K
Mean σ(P–O) = 0.015 Å
R factor = 0.076
wR factor = 0.106
Data-to-parameter ratio = 19.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Hydrogen diphosphates $M^{III}HP_2O_7$ have the ability to incorporate monovalent cations in place of hydrogen to give double salts $M^{III}M^{I}P_2O_7$ (Lyutsko & Prisedskaya, 1986), which are of interest because of their ionic conductivity at high temperatures (Vītiņš *et al.*, 2000).

Structural investigations of $M^{III}HP_2O_7$ have been performed only for M^{III} = Mn and Fe, including an α form for M^{III} = Mn (Ivashkevich *et al.*, 2006), a β form for M^{III} = Mn (Durif & Averbuch-Pouchot, 1982) and Fe (Selevich *et al.*, 2006), and an unnamed form for M^{III} = Fe (Genkina *et al.*, 1988). All these structures are monoclinic and based on three-dimensional networks of metal atoms and diphosphate groups. Because the Mn^{III} and Fe^{III} cations are rather small in size, it is of interest to know whether the above crystal forms are also typical for larger trivalent cations. Two such compounds have been synthesized to date, including $TlHP_2O_7$ (Selevich & Lesnikovich, 1996) and $YbHP_2O_7$ (Selevich *et al.*, 2005). However, their crystal structures have not been determined. In the present paper, we report the crystal structure of $TlHP_2O_7$ determined from X-ray powder diffraction data.

The unit-cell dimensions of $TlHP_2O_7$ unambiguously show that the compound does not belong to the α or β crystal forms mentioned above. However, $TlHP_2O_7$ shows similarities with the second form of $FeHP_2O_7$ investigated previously (Genkina *et al.*, 1988). The two compounds crystallize in the same space

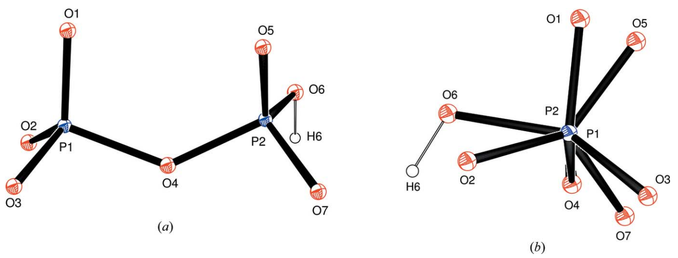

Figure 1
The conformation of the diphosphate anion in $TlHP_2O_7$. (*a*) Viewed approximately perpendicular to the plane P1/O4/P2. (*b*) Viewed along the P1···P2 vector. Displacement parameters are drawn at the 50% probability level. The H atom is shown as a sphere of arbitrary radius.

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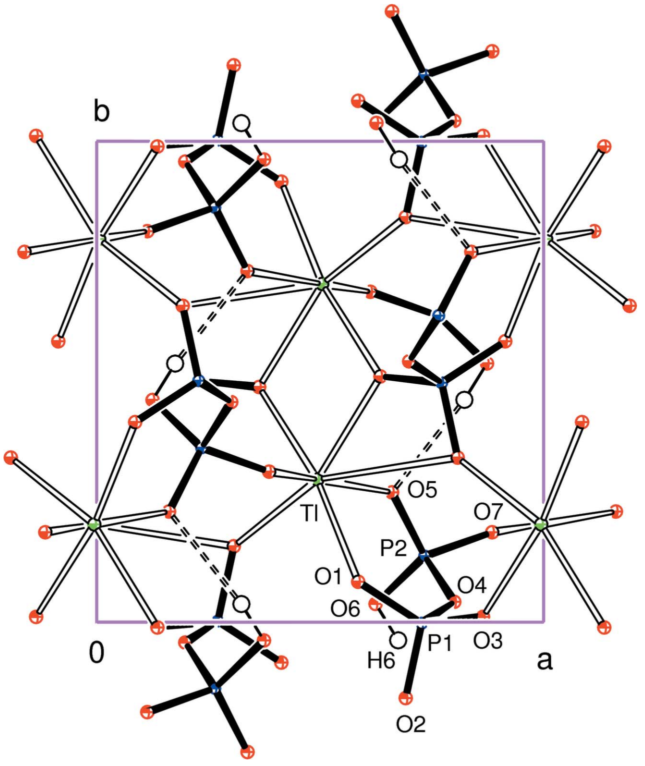

Figure 2
The crystal structure of $TlHP_2O_7$, viewed along the *c* axis. Dashed lines indicate hydrogen bonds.

group and show similar atomic arrangements. The unit-cell setting for $FeHP_2O_7$ (Genkina *et al.*, 1988) differs from that for $TlHP_2O_7$ and the latter is used for the purpose of comparing the two structures.

The asymmetric unit of $TlHP_2O_7$ contains one Tl^{III} ion and one $HP_2O_7^{3-}$ group with a conformation intermediate between eclipsed and staggered (Fig. 1). The average of the pseudo-torsion angles O1—P1···P2—O5, O2—P1···P2—O6 and O3—P1···P2—O7 is *ca* 24°. The Tl^{III} ions have a distorted octahedral environment of O atoms from four diphosphate groups. By sharing one edge, two adjacent TlO_6 octahedra form a Tl_2O_{10} dimer [with a Tl···Tl distance of 3.742 (2) Å] located near the $(10\overline{1})$ plane and aligned approximately along the *b* axis (Fig. 2). The dimers and the diphosphate groups share O atoms to build a three-dimensional polymeric structure. Atom O6 is not bonded to Tl and most likely carries the H atom of the HP_2O_7 group. The probable hydrogen bonds (Table 2) connect neighbouring diphosphate anions to form polymeric macroanions extending along the *b* axis.

Although the structures of $TlHP_2O_7$ and $FeHP_2O_7$ show a strong similarity, a number of differences should be mentioned. Firstly, the elongation of the unit cell in $TlHP_2O_7$ [b = 9.09283 (17) Å] relative to $FeHP_2O_7$ [b = 8.270 (4) Å] may be caused by the presence of the rather rigid $M^{III}{}_2O_{10}$ dimers aligned along the *b* axis and the elongation of the M^{III}—O bonds (mean Tl—O = 2.250 Å *versus* mean Fe—O = 2.004 Å). Secondly, the P_2O_7 groups show opposite orientations of the terminal PO_3 groups relative to each other (pseudo-torsion angle of *ca* 24° in $TlHP_2O_7$ *versus ca* −22° in $FeHP_2O_7$). Nevertheless, there is one-to-one correspondence between the O atoms in the two structures, so that the OH group in $FeHP_2O_7$ corresponds to atom O7 in $TlHP_2O_7$. Finally, the hydrogen bonding also differs in the two structures. In $FeHP_2O_7$, the hydrogen-bonded diphosphate anions form macroanions extending along the *a* axis, whereas they are parallel to the *b* axis in $TlHP_2O_7$.

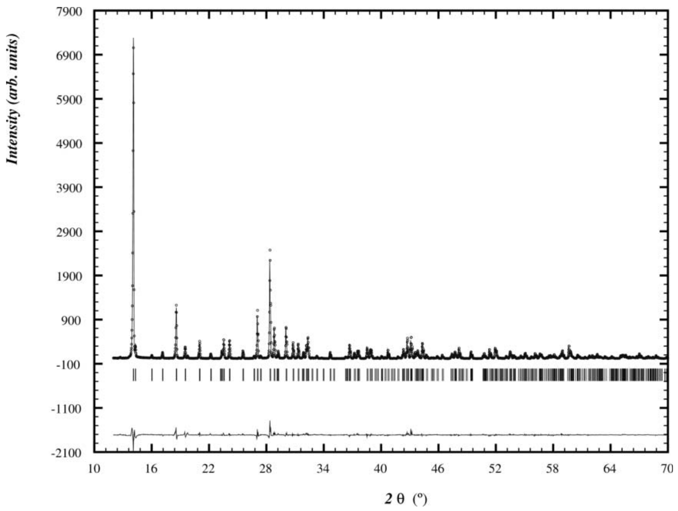

Figure 3
Rietveld refinement plots of $TlHP_2O_7$, showing the experimental diffraction pattern (circles), the calculated pattern (full line), their difference (bottom) and the positions of the Bragg reflections (vertical lines). Only the low-angle region is shown (10–70° 2θ).

Experimental

The title compound was synthesized by the thin-layer method described by Selevich & Lesnikovich (1996). A mixture of $Tl(OH)_3$ (3.83 g) and H_3PO_4 (5 ml, D = 1.7 Mg m^{-3}), in the molar ratio 1:5, was placed in a quartz crucible and heated in steps up to 423 K. The mixture was kept at this temperature until crystallization of $TlHP_2O_7$ occurred after 2–3 d. The crystalline product was separated from the unreacted mixture by washing with water, and was dried at room temperature. The product was identified by chemical analysis, X-ray diffraction, quantitative thin-layer chromatography and IR spectroscopy.

Crystal data

$TlHP_2O_7$
M_r = 379.33
Monoclinic, $P2_1/n$
a = 8.78516 (15) Å
b = 9.09283 (17) Å
c = 7.24420 (12) Å
β = 105.8725 (9)°
V = 556.62 (2) Å^3
Z = 4
D_x = 4.527 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.54180 Å
T = 295 K
Specimen shape: flat sheet
30 × 30 × 1 mm
Specimen prepared at 423 K
Particle morphology: plate-like, colourless

Data collection

HZG-4A (Carl Zeiss, Jena) diffractometer
Specimen mounting: packed powder pellet
Specimen mounted in reflection mode
Scan method: step
$2\theta_{min}$ = 12.0, $2\theta_{max}$ = 137.0°
Increment in 2θ = 0.02°

Refinement

Refinement on $I_{\rm net}$
$R_{\rm p} = 0.076$
$R_{\rm wp} = 0.106$
$R_{\rm exp} = 0.135$
$R_{\rm B} = 0.055$
$S = 0.79$
Excluded region(s): none
Profile function: pseudo-Voigt profile function; $\eta = 0.62$.
1036 reflections
52 parameters
H-atom parameters constrained
Weighting scheme based on $1/\sigma^2$
$(\Delta/\sigma)_{\rm max} = 0.03$
Preferred orientation correction: A Marsh–Dollase correction of intensities (Marsh, 1932; Dollase, 1986) for the $(10\overline{1})$ preferred orientation of plate-like grains was applied. The refined values of coefficients are $G_1 = 0.668(6)$, $G_2 = 0.316(19)$.

Table 1
Selected geometric parameters (Å, °).

Tl—O1	2.195 (19)	P1—O2	1.448 (15)
Tl—O5	2.250 (19)	P1—O3	1.487 (15)
Tl—O3$^{\rm i}$	2.33 (2)	P1—O4	1.656 (16)
Tl—O2$^{\rm ii}$	2.253 (18)	P2—O4	1.618 (16)
Tl—O3$^{\rm iii}$	2.31 (2)	P2—O5	1.455 (17)
Tl—O7$^{\rm iv}$	2.160 (19)	P2—O6	1.584 (18)
P1—O1	1.452 (19)	P2—O7	1.486 (18)
O1—P1—O2	111.0 (11)	O4—P2—O6	109.9 (10)
O1—P1—O3	120.1 (12)	O4—P2—O7	100.6 (11)
O1—P1—O4	108.7 (11)	O5—P2—O6	115.9 (11)
O2—P1—O3	105.0 (14)	O5—P2—O7	105.3 (11)
O2—P1—O4	106.9 (11)	O6—P2—O7	115.9 (11)
O3—P1—O4	104.4 (9)	P1—O4—P2	133.8 (12)
O4—P2—O5	108.0 (11)		

Symmetry codes: (i) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$; (ii) $-x+1, -y, -z+1$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O6—H6$\cdots$O5$^{\rm v}$	0.85	2.23	3.06 (2)	165

Symmetry code: (v) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

The diffraction pattern was indexed on a monoclinic cell ($M_{20} = 71$, $F_{20} = 138$, $M_{40} = 52$, $F_{40} = 110$) using the program *TREOR90* (Werner *et al.*, 1985). All non-H atoms were located as part of the structure solution with $R_{\rm F} = 0.180$. The structure was subsequently refined against the full data set using the Rietveld method, as implemented in the *FULLPROF* program (Rodríguez-Carvajal, 2001). A correction for profile asymmetry was made for reflections up to $2\theta = 40°$. The atomic displacement parameters were refined isotropically, with one common parameter for the O atoms. The identification of O6 as an OH group was confirmed by bond-valence analysis (Brese & O'Keeffe, 1991; Brown, 2002) performed using the program *PLATON* (Spek, 2003), resulting in a bond-valence sum of 1.13 for O6. The H atom was placed in a calculated position (O—H = 0.85 Å; Sheldrick, 1997) with a displacement parameter $U_{\rm iso}({\rm H}) = 0.05$ Å^2. The final structure refinement (Fig. 3) used soft restraints for the interatomic distances of the diphosphate group, based on a geometric analysis of a large number of diphosphates.

Data collection: local program; cell refinement: *FULLPROF* (Rodríguez-Carvajal, 2001); data reduction: local program; program(s) used to solve structure: *EXPO* (Altomare *et al.*, 1999); program(s) used to refine structure: *FULLPROF*; molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *FULLPROF* and *PLATON* (Spek, 2003).

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