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Mercury(II) polyphosphate, $Hg(PO_3)_2$

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Single crystals of mercury(II) polyphosphate, $Hg(PO_3)_2$, were prepared from HgO in an acidic polyphosphate melt. The structure is isotypic with α-$Cd(PO_3)_2$ and comprises infinite polyphosphate chains with a period of four phosphate units. Chains of the form ${}^1_\infty[PO_3{}^-]$ are linked by Hg^{2+} to form a three-dimensional network. The Hg atom is located at the centre of a distorted octahedron of O atoms with distances 2.173 (5) < $(Hg-O)_{mean}$ < 2.503 (6) Å. The $[HgO_6]$ polyhedra form zigzag-like chains of the form ${}^1_\infty[HgO_2O_{4/2}]$ parallel to the *c* axis.

Comment

Anhydrous mercury(II) phosphates have been known for a long time (*Gmelins Handbuch der anorganischen Chemie*, 1969), but only $Hg_3(PO_4)_2$ (Aurivillius & Nilsson, 1975) and $Hg_2P_2O_7$ (Weil & Glaum, 1997) have been characterized by single-crystal structure analysis so far. The first experiments to synthesize a compound with the molar ratio Hg:P:O = 1:2:6 were described by Glatzel (1880) and Warschauer (1903). Later, Thilo & Grunze (1957) showed by paper chromatography during their systematic investigations of the dehydration of acidic phosphates of divalent metals that this phase is not a tetrametaphosphate. According to them, HgP_2O_6 is a high molecular polyphosphate, which is isotypic with the low-temperature modification of cadmium polyphosphate, α-$Cd(PO_3)_2$. Some years later, for both polyphosphates, powder diagrams were indexed and lattice parameters given (Beucher & Tordjman, 1968). The structure of α-$Cd(PO_3)_2$ was solved from Weissenberg data by Tordjman *et al.* (1968) and refined some years later from single-crystal diffractometer data by Bagieu-Beucher *et al.* (1974).

In parallel with our investigations into the crystal chemistry of phosphates containing $Hg_2{}^{2+}$, $Hg_3{}^{4+}$ or Hg^{2+}, we have focused our interest on the thermal behaviour of these compounds (Weil, 1999). In the case of $Hg(PO_3)_2$, this is of particular interest because the isotypic compound α-$Cd(PO_3)_2$ is polymorphic and transforms into the *cyclo*-tetrametaphosphate $Cd_2P_4O_{12}$ (Laügt *et al.*, 1973) and β-$Cd(PO_3)_2$ (Bagieu-Beucher *et al.*, 1979). Therefore, detailed structural and thermal analyses of the title compound, $Hg(PO_3)_2$, have been undertaken and the results are presented here.

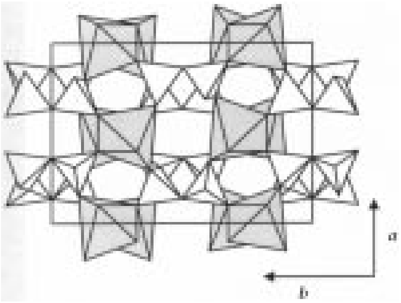

Figure 1
Projection of the $Hg(PO_3)_2$ structure along [001]. Polyphosphate chains are white and ${}^1_\infty[HgO_2O_{4/2}]$ chains are grey.

The structure of $Hg(PO_3)_2$ consists of polyphosphate chains of the type ${}^1_\infty[PO_3{}^-]$ extending parallel to the *c* axis. In a topological description, layers of polyphosphate chains and those formed by Hg atoms (Fig. 1) alternate along the *a* and *b* axes. The Hg atom shows sixfold distorted octahedral coordination by the terminal O atoms of the polyphosphate chains. The Hg—O distances are in the range 2.173 (5)–2.503 (6) Å, with a mean value of 2.346 Å, which is slightly longer and more irregular than for Cd—O in α-$Cd(PO_3)_2$, where the mean Cd—O distance is 2.301 Å (Bagieu-Beucher *et al.*, 1974).

In the title compound, $[HgO_6]$ units are linked *via* two *cis* edges, thus forming ${}^1_\infty[HgO_2O_{4/2}]$ zigzag chains parallel to the *c* axis (Fig. 2). The phosphate groups show the typical distri-

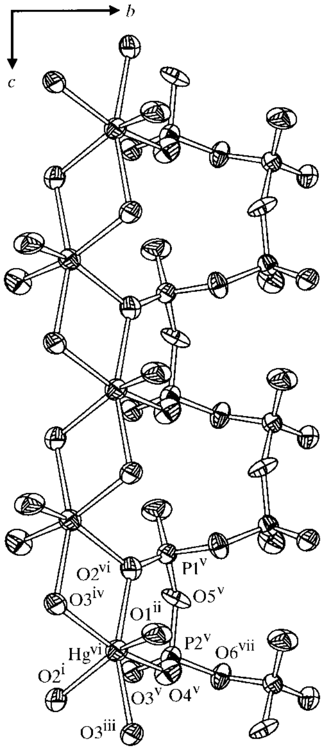

Figure 2
A plot with displacement ellipsoids of a section of ${}^1_\infty[HgO_2O_{4/2}]$ and ${}^1_\infty[PO_2O_{2/2}]$ chains running parallel to the *c* axis. Ellipsoids are drawn at the 90% probability level [symmetry codes: (i) $x, \frac{1}{2}-y, z+\frac{3}{2}$; (ii) $x-\frac{1}{2}, y, \frac{3}{2}-z$; (iii) $x-\frac{1}{2}, y, \frac{5}{2}-z$; (iv) $x-\frac{1}{2}, \frac{1}{2}-y, 2-z$; (v) $x, y, z+1$; (vi) $x-1, \frac{1}{2}-y, z+\frac{3}{2}$; (vii) $\frac{1}{2}-x, 1-y, z+\frac{3}{2}$].

bution of P—O distances which is observed for many other polyphosphate structures (Durif, 1995). There are two longer P—O distances with a mean of 1.594 Å to the bridging atoms O5 and O6 and two shorter distances with a mean of 1.489 Å to the terminal atoms. The dihedral angle (P2/O5/P1/O6/P2) between two phosphate groups within the polyphosphate chain is 76.5 (3)°. The polyphosphate anion shows a period of four tetrahedra. The terminal O1 and O4 atoms with the shortest P—O bond distances also exhibit the shortest distances to the Hg atom. Except for O2 and O5, which are the bridging atoms within the Hg—O chains and which have a coordination number of 3 (2 Hg, 1 P), all O atoms have a coordination number of 2 (O5 and O6: 2 P, O1; O4: 1 Hg, 1 P).

Surveys of the unique crystal chemistry of Hg^{2+} with its d^{10} electronic configuration have been published in the past (*e.g.* Grdenić, 1965; Aurivillius, 1965; Stålhandske, 1980; Müller-Buschbaum, 1995; Wessels, 1996), likewise the influence of relativistic effects (Norrby, 1991) for the preference of the linear coordination. Frequently, a [2+*x*] coordination with two short axial distances or an [*x*+2] coordination with two long axial distances is observed. In case of the anhydrous mercury(II) phosphates, for $Hg_3(PO_4)_2$ [2+3] and [2+4] coordination is found for the Hg atoms. The Hg—O distances range from 2.114–2.599 Å, with a mean of 2.389 Å, and the O_{ax}—Hg—O_{ax} angles are in the range 163.3–169.9° (Aurivillius & Nilsson, 1975). In mercury(II) diphosphate, a [2+4] and a [4+2] coordination is observed, with Hg—O distances in the range 2.120–2.793 Å (mean 2.392 Å) and O_{ax}—Hg—O_{ax} angles in the range 166.0–176.1° (Weil & Glaum, 1997). For the title compound, a [4+2] coordination and an O_{ax}—Hg—O_{ax} angle of 161.1° are observed. In $HgHPO_4$ (Dubler *et al.*, 1981), two independent Hg atoms are surrounded in a [2+5] and a [2+4] coordination with Hg—O distances in the range 2.060–2.924 Å (mean 2.528 Å) and O_{ax}—Hg—O_{ax} angles in the range 160.6–166.6°. In other mercury(II)-containing phosphates listed in the ICSD (FIZ–Karlsruhe, 1998), such as $HgLi_2(PO_3)_4$ (Averbuch-Pouchot *et al.*, 1976), $HgNaPO_4$ (Hata & Marumo, 1982), $HgKP_3O_9$ (Averbuch-Pouchot & Durif, 1986*a*), $Hg(NH_4)_2Na_2(P_3O_9)_2$ (Averbuch-Pouchot & Durif, 1986*b*) and $HgV_2(P_2O_7)_2$ (Boudin *et al.*, 1994), similar coordination geometries around the Hg atom are found.

In contrast to α-$Cd(PO_3)_2$, which transforms into β-$Cd(PO_3)_2$ upon heating above 1008 K (Bagieu-Beucher *et al.*, 1979), and under particular thermal conditions into $Cd_2P_4O_{12}$ (Thilo & Grunze, 1957; Laügt *et al.*, 1973), neither a high-temperature modification of $Hg(PO_3)_2$ nor a transformation into the possible *cyclo*-tetraphosphate $Hg_2P_4O_{12}$ could be detected by thermal analysis nor temperature-dependent Guinier photographs. Our own results confirm earlier observations performed by Thilo & Grunze (1957).

Experimental

Microcrystalline $Hg(PO_3)_2$ was synthesized by heating a solution of HgO (*e.g.* 4.93 g, Merck, p.a.) in 50% nitric acid, together with a small excess (*ca* 2%) of the stoichiometric amount of 85% H_3PO_4 (5.34 g, Merck, pure) in a silica crucible up to 773 K for 3 d. After cooling, the solid obtained was homogenized in an agate mortar and tempered again at 673 K for 1 d. According to Guinier photographs, the white product showed no impurities. Single crystals of $Hg(PO_3)_2$ were synthesized in a slight modification of the procedure given by Beucher (1968). HgO and H_3PO_4 (85%) were mixed in the molar ratio Hg:P = 1:11 (*e.g.* 0.747 g HgO, 4.46 g H_3PO_4) and heated in a glassy carbon crucible up to 693 K. The reaction mixture was kept at this temperature for about 3 d, then cooled over a period of 10 h to 573 K and kept at that temperature for 2 d. It was then quenched to room temperature. After extraction with hot water, colourless transparent crystals were obtained in mainly plate-like crystal form with edge lengths up to 8 mm.

Crystal data

$Hg(PO_3)_2$
$M_r = 358.53$
Orthorhombic, *Pbca*
$a = 9.709$ (2) Å
$b = 13.748$ (2) Å
$c = 7.128$ (1) Å
$V = 951.4$ (3) Å^3
$Z = 8$
$D_x = 5.006$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 45 reflections
$\theta = 6.44$–25.85°
$\mu = 32.973$ mm^{-1}
$T = 293$ (2) K
Irregular, colourless
0.28 × 0.18 × 0.12 mm

Data collection

Siemens AED-2 diffractometer
$\theta/2\theta$ scans
Absorption correction: numerical (*HABITUS*; Herrendorf, 1993)
$T_{min} = 0.023, T_{max} = 0.085$
10 112 measured reflections
1379 independent reflections
1223 reflections with $I > 2\sigma(I)$
$R_{int} = 0.082$
$\theta_{max} = 29.99°$
$h = -13 \rightarrow 13$
$k = -19 \rightarrow 19$
$l = -10 \rightarrow 10$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.034$
$wR(F^2) = 0.093$
$S = 1.108$
1379 reflections
83 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 18.4224P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 3.01$ e Å^{-3}
$\Delta\rho_{min} = -2.88$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 3.2 (2) × 10^{-3}

Table 1
Selected geometric parameters (Å, °).

Hg—O4^{i}	2.173 (5)	P1—O2	1.494 (6)
Hg—O1^{ii}	2.251 (6)	P1—O5	1.589 (6)
Hg—O3^{iii}	2.285 (5)	P1—O6	1.600 (5)
Hg—O2	2.369 (5)	P2—O4	1.493 (6)
Hg—O3^{iv}	2.493 (5)	P2—O3	1.494 (5)
Hg—O2^{i}	2.503 (6)	P2—O6^{v}	1.586 (5)
P1—O1	1.475 (6)	P2—O5	1.599 (6)
O4^{i}—Hg—O1^{ii}	110.3 (2)	O1—P1—O2	119.3 (3)
O4^{i}—Hg—O3^{iii}	155.0 (2)	O1—P1—O5	107.7 (3)
O1^{ii}—Hg—O3^{iii}	84.5 (2)	O2—P1—O5	109.5 (3)
O4^{i}—Hg—O2	88.6 (2)	O1—P1—O6	108.4 (3)
O1^{ii}—Hg—O2	146.2 (2)	O2—P1—O6	106.6 (3)
O3^{iii}—Hg—O2	89.3 (2)	O5—P1—O6	104.3 (3)
O4^{i}—Hg—O3^{iv}	84.5 (2)	O4—P2—O3	120.1 (3)
O1^{ii}—Hg—O3^{iv}	77.89 (19)	O4—P2—O6^{v}	108.8 (3)
O3^{iii}—Hg—O3^{iv}	119.1 (2)	O3—P2—O6^{v}	106.1 (3)
O2—Hg—O3^{iv}	76.27 (18)	O4—P2—O5	110.5 (3)
O4^{i}—Hg—O2^{i}	80.80 (19)	O3—P2—O5	106.5 (3)
O1^{ii}—Hg—O2^{i}	96.0 (2)	O6^{v}—P2—O5	103.6 (3)
O3^{iii}—Hg—O2^{i}	77.57 (18)	P1—O5—P2	135.0 (4)
O2—Hg—O2^{i}	115.1 (2)	P2^{vi}—O6—P1	128.4 (3)
O3^{iv}—Hg—O2^{i}	161.07 (18)		

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

The lattice parameters given were refined with the program *SOS* (Soose, 1980), using 45 reflections from a Guinier photograph. The highest and lowest electron density in the final difference electron-density map were found to be 0.06 and 0.66 Å, respectively, from the Hg atom.

Data collection: *STADI*4 (Stoe & Cie, 1995); cell refinement: *STADI*4; data reduction: *STADI*4; program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 1998); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GS1057). Services for accessing these data are described at the back of the journal.

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