Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Dilead(II) trimercury(II) tetraoxide chromate(VI), $Pb_2(Hg_3O_4)(CrO_4)$

Wilhelm Klein, Jan Curda and Martin Jansen*

Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany
Correspondence e-mail: m.jansen@fkf.mpg.de

Received 17 December 2004
Accepted 21 April 2005
Online 13 May 2005

$Pb_2(Hg_3O_4)(CrO_4)$ consists of $[CrO_4]^{2-}$ tetrahedra, linear O—Hg—O dumbbells and divalent Pb atoms in [3+5]-coordination. The HgO_2 dumbbells are condensed into $[Hg_3O_4]^{2-}$ units and can be regarded as a section of the HgO structure. The $[Hg_3O_4]^{2-}$ complex anions are connected by interstitial Pb^{2+} ions, while the $[CrO_4]^{2-}$ tetrahedra are isolated.

Comment

$Pb_2(Hg_3O_4)(CrO_4)$ consists of three different structural building units, *viz.* $[CrO_4]^{2-}$ tetrahedra, anionic $[Hg_3O_4]^{2-}$ strips and, connecting the latter, Pb^{2+} ions. The $[CrO_4]^{2-}$ ion is only slightly distorted; all Cr—O distances are identical within the 1σ limit, and the angles are close to the tetrahedral value.

All crystallographically independent Hg atoms are linearly coordinated by O atoms, and the Hg—O distances decrease remarkably from the central [2.094 (9) and 2.097 (9) Å] to the terminal bonds [2.006 (10) and 2.015 (10) Å]. The Hg—O—Hg angles of 111.2 (4) and 114.7 (4)° result in a zigzag shape of the $[Hg_3O_4]^{2-}$ anion. The dihedral angle between the two terminal O—Hg—O dumbbells is *ca* 0.9°, so all atoms are approximately coplanar. These characteristic $[Hg_3O_4]^{2-}$ units represent a section of the HgO structure and are linked by Pb^{2+} ions, forming a three-dimensional framework (Figs. 1 and 2).

The two Pb atoms exhibit a stereochemically active lone pair; each atom has three close O-atom contacts on one side [Pb1 2.246 (10)–2.512 (11) Å and Pb2 2.309 (10)–2.380 (9) Å] and five considerably more remote neighbours on the other [Pb1 2.868 (15)–3.610 (10) Å and Pb2 2.761 (12)–3.228 (11) Å; Table 1 and Fig. 3]. Considered as pyramidal PbO_3 units, the polyhedra containing Pb2 form dimers *via* common O8–O8^{iii} [symmetry code: (iii) $2 - x$, $-y$, $2 - z$] edges, while those containing Pb1 are arranged as infinite chains along [001], linked *via* common vertices. The close contacts are formed exclusively with O atoms of the $[Hg_3O_4]^{2-}$ group, each coordinating to three heavy metal cations (O5 and O8: 1 Hg + 2 Pb; O6 and O7: 2 Hg + 1 Pb).

Atoms O1–O4, belonging to the $[CrO_4]^{2-}$ tetrahedra, find their closest Hg and Pb neighbours at distances of 2.576 (12) (O1—Hg2) and 2.761 (12) Å (O4—Pb2), respectively, *i.e.* atoms O1–O4 reside in the second coordination sphere of Hg and Pb atoms only.

The title compound is closely related to $Pb_2(HgO_2)(CrO_4)$ (Klein *et al.*, 2002), which was found under similar synthetic conditions. The crystal structure also consists of isolated

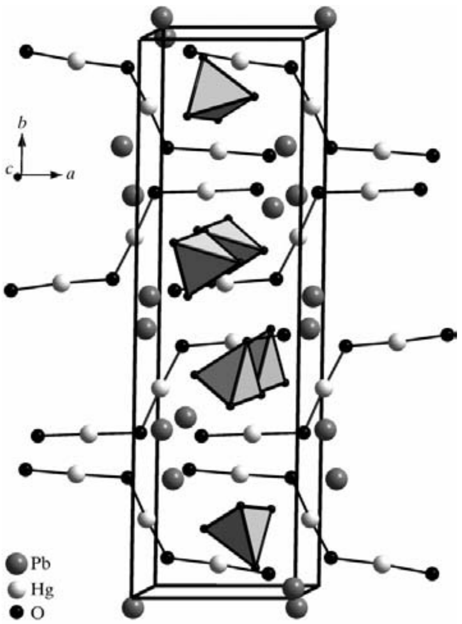

Figure 1
A perspective view of $Pb_2(Hg_3O_4)(CrO_4)$ along [001], showing Pb atoms, $[Hg_3O_4]^{2-}$ units and $[CrO_4]^{2-}$ tetrahedra.

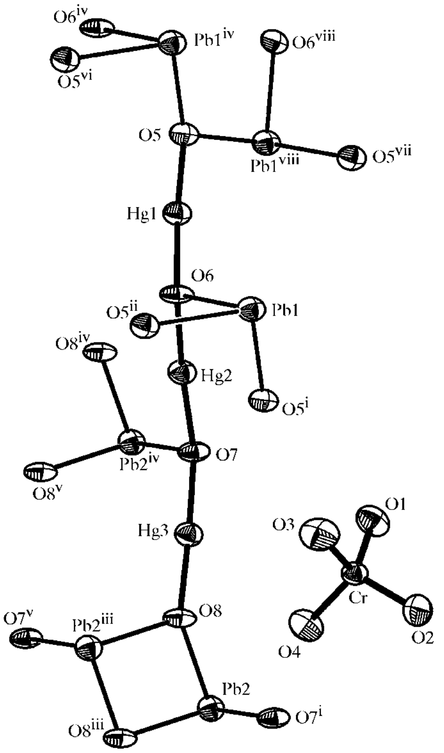

Figure 2
The environment of the $[Hg_3O_4]^{2-}$ unit, showing the six-coordinate PbO_3 pyramids and a $[CrO_4]^{2-}$ tetrahedron. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $x + 1, y, z$; (ii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + 2, -y, -z + 2$; (iv) $x - 1, y, z$; (v) $-x + 1, -y, -z + 2$; (vi) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (vii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (viii) $x - 1, -y + \frac{1}{2}, z - \frac{1}{2}$.]

DOI: 10.1107/S0108270105012552

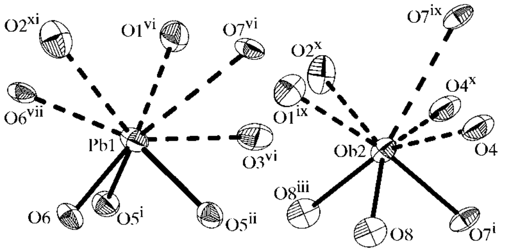

Figure 3
The [3+5]-coordination of the two Pb^{2+} ions; dashed bonds are longer than 2.52 Å. Displacement ellipsoids are shown at the 50% probability level. [Symmetry codes: (i) $x + 1, y, z$; (ii) $x + 1, -y + \frac{1}{2}, z + \frac{1}{2}$; (iii) $-x + 2, -y, -z + 2$; (vi) $x, -y + \frac{1}{2}, z + \frac{1}{2}$; (vii) $x, -y + \frac{1}{2}, z - \frac{1}{2}$; (ix) $-x + 1, -y, -z + 1$; (x) $-x + 2, -y, -z + 1$; (xi) $x - 1, -y + \frac{1}{2}, z + \frac{1}{2}$.]

$[CrO_4]^{2-}$ tetrahedra, $[HgO_2]^{2-}$ dumbbells and Pb^{2+} ions in an O-atom [3+5]-coordination with closest contacts to O atoms that are not bonded to chromium. Both compounds described here belong to the series of $Pb_2(Hg_nO_{n+1})(CrO_4)$ composition and differ in the chain length of the Hg_nO_{n+1} fragment. Another formal member of this family, with $n = 0$, the naturally occurring phoenicochroit, Pb_2OCrO_4 (Williams *et al.*, 1970), was also observed in our experiments.

Inspecting oxochromate(VI) compounds containing divalent Pb and/or Hg, such as $PbCrO_4$ (Quareni & de Pieri, 1965), $HgCrO_4$ (Stalhandske, 1978), Hg_3CrO_6 (Hansen *et al.*, 1995) and the compounds mentioned above, general structural trends become obvious. With increasing amounts of the heavy metal cations, the $[CrO_4]^{2-}$ tetrahedra tend to separate from Hg-containing entities and the number of short $Pb—OCrO_3$ contacts is subsequently reduced. As a second structural constant besides the $[CrO_4]^{2-}$ tetrahedra, Hg appears in a linear coordination in all compounds mentioned here, and structural motifs strongly reminiscent of the HgO structure are formed, *i.e.* $[HgO_2]^{2-}$ dumbbells in $Pb_2(HgO_2)(CrO_4)$, $[Hg_3O_4]^{2-}$ zigzag chains in the title compound and two-dimensional networks in Hg_3CrO_6. The Pb^{2+} ion, mostly occurring in an O-atom [3+x]-coordination ($x \simeq 5$), exhibits the highest flexibility in its coordination sphere among the present cations, and separates and shortens the $[HgO]_n$ chains and fragments.

Experimental

Single crystals of $Pb_2(Hg_3O_4)(CrO_4)$ were obtained at elevated oxygen pressures using steel autoclaves. In a typical experiment, HgO, PbO and CrO_3 were used as starting materials, and distilled water (2 ml) was added to accelerate the reaction. The ground mixture, placed in gold crucibles, was annealed for 120 h at 753 K and 12 MPa oxygen pressure in stainless steel autoclaves (Linke & Jansen, 1997).

Crystal data

$Pb_2(Hg_3O_4)(CrO_4)$
$M_r = 1196.15$
Monoclinic, $P2_1/c$
$a = 6.5408$ (9) Å
$b = 21.947$ (3) Å
$c = 6.9672$ (10) Å
$\beta = 109.304$ (11)°
$V = 943.9$ (2) Å^3
$Z = 4$

$D_x = 8.417$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 17 644 reflections
$\theta = 0.0$–44.2°
$\mu = 85.28$ mm^{-1}
$T = 293$ (2) K
Block, red
0.2 × 0.2 × 0.2 mm

Data collection

Stoe IPDS-II diffractometer
ω scans
Absorption correction: integration (*X-SHAPE*; Stoe & Cie, 2002)
$T_{min} = 0.003$, $T_{max} = 0.023$
18 557 measured reflections
2292 independent reflections

2016 reflections with $I > 2\sigma(I)$
$R_{int} = 0.138$
$\theta_{max} = 28.0°$
$h = -8 \rightarrow 8$
$k = -28 \rightarrow 28$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.045$
$wR(F^2) = 0.119$
$S = 1.01$
2292 reflections
128 parameters

$w = 1/[\sigma^2(F_o^2) + (0.079P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 3.79$ e Å^{-3}
$\Delta\rho_{min} = -4.97$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.00073 (10)

Table 1
Selected geometric parameters (Å, °).

Cr—O1	1.661 (12)	Pb1—O3^{vi}	2.868 (15)
Cr—O2	1.656 (13)	Pb1—O6^{vii}	2.910 (11)
Cr—O3	1.675 (12)	Pb1—O1^{vi}	2.928 (13)
Cr—O4	1.661 (11)	Pb1—O2^{xi}	2.943 (14)
Hg1—O5	2.015 (10)	Pb1—O7^{vi}	3.610 (10)
Hg1—O6	2.022 (9)	Pb2—O8	2.309 (10)
Hg2—O6	2.094 (9)	Pb2—O8^{iii}	2.349 (11)
Hg2—O7	2.097 (9)	Pb2—O7^{i}	2.380 (9)
Hg3—O7	2.029 (10)	Pb2—O4	2.761 (12)
Hg3—O8	2.006 (10)	Pb2—O1^{ix}	2.771 (13)
Pb1—O5^{i}	2.246 (10)	Pb2—O4^{x}	2.972 (14)
Pb1—O6	2.367 (10)	Pb2—O2^{x}	3.202 (13)
Pb1—O5^{ii}	2.512 (11)	Pb2—O7^{ix}	3.228 (11)
O5—Hg1—O6	176.0 (5)	O6—Pb1—O5^{ii}	72.3 (3)
O6—Hg2—O7	175.6 (4)	O8—Pb2—O8^{iii}	75.7 (4)
O7—Hg3—O8	176.4 (4)	O8—Pb2—O7^{i}	81.3 (4)
O5^{i}—Pb1—O6	80.9 (3)	O8^{iii}—Pb2—O7^{i}	91.9 (4)
O5^{i}—Pb1—O5^{ii}	100.0 (3)		

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

Data collection and cell refinement: *X-AREA* (Stoe & Cie, 2002); data reduction: *X-RED* (Stoe & Cie, 2002); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2001).

The authors thank Dr Martin Panthöfer for data recording.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1488). Services for accessing these data are described at the back of the journal.

References

Brandenburg, K. (2001). *DIAMOND*. Version 2.1e. Crystal Impact GbR, Bonn, Germany.
Hansen, T., Müller-Buschbaum, H. & Walz, L. (1995). *Z. Naturforsch. Teil B*, **50**, 47–50.
Klein, W., Curda, J., Friese, K. & Jansen, M. (2002). *Acta Cryst.* C**58**, i23–i24.
Linke, C. & Jansen, M. (1997). *Z. Anorg. Allg. Chem.* **623**, 1441–1446.
Quareni, S. & de Pieri, R. (1965). *Acta Cryst.* **19**, 287–289.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
Stålhandske, C. (1978). *Acta Cryst.* B**34**, 1968–1969.
Stoe & Cie (2002). *X-AREA*, *X-RED* and *X-SHAPE*. Stoe & Cie, Darmstadt, Germany.
Williams, S. A., McLean, W. J. & Anthony, J. W. (1970). *Am. Mineral.* **55**, 784–792.