O(3^{ii})	86.1 (1)	90.1 (1)	1.963 (3)	2.888 (7)	3.912 (9)	2.813 (5)
O(7^{iii})	91.3 (2)	174.4 (7)	95.1 (2)	1.951 (3)	2.733 (6)	2.786 (7)
O(8^{iv})	86.3 (2)	85.9 (1)	171.5 (4)	88.7 (2)	1.960 (3)	2.902 (7)
O(10^{v})	177.0 (8)	91.0 (1)	91.8 (1)	91.1 (2)	95.7 (2)	1.954 (2)

M(2)	O(4^{iv})	O(5^{i})	O(6^{ii})	O(9^{v})	O(11^{vi})	O(12)
O(4^{iv})	1.959 (3)	2.885 (6)	2.935 (7)	3.998 (7)	2.923 (5)	2.785 (5)
O(5^{i})	94.1 (2)	1.981 (3)	2.803 (7)	2.863 (5)	2.860 (6)	4.018 (9)
O(6^{ii})	95.3 (2)	89.2 (1)	2.012 (3)	2.865 (5)	3.228 (5)	2.690 (6)
O(9^{v})	173.1 (4)	90.6 (2)	89.8 (1)	2.046 (3)	2.677 (6)	2.841 (7)
O(11^{vi})	93.4 (1)	90.2 (2)	171.3 (4)	81.5 (1)	2.055 (3)	3.078 (7)
O(12)	88.1 (1)	172.1 (5)	83.0 (1)	87.9 (1)	97.3 (1)	2.046 (3)

P(1)	O(1)	O(2)	O(3)	O(4)
O(1)	1.532 (2)	2.477 (6)	2.516 (6)	2.471 (4)
O(2)	107.7 (2)	1.535 (3)	2.452 (6)	2.512 (5)
O(3)	110.6 (2)	106.3 (2)	1.529 (3)	2.497 (5)
O(4)	109.2 (2)	111.8 (2)	111.1 (2)	1.499 (2)

P(2)	O(5)	O(6)	O(7)	O(8)
O(5)	1.513 (2)	2.450 (6)	2.519 (6)	2.509 (6)
O(6)	107.5 (2)	1.525 (2)	2.532 (6)	2.477 (6)
O(7)	112.1 (2)	112.4 (2)	1.523 (3)	2.440 (6)
O(8)	110.8	108.1 (2)	105.9 (2)	1.535 (3)

P(3)	O(9)	O(10)	O(11)	O(12)
O(9)	1.528 (2)	2.443 (4)	2.517 (6)	2.491 (6)
O(10)	106.0 (2)	1.529 (2)	2.528 (5)	2.521 (5)
O(11)	110.8 (2)	111.6 (2)	1.528 (3)	2.484 (6)
O(12)	109.0 (2)	110.9 (2)	108.5 (2)	1.532 (3)

Li(1)	O(6^{vii})	O(9^{viii})	O(11^{ix})	O(12^{x})
O(6^{vii})	2.06 (2)	3.786 (8)	3.228 (5)	2.690 (6)
O(9^{viii})	140.7 (4)	1.96 (2)	2.677 (6)	3.638 (8)
O(11^{ix})	102.2 (2)	82.8 (4)	2.09 (1)	3.442 (7)
O(12^{x})	82.3 (5)	131.8 (3)	113.6 (8)	2.03 (2)

Li(2)	O(1^{iv})	O(1^{xi})	O(2^{v})	O(2^{iii})	O(8^{xii})	O(8^{ii})
O(1^{iv})	2.448 (4)	4.90 (1)	2.723 (6)	3.890 (9)	2.698 (7)	4.00 (1)
O(1^{xi})	180	2.448 (4)	3.890 (9)	2.723 (6)	4.00 (1)	2.698 (7)
O(2^{v})	69.9 (1)	110.1 (1)	2.297 (4)	4.59 (1)	2.680 (6)	3.83 (1)
O(2^{iii})	110.1 (1)	69.9 (1)	180	2.297 (4)	3.83 (1)	2.680 (6)
O(8^{xii})	68.0 (1)	112.0 (1)	70.0 (1)	110.0 (1)	2.374 (5)	4.75 (1)
O(8^{ii})	112.0 (1)	68.0 (1)	110.0 (1)	70.0 (1)	180	2.374 (5)

Symmetry codes: (i) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (ii) $1-x, 1-y, 1-z$; (iii) $\frac{1}{2}-x, 1-y, z-\frac{1}{2}$; (iv) $x, \frac{1}{2}-y, z-\frac{1}{2}$; (v) $\frac{1}{2}+x, y, \frac{1}{2}-z$; (vi) $\frac{1}{2}-x, y-\frac{1}{2}, z$; (vii) $x-\frac{1}{2}, y, \frac{3}{2}-z$; (viii) $x, \frac{1}{2}-y, \frac{1}{2}+z$; (ix) $-x, 1-y, 1-z$; (x) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (xi) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$; (xii) $x, y, z-1$.

The ω scan width was $(0.8+0.345\tan\theta)^\circ$ with a variable ω scan speed of 1.2–20° min^{-1} and a background/peak counting time ratio of 0.5. Data were corrected for Lorentz and polarization effects. *SHELXS*86 (Sheldrick, 1985) was used to solve the structure by direct methods, and *CRYSTALS* (Watkin, Carruthers & Betteridge, 1987) was used to refine the structure on a MicroVAXII. *MOLVIEW* (Cense, 1990) was used to prepare the view of the structure on a Macintosh LC.

Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: DU1115). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Lead(II) Hydrogenselenite

MARKUS KOSKENLINNA

Technology Development Centre, PO Box 69 (Malminkatu 34), FIN-00101 Helsinki, Finland

JUSSI VALKONEN

University of Jyväskylä, Department of Chemistry, PO Box 35 (Survontie 9), FIN-40351 Jyväskylä, Finland

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Abstract

The title structure, $Pb(HSeO_3)_2$, consists of layers of Pb—O polyhedra connected into a two-dimensional network by Se atoms. The layers are parallel to the *bc* plane and are not interconnected by chemical bonds. Hydrogen bonding between layers is improbable. The coordination polyhedron of Pb consists of eight O atoms in the form of a square antiprism, with all Pb—O distances less than 3.0 Å. There is no apparent lone-pair effect on the lead ion.

Comment

The coordination geometry of the Pb^{II} ion is interesting because of the stereochemical effects occasionally exhibited by the lone electron pair, either as an apparent gap or as other distortions in the coordination geometry (Lawton & Kokotailo, 1972). Sometimes the effect is not detected, as in the lead(II)–carboxylate compound $Pb[O_2(CH_3)_2](18\text{-crown-}6).3H_2O$, where the lead ion is decacoordinate, or in lead(II) aminosquarate, $Pb(C_4O_3HNH_2)_2(OH_2)_2$, where it is octacoordinate, while in $PbSe_2O_5$ with a 6 + 2 coordination scheme the effect is clearly manifested (Shin, Hampden-Smith, Kodas & Duesler, 1993; Narinesingh, Ramcharitar, Hall & Williams, 1994; Koskenlinna & Valkonen, 1995). In $PbSeO_3$, the lone-pair effect is also evident (Koskenlinna & Valkonen, 1977). As part of this study, we prepared lead(II) hydrogenselenite, $Pb(HSeO_3)_2$, and now describe its structure.

The coordination polyhedron of lead in the title compound is a square antiprism composed of eight hydrogenselenite O atoms, O1 and O2. The Pb—O bond distances are between 2.555 (10) and 2.949 (11) Å. Four O1 atoms form one side of the square antiprism, while four O2 atoms form the other side. Pb—O1 distances [2.760 (11)–2.949 (11) Å] are longer than Pb—O2 distances [2.555 (10)–2.573 (10) Å], but an examination of the O—Pb—O bond angles and O· · ·O distances of the square antiprism does not conclusively reveal a gap large enough to contain a lone pair. In lead(II) aminosquarate, the coordination polyhedron is also a square antiprism, with Pb—O distances between 2.535 (8) and 2.798 (8) Å (Narinesingh, Ramcharitar, Hall & Williams, 1994).

The structure of the title compound is depicted in Fig. 1. An outstanding feature is the array of Pb–O polyhedra in the form of layers parallel to the *bc* plane. The polyhedra are connected to one another through Se atoms, thus forming a two-dimensional network. A hydrogenselenite group unites four Pb ions, with atoms O1 and O2 both within bonding distance of two Pb ions simultaneously. There are eight independent hydrogenselenites grouped around a Pb ion.

The atoms which are closest to one another in adjacent layers are the protonated O atoms, O3 and O3($\frac{1}{2}-x$, $\frac{1}{2}+y$, z), which are 3.409 (17) Å apart. This large distance makes hydrogen bonding between layers improbable. The layers in the title compound are held together by other forces, probably van der Waals. The notable fragility of the crystals also points to weak bonding within the crystal.

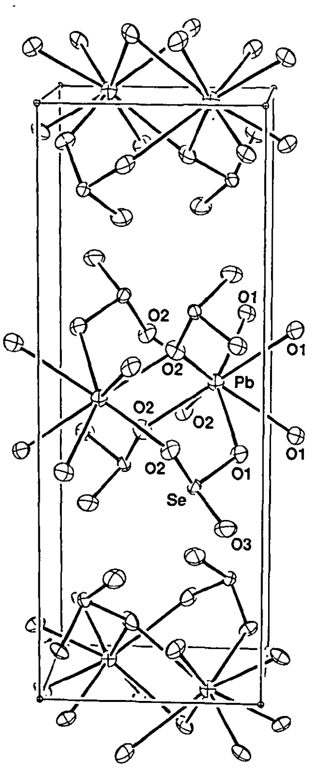

Fig. 1. An *ORTEPII* (Johnson, 1976) drawing of the unit cell showing the layers parallel to the *bc* plane with 75% probability ellipsoids. The *b* axis is horizontal and the *a* axis vertical.

The H atoms could not be located in difference Fourier maps. A probable location for a hydrogen bond, judging from the distance of 2.625 (16) Å, is between atoms O3 and O1(x, $1-y$, $\frac{1}{2}+z$) of two neighbouring hydrogenselenites within the same layer. The other O3· · ·O distances under 3.4 Å are to O atoms of the same hydrogenselenite group. This distance is comparable to that found in $[\mathrm{Fe(SeO_2OH)(SeO_4)}].\mathrm{H_2O}$, where the protonated O atom of the hydrogenselenite group is at a distance of 2.686 Å from the counterpart O atom (Giester, 1992). These distances are within normal ranges, although the distance of 1.727 (11) Å for the Se—OH bond is somewhat shorter than usually encountered in compounds of hydrogenselenite. However, corresponding Se—OH bond lengths have been reported, as in, for example, $\mathrm{FeH(SeO_3)_2}$ [1.734 (10) Å] and $\mathrm{Fe(SeO_2OH)(SeO_4).H_2O}$ [1.710 (9) and 1.730 (8) Å] (Valkonen & Koskenlinna, 1978; Giester, 1992).

Experimental

The title compound can be crystallized by allowing crystals of either $\mathrm{PbSeO_3}$ or $\mathrm{PbSe_2O_5}$ (Koskenlinna & Valkonen, 1977, 1995) to stand for several weeks in an aqueous solution of $\mathrm{H_2SeO_3}$, partly neutralized with KOH or $\mathrm{Mg(CO_3)_2}$, at a temperature between 350 and 370 K. The fragile colourless needles grow on the crystals of the starting material making the solids mixed phase.

Crystal data

$\mathrm{Pb(HSeO_3)_2}$
$M_r = 463.12$
Orthorhombic
Pbcn
$a = 16.381$ (5) Å
$b = 6.111$ (1) Å
$c = 5.896$ (1) Å
$V = 590.3$ (2) Å^3
$Z = 4$
$D_x = 5.21$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 15.0$–$16.0°$
$\mu = 41.0$ mm^{-1}
$T = 295$ K
Prism
0.13 × 0.06 × 0.05 mm
White

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{\min} = 0.58$, $T_{\max} = 1.00$
1049 measured reflections
1049 independent reflections

501 observed reflections [$I > 3\sigma(I)$]
$\theta_{\max} = 30.0°$
$h = 0 \rightarrow 23$
$k = 0 \rightarrow 8$
$l = 0 \rightarrow 8$
2 standard reflections monitored every 35 reflections
intensity decay: none

Refinement

Refinement on F
$R = 0.032$
$wR = 0.040$
$S = 0.46$
501 reflections
43 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.0049$
$\Delta\rho_{\max} = 1.52$ e Å^{-3}
$\Delta\rho_{\min} = -3.82$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: $5.82(6) \times 10^{-7}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.3.1 and 2.2B)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	$U_{\rm eq}$
Pb	0	0.2513 (1)	1/4	0.0036 (1)
Se	0.1492 (1)	0.1796 (2)	0.7378 (2)	0.0026 (1)
O1	0.1018 (6)	0.3781 (18)	0.5993 (18)	0.004 (1)
O2	0.0749 (6)	0.0821 (18)	0.9086 (17)	0.004 (1)
O3	0.2039 (6)	0.3335 (20)	0.9309 (20)	0.005 (1)

Table 2. *Selected geometric parameters* (Å, °)

Pb—O1	2.760 (11)	Pb—O2$^{\rm vi}$	2.573 (10)
Pb—O1$^{\rm i}$	2.949 (11)	Pb—O2$^{\rm vii}$	2.555 (10)
Pb—O1$^{\rm ii}$	2.760 (11)	Se—O1	1.655 (11)
Pb—O1$^{\rm iii}$	2.949 (11)	Se—O2	1.688 (10)
Pb—O2$^{\rm iv}$	2.573 (10)	Se—O3	1.727 (11)
Pb—O2$^{\rm v}$	2.555 (10)		
O1—Se—O2	102.4 (5)	O2—Se—O3	99.9 (5)
O1—Se—O3	99.7 (5)		

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

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Re-Examination Shows that Copper(II) Tetrachloroaluminium, Cu(AlCl$_4$)$_2$, is Monoclinic and not Triclinic as Originally Stated

FRANK H. HERBSTEIN AND MOSHE KAPON

Department of Chemistry, Technion-Israel Institute of Technology, Haifa, Israel 32000

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Abstract

Analysis of the published diffraction data for copper(II) tetrachloroaluminium, Cu(AlCl$_4$)$_2$ [Kitajima, Shimanouchi, Ono & Sasada (1982). *Bull. Chem. Soc. Jpn*, **55**, 2064–2067], shows that the crystals are monoclinic (space group $P2_1/c$, $Z = 2$) and not triclinic ($P\bar{1}$, $Z = 2$) as originally stated. Refinement on this basis gives $R = 0.0883$ for all 1218 data compared with 0.1191 for the triclinic cell. Revised coordinates are given. The changes in the structure are small.

Comment

The crystal structure of copper(II) tetrachloroaluminium, Cu(AlCl$_4$)$_2$, was determined from four-circle diffractometer measurements using graphite-monochromated Mo $K\alpha$ radiation (Kitajima, Shimanouchi, Ono & Sasada, 1982; hereinafter KSOS82) and reported to be triclinic with $a = 6.582(6)$, $b = 7.362(5)$, $c = 12.265(5)$ Å, $\alpha = 89.99(5)$, $\beta = 85.97(6)$, $\gamma = 89.76(6)$°, space group $P\bar{1}$, $Z = 2$. Some 2600 reflections were used in a block-diagonal least-squares refinement, giving $R_F = 0.110$ for 2594 non-zero [$|F_o| > 3\sigma(F_o)$] reflections. The structure was stated to have pseudo $P2_1/c$ symmetry 'inferred from the systematically weak intensities of $0k0$ and $h0l$ reflections'. We show that the true