

INORGANIC COMPOUNDS

Acta Cryst. (1995). C51, 1–3

Lead Diselenite

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(Received 21 February 1994; accepted 11 May 1994)

Abstract

The structure of the title compound, PbSe_2O_5 , is a three-dimensional network with each diselenite ion bridging five Pb ions and with five diselenite ions grouped around each Pb ion. The coordination around Pb comprises six O atoms forming a dented one-sided octahedron with Pb—O distances between 2.483 (10) and 2.884 (10) Å. There are also 2 + 2 O atoms near Pb but with longer Pb—O distances [3.100 (10), 3.136 (10) and 3.291 (10), 3.479 (10) Å]. The first two of these O atoms may be coordinated to Pb, but the other two seem unlikely to be.

Comment

The structures of several complex compounds of lead which contain selenite and some other anions and cations are known, *e.g.* $\text{PbCu}_2(\text{SeO}_3)_3$, $\text{Pb}_2\text{Cu}_2(\text{OH})_4(\text{SeO}_3)(\text{SeO}_4)$, $\text{PbCu}_3(\text{OH})(\text{NO}_3)(\text{SeO}_3)_3 \cdot \frac{1}{2}\text{H}_2\text{O}$, $\text{Pb}_2\text{Cu}_3\text{O}_2(\text{NO}_3)_2(\text{SeO}_3)_2$, $\text{Pb}_2(\text{NO}_3)(\text{NO}_3)(\text{SeO}_3)$ and $\text{Pb}_2\text{Cu}_5(\text{SeO}_3)_6(\text{UO}_2)_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ (Effenberger, 1986, 1987*a,b*, 1988; Ginderow & Cesbron, 1983). The structure of the simple lead selenite PbSeO_3 has also been reported (Koskenlinna & Valkonen, 1977*a*). A common feature of all of these compounds is the irregularity of the coordination geometry around the Pb ions, probably caused by the stereochemical effects of the lone-pair electrons in the valence shell of Pb^{2+} (Lawton & Kokotailo, 1972). Thus, the difference between the shortest and longest Pb—O distances in the coordination polyhedra in these compounds varies between 0.5 and 1.2 Å. In addition, the presence of three, four, or most frequently, five short Pb—O distances at one side of the Pb atom is observed in at least five of the eleven (crystallographically) different Pb coordination polyhedra. In order to clarify these aspects of the coordination of Pb in selenites further, we report here the structure of lead diselenite, PbSe_2O_5 .

The structure is illustrated in Fig. 1, which shows the packing of the four PbSe_2O_5 units within the unit cell. The structure is a three-dimensional network. There is a cavity in the structure, lined by the Se, O1, O3 and O4 atoms of the diselenite ion.

The Pb ion is coordinated by six O atoms at distances ranging from 2.483 (10) to 2.884 (10) Å. The seventh (O4^v) is 3.100 (10) Å from Pb. The six O atoms form a dented, angularly distorted octahedron with O5^{vi} and O2 at the apices [Pb—O5^{vi} 2.522 (10), Pb—O2 2.884 (10) Å]. The bond angle O5^{vi}—Pb—O2 is 148.9 (3)°. The equatorial O atoms (O1ⁱ, O2ⁱⁱⁱ, O5 and O4^{iv}) and the apical O atom O5^{vi} lie on the same side of the Pb ion. [Symmetry codes (i) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$; (iii) $x - 1, y, z$; (iv) $1 - x, -y, 1 - z$; (v) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $-x, -y, 1 - z$.] Similar one-sided coordination has been observed in $\text{PbCu}_2(\text{SeO}_3)_3$, in which five short bonds are also oriented on the same side of the Pb ion (Effenberger, 1988).

The angle O1ⁱ—Pb—O2 between the equatorial O1ⁱ atom and the apical O2 atom is exceptionally large [140.1 (3)°] and the adjacent angles O2ⁱⁱⁱ—Pb—O2 and O4^{iv}—Pb—O2 are also large [114.3 (3) and 104.8 (3)°, respectively]. The fourth angle, O5—Pb—O2, on the opposite side, is compressed to 79.6 (3)°. The lone pair of the Pb^{2+} ion probably lies within the cavity defined by the large angle O1ⁱ—Pb—O2; this has been postulated in the case of Pb^{2+} within a PbS_6 octahedron, where the lone pair is thought to lie within an S—Pb—S angle of

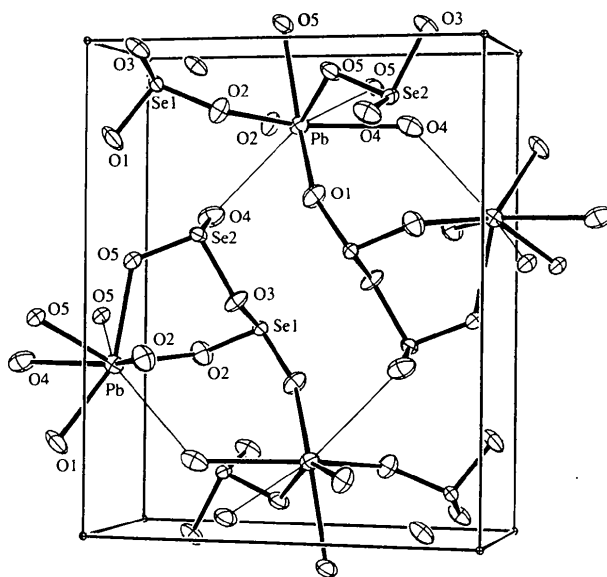


Fig. 1. An ORTEP (Johnson, 1976) drawing of the unit cell with displacement ellipsoids shown at the 75% probability level. The *b* axis is horizontal and the *c* axis is vertical. Thin lines indicate the long Pb—O distances of 3.100 (10) and 3.136 (10) Å.

152.3°, the opposite angle being compressed to 75.5° (Lawton & Kokotailo, 1972).

The coordination geometry of the Pb ion is, however, complicated by four O atoms (O1ⁱⁱ, O3, O4^v and O5^{iv}) which lie at distances ranging from 3.100 (10) to 3.479 (10) Å from Pb [symmetry code: (ii) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{3}{2}-z$]. A fifth O atom (O2^{iv}) lies significantly further away [4.051 (10) Å]. The coordination number of Pb has been reported to be 10 in four of the eleven crystallographically different coordination polyhedra in the compounds mentioned above, but the Pb—O distances in these are shorter. In Pb₂(NO₂)(NO₃)(SeO₃), one of the two independent Pb atoms is ten-coordinate with all Pb—O distances lying within the range 2.508 (6)–2.964 (8) Å (Effenberger, 1987*b*). Tenfold coordination is also observed in PbCu₃(OH)(NO₃)(SeO₃)₃· $\frac{1}{2}$ H₂O and in Pb₂Cu₃O₂(NO₃)₂(SeO₃)₂; the Pb—O distances in these two compounds range from 2.475 (5) to 3.302 (5) Å and from 2.41 (3) to 3.08 (4) Å, respectively (Effenberger, 1986).

In the present compound 6 + 2 coordination is more plausible than 6 + 4. The two additional Pb—O distances to O4^v and O5^{iv} lie within the range usually reported for lead selenites (Effenberger, 1986, 1987*a,b*, 1988; Ginderow & Cesbron, 1983). The lone pair, if assumed to occupy the cavity described above, protrudes approximately in the direction of O1ⁱⁱ. The role of O4^v and O5^{iv} in the coordination scheme of the Pb ion may nonetheless remain small, since they lie at significantly longer distances from the Pb ion than the six O atoms of the octahedron.

Of the six O atoms forming the distorted octahedron, O2 and O5 belong to the same diselenite group while O1ⁱ, O2ⁱⁱ, O4^{iv} and O5^{vi} each belong to a different anion. O2 and O5 lie within bonding distance from two Pb ions. Each diselenite ion connects five Pb ions, acting as a bidentate ligand to one ion and as a monodentate ligand to the other four.

The bond distances and selected bond angles within the diselenite ions are given in Table 2, and are comparable to the corresponding distances and angles in MnSe₂O₅ and PrH₃(SeO₃)₂(Se₂O₅) (Koskenlinna, Niinistö & Valkonen, 1976; Koskenlinna & Valkonen, 1977*b*). The Se—O—Se angle formed by the bridging O atom differs slightly in each compound, being 117.1 (5)° in the title compound, 121.6 (9)° in MnSe₂O₅ and 123.8 (8)° in PrH₃(SeO₃)₂(Se₂O₅).

Experimental

The title compound was prepared by the precipitation of amorphous PbSeO₃ from an aqueous solution of Pb(NO₃)₂ with selenous acid. The precipitate was added to a concentrated (> 1.0 M) aqueous solution of SeO₂ with a stoichiometric ratio of Pb to SeO₂ of 1:2. Well formed crystals with yellowish tint were grown by allowing the suspension to stand at temperatures between 330 and 373 K for a few days.

Crystal data

PbSe₂O₅
 $M_r = 445.11$
 Monoclinic
 $P2_1/n$
 $a = 4.515 (1) \text{ \AA}$
 $b = 9.503 (3) \text{ \AA}$
 $c = 11.618 (2) \text{ \AA}$
 $\beta = 90.33 (1)^\circ$
 $V = 498.5 (2) \text{ \AA}^3$
 $Z = 4$
 $D_x = 5.93 \text{ Mg m}^{-3}$

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: empirical (North, Phillips & Mathews, 1968)
 $T_{\min} = 0.844, T_{\max} = 1.000$
 1543 measured reflections
 1543 independent reflections

Refinement

Refinement on F
 $R = 0.034$
 $wR = 0.043$
 $S = 0.53$
 1165 reflections
 74 parameters
 Weighting scheme based on measured e.s.d.'s
 $(\Delta/\sigma)_{\max} = 0.0049$
 $\Delta\rho_{\max} = 2.64 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -3.00 \text{ e \AA}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 15.3\text{--}20.6^\circ$
 $\mu = 48.5 \text{ mm}^{-1}$
 $T = 295 \text{ K}$
 Prism
 $0.15 \times 0.06 \times 0.07 \text{ mm}$
 Yellowish

1165 observed reflections
 $[I > 3\sigma(I)]$
 $\theta_{\max} = 30.0^\circ$
 $h = 0 \rightarrow 6$
 $k = 0 \rightarrow 13$
 $l = -16 \rightarrow 16$
 2 standard reflections monitored every 50 reflections
 intensity variation: none

Extinction correction:

Zachariasen (1963)

Extinction coefficient:

$5.86 (9) \times 10^{-7}$

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 (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j.$$

| | x | y | z | U_{eq} |
|-----|------------|-------------|-------------|-----------------|
| Pb | 0.2046 (1) | 0.04305 (5) | 0.65436 (4) | 0.00352 (4) |
| Se1 | 0.7262 (3) | 0.3545 (1) | 0.5806 (1) | 0.0025 (1) |
| Se2 | 0.2938 (3) | 0.2497 (1) | 0.3872 (1) | 0.0025 (1) |
| O1 | 0.656 (2) | 0.457 (1) | 0.6924 (9) | 0.006 (1) |
| O2 | 0.757 (2) | 0.193 (1) | 0.6354 (9) | 0.005 (1) |
| O3 | 0.345 (2) | 0.343 (1) | 0.5235 (8) | 0.004 (1) |
| O4 | 0.641 (2) | 0.232 (1) | 0.3462 (8) | 0.005 (1) |
| O5 | 0.212 (2) | 0.090 (1) | 0.4421 (8) | 0.004 (1) |

Table 2. Selected geometric parameters ($\text{\AA}, ^\circ$)

| | | | |
|----------------------|------------|----------------------|------------|
| Pb—O1 ⁱ | 2.556 (10) | Pb—O5 ^{vi} | 2.522 (10) |
| Pb—O1 ⁱⁱ | 3.479 (10) | Pb—O5 ^{vii} | 3.136 (10) |
| Pb—O2 ⁱⁱⁱ | 2.483 (10) | Se1—O1 | 1.655 (10) |
| Pb—O2 | 2.884 (10) | Se1—O2 | 1.665 (10) |
| Pb—O3 | 3.291 (10) | Se1—O3 | 1.843 (9) |
| Pb—O4 ^{iv} | 2.709 (11) | Se2—O3 | 1.827 (9) |
| Pb—O4 ^v | 3.100 (10) | Se2—O4 | 1.652 (10) |
| Pb—O5 | 2.507 (9) | Se2—O5 | 1.689 (10) |
| O1—Se1—O2 | 104.9 (5) | O3—Se2—O5 | 97.7 (5) |
| O1—Se1—O3 | 97.8 (5) | O4—Se2—O5 | 103.3 (5) |

O2—Se1—O3 99.0 (5) Se1—O3—Se2 117.1 (5)
 O3—Se2—O4 100.4 (5)

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

Data collection and cell refinement: *CAD-4 Software* (Enraf-Nonius, 1989). Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *MULTAN11/82* (Main *et al.*, 1982). Program(s) used to refine structure: *MolEN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: AB1172). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Effenberger, H. (1986). *Monatsh. Chem.* **117**, 1099–1106.
 Effenberger, H. (1987a). *Mineral. Petrol.* **36**, 3–12.
 Effenberger, H. (1987b). *Monatsh. Chem.* **118**, 211–216.
 Effenberger, H. (1988). *J. Solid State Chem.* **73**, 118–126.
 Enraf-Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf-Nonius, Delft, The Netherlands.
 Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf-Nonius, Delft, The Netherlands.
 Ginderow, D. & Cesbron, F. (1983). *Acta Cryst.* **C39**, 824–827.
 Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 Koskenlinna, M., Niinistö, L. & Valkonen, J. (1976). *Acta Chem. Scand. Ser. A*, **30**, 836–837.
 Koskenlinna, M. & Valkonen, J. (1977a). *Cryst. Struct. Commun.* **6**, 813–816.
 Koskenlinna, M. & Valkonen, J. (1977b). *Acta Chem. Scand. Ser. A*, **31**, 457–460.
 Lawton, S. L. & Kokotailo, G. T. (1972). *Inorg. Chem.* **11**, 363–369.
 Main, P., Fiske, S. J., Hull, S. E., Lessinger, L., Germain, G., Declercq, J.-P. & Woolfson, M. M. (1982). *MULTAN11/82. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 Zachariasen, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1995). **C51**, 3–7

Lithium Perbromate Monohydrate at 296 and 173 K

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(Received 29 October 1993; accepted 18 July 1994)

Abstract

Lithium tetraoxobromate(1−) monohydrate, $\text{LiBrO}_4 \cdot \text{H}_2\text{O}$, whose perchlorate analog has not yet been de-

scribed, is found to be isomorphous with $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$ and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$. Each of the two inequivalent Li ions is coordinated by six O atoms, thus forming distorted octahedra, each of which has three inequivalent Li—O distances. At room temperature, the average Li(1)—O and Li(2)—O distances are 2.150 and 2.164 Å, respectively. The perbromate ion displays very nearly regular tetrahedral geometry, although it is not subject to symmetry constraints. At 296 K the average observed Br—O distance is 1.610 (4) Å and the average O—Br—O angle is 109.5 (6)°, while at 173 K the corresponding values are 1.613 (4) Å and 109.5 (7)°. The perbromate ion shows rigid-body behavior but the lithium coordination polyhedra do not. At 296 K, the average rigid-body corrected Br—O distance in the perbromate ion is 1.624 (3) Å, in excellent agreement with the corresponding value reported for $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$. Refinement of the two inequivalent H atoms allowed detailed analysis of the hydrogen bonding, which is more extensive than in $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$ or in $\text{NaClO}_4 \cdot \text{H}_2\text{O}$. The average observed *B* values for the H atoms [2.9 (3) Å² at 296 K and 2.8 (3) Å² at 173 K] are sufficiently small to suggest that dynamic disordering of the H atoms (determined by magnetic resonance methods for $\text{NaClO}_4 \cdot \text{H}_2\text{O}$) is not significant in the title salt.

Comment

This study of $\text{LiBrO}_4 \cdot \text{H}_2\text{O}$ is the sequel to an investigation of the structure of $\text{LiBrO}_4 \cdot 3\text{H}_2\text{O}$ (Blackburn, Gallucci, Gerkin & Reppart, 1993). It was of particular interest since the perchlorate analog, $\text{LiClO}_4 \cdot \text{H}_2\text{O}$, has not been described. The potentially similar structure of $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$, however, had been determined (Blackburn, Gallucci, Gerkin & Reppart, 1992).

A stereoview of the structure is given in Fig. 1; hydrogen bonds have been omitted for clarity. The structure is isomorphous with that of $\text{NaBrO}_4 \cdot \text{H}_2\text{O}$ (Blackburn *et al.*, 1992) and thus, also with that of $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (Berglund, Thomas & Tellgren, 1975; Berglund, Tellgren & Thomas, 1976).

Each of the two inequivalent Li ions is coordinated by six O atoms at three inequivalent distances. At room temperature, these Li(1)—O dis-

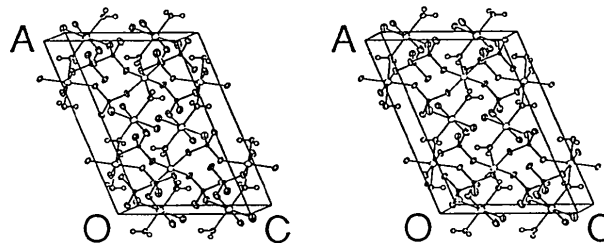


Fig. 1. Stereoview of a unit cell of the lithium perbromate structure at 296 K drawn using *ORTEPII* (Johnson, 1976). Displacement ellipsoids are drawn at 50% probability for all atoms except H, which have been set artificially small. Hydrogen bonds have been omitted for clarity.