Despite the appreciable absorption of the crystal and the empirical correction applied, which led to significant residual electron density, the Zn and Co sites for the title compound could be distinguished without ambiguity through several refinement steps; changing Co to Zn decreased all the crystallographic quality criteria. The coordination of the two metals, octahedral for Co and fivefold for Zn, is also compatible with that found in the literature. The cell parameters of the $ZnNiP_2O_7$ compound are as follows: a = 6.937 (4), b = 8.256 (1), c = 8.904 (5) Å and β = 112.18 (6)°, space group $P2_1/n$. We obtained the crystal structure, which is isotypic with $ZnCoP_2O_7$, but it was of poor quality.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *BEGIN* in *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: Patterson and Fourier methods in *SDP-Plus*. Program(s) used to refine structure: *LSFM* in *SDP-Plus*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *MolEN* (Fair, 1990).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1256). Services for accessing these data are described at the back of the journal.

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$Pb_5O_4MoO_4$

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Abstract

The structure of pentalead molybdenum octaoxide, Pb_5MoO_8, has been determined by single-crystal X-ray methods. The crystal structure is a 4:3:2 superstructure of tetragonal α-PbO (litharge), with embodied MoO_4^{2-} tetrahedra. Infinite double chains of OPb_4 tetrahedra are formed. Along these chains, the OPb_4 tetrahedra share vertices. Two of the O atoms form three nearly coplanar bonds with Pb atoms.

Comment

This work was carried out as part of a systematic study of the PbO–MoO_3 system (Nihtianova *et al.*, 1997), which was undertaken because of interest in the acousto-optical properties of single-crystal lead molybdates.

The lattice parameters and space group of Pb_5MoO_8 were determined by Mentzen *et al.* (1983). Considering the lattice parameters, a 4:3:2 superstructure of tetragonal α-PbO (litharge) can be expected. The low-temperature form of PbO (litharge) crystallizes in space group $P4/nmm$, with cell parameters a = 3.9744 (5) and c = 5.0220 (5) Å (Boher *et al.*, 1985). α-PbO is built up of layers of edge-sharing OPb_4 tetrahedra. The structure of the title compound can be represented as a litharge-like one, in which some of the Pb atoms are replaced by MoO_4^{2-} tetrahedra. The original litharge cell is multiplied four, three and two times in the **a**, **b** and **c** directions, respectively. Infinite double chains of OPb_4 tetrahedra are formed along the a axis by atoms O1–O4, Pb1–Pb4 and Pb7–Pb10. Two additional OPb_4 tetrahedra, with central atoms O5 and O6, are located on either side of the double chains. Pb—O bond lengths for the OPb_4 tetrahedra range from 2.201 (11) to 2.435 (10) Å, with a mean value of 2.315 Å, in good agreement with the Pb—O distance of 2.313 (1) Å found in α-PbO (Boher *et al.*, 1985). Pb—O—Pb angles are in the range 96.6 (4)–122.0 (5)°, with a mean value of 109.1°. All ten Pb atoms are part of OPb_4 tetrahedra, but only Pb7 and Pb9 are at the vertices of proper square pyramids, whose bases are formed by $O1^{iii}$, $O3^{ii}$, $O4^{ii}$

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and O5, and by O1^{ii}, O2^{ii}, O3^{iii} and O6, respectively [symmetry codes: (ii) $1-x$, $1-y$, $-z$; (iii) x, $1+y$, z]. The MoO_4^{2-} ions do not form detached columns but are incorporated in the litharge arrangement. Thus, infinite alternating –Mo1—Pb5—Mo2—Pb6– heavy-atom chains are formed along the a axis. Mo—O bond lengths are between 1.71 (2) and 1.767 (14) Å, with an average of 1.74 Å. The shortest distance between an O atom from an MoO_4^{2-} group and a Pb atom is 2.408 (14) Å.

Atoms O7 and O8 form three nearly coplanar bonds with Pb atoms from two different layers. The O atoms are at the greatest distance from the weighted least-squares planes through Pb3, Pb4, Pb5^{i}, O7 and Pb1, Pb2, Pb6^{i}, O8, at distances of 0.178 (13) and 0.095 (14) Å, respectively [symmetry code: (i) $1-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$] (Nardelli, 1995). Other interlayer connections are formed between O atoms from MoO_4^{2-} tetrahedra and Pb atoms. The thickness of the layers is 5.815 Å, which is longer than in litharge (5.0219 Å; Boher *et al.*, 1985), on account of the presence of the larger MoO_4^{2-} tetrahedra.

The heavy metal atoms in the structure are in a distorted cubic close-packed arrangement, and the distances between them range from 3.459 (1) to 4.542 (3) Å, with a mean value of 3.975 Å. Regarding the arrangement of the heavy metal atoms, the Pb atom sites have one, two or three Mo and, accordingly, 11, ten or nine Pb closest neighbours, giving the total of 12 required for cubic close packing. Each of the Mo atom sites has only one Mo neighbour, related by a centre of symmetry. The two non-equivalent MoO_4^{2-} tetrahedra have different orientations in the unit cell. This is the main reason that $Pb_5O_4MoO_4$ is represented as a 4:3:2 rather than as a 2:3:2 superstructure.

Considering the final ratios between the minimum and maximum principal axes of the displacement ellipsoids, exceptionally high values for atoms O1, O2, O3 and O21, O22, O23 are observed. This may be caused by disorder in the structure, residual uncorrected absorption effects or both.

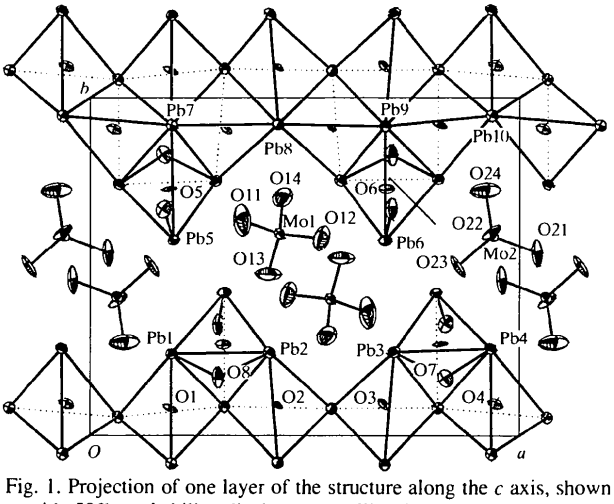

Fig. 1. Projection of one layer of the structure along the c axis, shown with 50% probability displacement ellipsoids. Bonds between Pb and O atoms are not given for clarity.

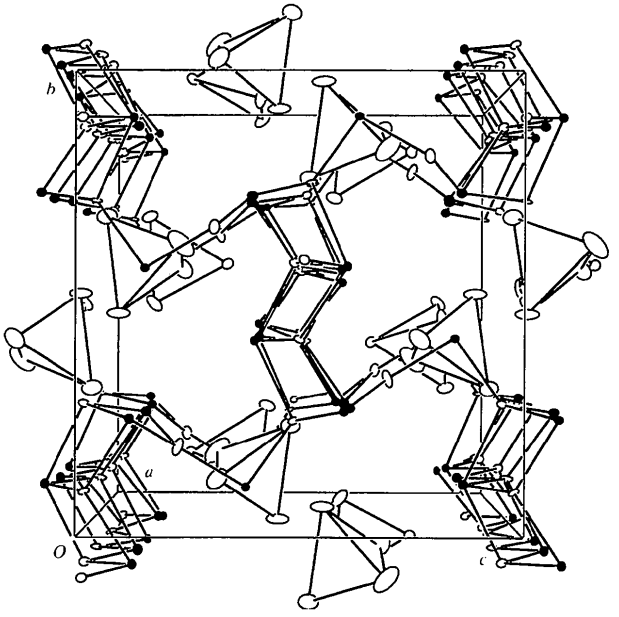

Fig. 2. View of the structure along the a axis. Pb atoms are represented by black ellipsoids and Mo atoms are not shown for clarity.

Experimental

The Pb_5MoO_8 crystals used for the single-crystal investigation were grown from a high-temperature solution by spontaneous crystallization (Nihtianova *et al.*, 1997). The PbO and MoO_3 used were first dried for 3 h at 673 K. The flux was prepared from a mixture of PbO and MoO_3 (5.5:1 molar ratio), and then heated in a platinum crucible to 1163 K at a rate of 200 K h^{-1}. After homogenization of the flux at 1163 K for 1 h, the temperature was decreased to 1037 K for 2.5 h. A Pt wire with a diameter of 0.8 mm was immersed in the solution and removed after 5–10 min, the flux being kept at 1037 K. The Pb_5MoO_8 crystals grew spontaneously on the Pt wire.

Crystal data

Pb_5MoO_8
M_r = 1259.89
Monoclinic
$P2_1/c$
a = 15.330 (1) Å
b = 11.829 (2) Å
c = 11.631 (2) Å
β = 90.104 (14)°
V = 2109.1 (5) Å^3
Z = 8
D_x = 7.936 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 20.73–21.48°
μ = 80.702 mm^{-1}
T = 293 (2) K
Cubic
0.1 × 0.1 × 0.1 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
Profile data from $\omega/2\theta$ scans
Absorption correction: Gaussian using *ABSORB* over a 16 × 16 × 16 grid (DeTitta, 1985)
T_{min} = 0.007, T_{max} = 0.040
9755 measured reflections
4139 independent reflections
2747 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 25.92°
$h = 0 \rightarrow 18$
$k = -14 \rightarrow 14$
$l = -14 \rightarrow 14$
3 standard reflections frequency: 120 min intensity decay: −6.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.034
$wR(F^2)$ = 0.076
S = 1.076
4136 reflections
254 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0284P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 3.616 e Å^{-3}
$\Delta\rho_{min}$ = −2.369 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 0.000307 (9)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Pb1—O8	2.226 (13)	Pb5—O7^{iii}	2.203 (13)
Pb1—O22^{i}	2.756 (12)	Pb5—O21^{iv}	2.408 (14)
Pb1—O24^{ii}	2.85 (2)	Pb5—O11	2.68 (2)
Pb2—O8	2.275 (13)	Pb6—O8^{iii}	2.194 (12)
Pb2—O14^{ii}	2.74 (2)	Pb6—O12	2.44 (2)
Pb2—O13	2.84 (2)	Pb6—O13^{ii}	2.73 (2)
Pb2—O12^{i}	2.86 (2)	Pb6—O23	2.77 (2)
Pb3—O7	2.283 (14)	Pb8—O14	2.71 (2)
Pb3—O11^{i}	2.57 (2)	Pb10—O24	2.63 (2)
Pb4—O7	2.263 (13)	Pb10—O22^{v}	2.871 (13)
Pb5^{i}—O7—Pb4	143.1 (7)	Pb6^{i}—O8—Pb1	137.6 (6)
Pb5^{i}—O7—Pb3	115.6 (6)	Pb6^{i}—O8—Pb2	119.6 (6)
Pb4—O7—Pb3	99.1 (5)	Pb1—O8—Pb2	102.3 (5)

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

Reflection background subtraction, based on the peak profile analysis, and Lorentz and polarization corrections, were performed using programs *REFPK* and *BGLP* (Blessing, 1989). Time-dependent scaling of the measured data with cubic polynomials (*SCALE*3; Blessing, 1989) gave scale factors varying from 1.000 to 0.940 (average 0.979). Multiple-repeated and symmetry-equivalent measurements were averaged, after Gaussian absorption correction using the *SORTAV* program (Blessing, 1995), by a least-squares fit of real spherical harmonic functions (y_{lm}, with an even-order limit of l_{0max} = 4 and an odd-order limit of l_{1max} = 1). The 'relative weighting factor' parameter of the program was set to w_a = 4.0. This yielded corrections corresponding to effective transmission factors varying from 0.985 to 1.020 (average 0.999), and improved the residuals for symmetry-equivalent measurements from R_{int} = 0.0306 (using the conventional averaging procedure) to R_{int} = 0.0259. Bayesian statistical treatment was applied using the *BAYES* program (Blessing, 1989) to calculate the estimates of F^2, $\sigma(F^2)$, F and $\sigma(F)$. Anisotropic displacement parameters were refined for all atoms. The first 25 peaks in the final electron density in the difference Fourier map were found to be ghosts to Pb or Mo atoms at distances less than 1.05 Å.

Data collection: *CAD-4 Users Manual* (Enraf–Nonius, 1988). Cell refinement: *CAD-4 Users Manual*. Data reduction: data reduction and error analysis programs (Blessing, 1989, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Neutron Powder Diffraction Study on Highly Deuterated $Ca(IO_3)_2.D_2O$

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Abstract

Neutron powder diffraction experiments were performed on highly deuterated calcium iodate monohydrate (bruggenite) to examine possible H/D enrich-

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