Acta Cryst E CRYSTALLOGRAPHIC COMMUNICATIONS

ISSN 2056-9890

Synthesis and structure of poly[hydroxonium [μ_4-bromido-tetra-μ_3-bromido-diplumbate(II)]]

Danylo S. Kreiman,[a]* Olesia I. Kucheriv,[a] Alexandru-Constantin Stoica,[b] Sergey O. Malinkin[a] and Il'ya A. Gural'skiy[a]

[a]Department of Chemistry, Taras Shevchenko National University of Kyiv, Volodymyrska st. 64/13, 01601 Kyiv, Ukraine, and [b]Department of Inorganic Polymers, "Petru Poni" Institute of Macromolecular Chemistry, Aleea Grigore Ghica Voda 41A, 700487 Iasi, Romania. *Correspondence e-mail: danylo.kreiman@knu.ua

Received 8 October 2026
Accepted 29 October 2026

Edited by M. Weil, Vienna University of Technology, Austria

Keywords: hydronium bromidoplumbate(II); lead(II) bromide; two-periodic network; tetragonal crystal structure; Pb—Br coordination; disorder.

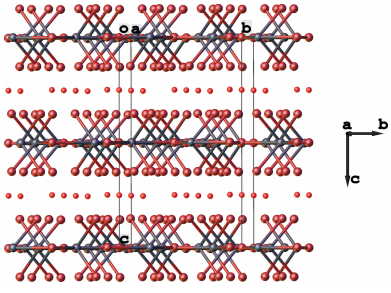
Supporting information: this article has supporting information at journals.iucr.org/e

The title compound, $\{(H_3O)[Pb_2Br_5]\}_n$, crystallizes in the tetragonal space group $I4/mcm$. The asymmetric unit comprises one Pb, two Br and one O sites with site symmetry $m.2m$, $4/m..$, $..m$ and 422, respectively. Bromide ions link the Pb^{II} atoms to form a two-periodic $Pb_2Br_5^-$ anion extending parallel to the ab plane, whilst hydroxonium cations are embedded between neighbouring inorganic layers. Although the hydrogen positions of the hydroxonium cation could not be determined, close O···Br contacts suggest possible O—H···Br hydrogen-bonding interactions between cations and the anionic layers.

1. Chemical context

Lead(II) halide and halidoplumbate(II) compounds display various coordination environments and structural connectivities, both of which are influenced by the stereochemical activity of the Pb^{II} $6s^2$ lone pair and by the terminal or bridging character of the halido ligands (Shimoni-Livny *et al.*, 1998; Mitzi, 2001). Lead(II) halides are widely used as precursors for hybrid lead-halide perovskites. The latter have attracted considerable interest due to their semiconducting properties and potential applications in photovoltaics and optoelectronics (Yuan *et al.*, 2025; Kucheriv *et al.*, 2023, 2025). The chemistry of halidoplumbate species in solution is also central to the formation of lead-halide perovskites. Studies of lead-halide precursor solutions and solvent-dependent phase formation highlight the importance of halidoplumbate speciation and the coordination environment of Pb^{II} (Sharenko *et al.*, 2017). Hydroxonium ions can exhibit different hydrogen-bonding arrangements in crystalline solids, with their local structure influenced by interactions with the surrounding atoms (Bernal, 2006).

In this paper, the crystal structure of the title compound, $(H_3O)Pb_2Br_5$, (**I**), containing a two-periodic Pb–Br network, is reported.



2. Structural commentary

The asymmetric unit of (**I**) comprises four sites, Pb1, Br1, Br2 and O1. They occupy the special Wyckoff positiosn 8 *h*, 4 *c*, 16 *l* and 4 *a*, with site symmetry $m.2m$, $4/m..$, $..m$ and 422, respectively, in the tetragonal space group $I4/mcm$. The asymmetric unit, together with selected symmetry-generated bromide ions that complete the local environment of Pb1, is shown in Fig. 1. The Pb1 atom is eight-coordinated by bromide ions, with Pb1—Br2 and Pb1—Br1 distances of 2.8863 (10)/3.3470 (9) and 3.1287 (2) Å, respectively. The Br—Pb1—Br

OPEN ACCESS
Published under a CC BY 4.0 licence

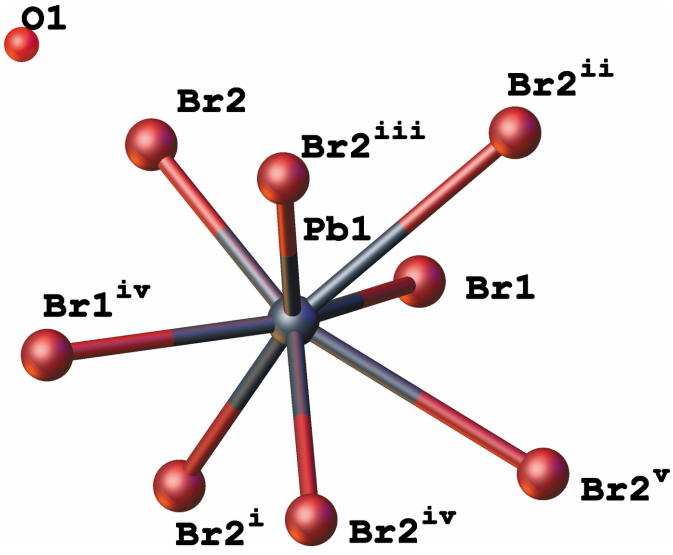


Figure 1
Fragment of the crystal structure showing the coordination environment of Pb1 in the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry codes: (i) $\frac{1}{2}+y, -\frac{1}{2}+x, 1-z$; (ii) $1+y, 1-x, z$; (iii) $1-y, x, z$; (iv) $\frac{3}{2}-x, \frac{1}{2}+y, 1-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$.]

bond angles range from 66.989 (2)° for Br2($\frac{3}{2}-x, \frac{1}{2}+y, 1-z$)—Pb1—Br2($\frac{1}{2}+x, \frac{1}{2}-y, 1-z$) to 146.5601 (14)° for Br2—Pb1—Br2($\frac{1}{2}+x, \frac{1}{2}-y, 1-z$). A continuous shape-measure analysis using *SHAPE 2.1* (Llunell *et al.*, 2013) identifies a distorted biaugmented trigonal prism (BTPR-8) as the closest ideal figure for the $PbBr_8$ coordination polyhedron (CShM = 1.278). Bromide anions link neighbouring Pb^{II} atoms into a two-periodic $Pb_2Br_5^-$ anion extending parallel to the *ab* plane (Figs. 2, 3).

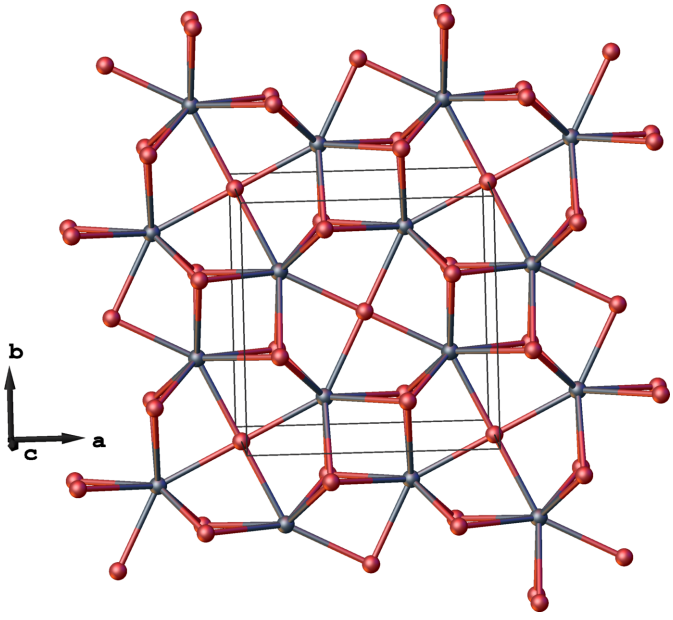


Figure 2
Fragment of the two-periodic Pb–Br network extending parallel to the *ab* plane.

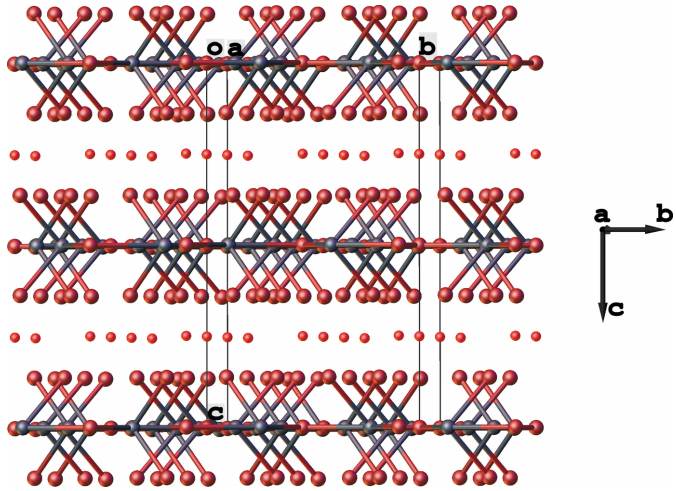


Figure 3
View of the crystal packing, showing the $Pb_2Br_5^-$ anion layers and the O1-centred hydroxonium ion (small red spheres) between neighbouring layers.

3. Supramolecular features

The O1-centred hydroxonium ion is embedded between two neighbouring Pb–Br layers and forms fourselected O1···Br contacts with bromide ions of symmetry-related Pb—Br units (Fig. 4). These contacts involve both the Br1 and Br2 sites. The observed O1···Br contacts (Table 1) suggest possible O—H···Br hydrogen-bonding interactions between the hydroxonium ion and the anionic layers. However, the hydrogen atom(s) could not be located from the available X-ray data and were therefore omitted from the refinement

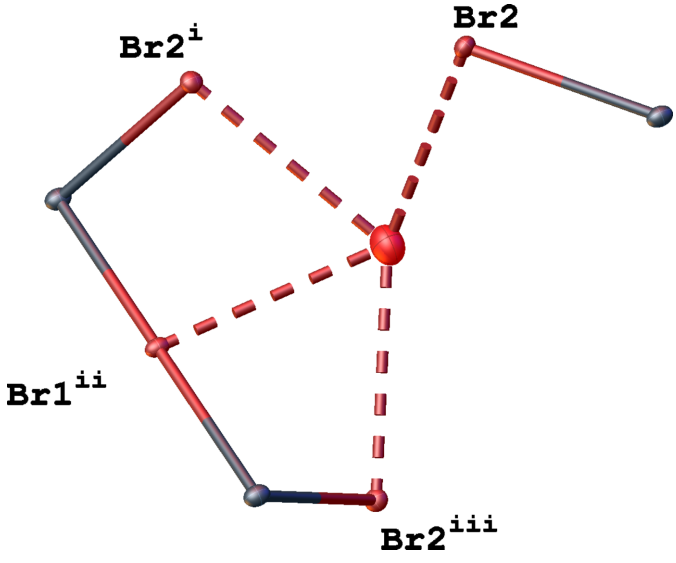


Figure 4
Local environment of the O1-centred hydroxonium ion, showing four selected O1···Br contacts with bromide ions of neighbouring Pb–Br layers. Dashed lines indicate O1···Br contacts associated with possible O—H···Br hydrogen-bonding; hydrogen atom positions remain undetermined. [Symmetry codes: (i) $1-x, y, \frac{1}{2}-z$; (ii) $x-\frac{1}{2}, y+\frac{1}{2}, z$ - 1/2; (iii) $x, 1-y, \frac{1}{2}-z$.]

Table 1
Selected interatomic distances (Å).

O1···Br1^{i}	3.5848 (3)	O1···Br2^{ii}	3.5604 (1)
O1···Br2	3.5604 (1)	O1···Br2^{iii}	3.5604 (1)

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

model. Consequently, the O—H bond orientations and further numerical details of the hydrogen-bonding scheme remain undetermined, and no specific hydrogen-bonding topology is assigned. A view of the overall crystal packing, including the two-periodic Pb–Br networks and the O1-centred hydroxonium ion, is shown in Fig. 3.

4. Database survey

A search of the Crystallography Open Database (COD; Gražulis *et al.*, 2012) identified related Pb^{II} bromide compounds, of which two were selected for structural comparison: the hydrated lead(II) bromide phase $3PbBr_2{\cdot}2H_2O$ (Liu *et al.*, 2018) and the oxyhydroxybromide Pb_2OOHBr (Kunisawa *et al.*, 2026). The former contains eight-coordinate Pb^{II} atoms with $PbBr_8$ or $PbBr_7O$ coordination environments, whereas the latter contains $PbBr_4O_4$ coordination polyhedra within a Pb–O–Br framework.

5. Synthesis and crystallization

Lead(II) bromide (50 mg, 0.136 mmol) was dissolved in concentrated hydrobromic acid (0.5 ml). After 2 days, light-yellow single crystals suitable for single-crystal X-ray diffraction were formed. They were stored in the mother liquor prior to measurement.

6. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Due to the site symmetry (422) of the oxygen atom, the hydrogen-atom positions of the hydroxonium cation are orientationally disordered. This fact, combined with the high absorption coefficient of (**I**), has made it impossible to determine the relevant H positions from difference-Fourier syntheses. Therefore, they were not included in the final model; the contribution from the H atoms is accounted for in the molecular weight given in Table 2.

Acknowledgements

The authors are grateful to the FAIRE programme provided by the Cambridge Crystallographic Data Centre (CCDC) for the opportunity to use the Cambridge Structural Database (CSD) and associated software.

Funding information

Funding for this research was provided by: Ministry of Education and Science of Ukraine (grant Nos. 24BF037-01M and 24BF037-02).

Table 2
Experimental details.

Crystal data	
Chemical formula	$(H_3O)[Pb_2Br_5]$
M_r	832.95
Crystal system, space group	Tetragonal, *I*4/*mcm*
Temperature (K)	100
a, *c* (Å)	8.3948 (4), 14.3392 (10)
V (Å^3)	1010.52 (12)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	52.98
Crystal size (mm)	0.20 × 0.17 × 0.06
Data collection	
Diffractometer	XtaLAB Synergy, Dualflex, HyPix
Absorption correction	Analytical [*CrysAlis PRO* (Rigaku OD, 2024), based on expressions derived by Clark & Reid, 1995]
T_{min}, T_{max}	0.011, 0.094
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	1765, 368, 317
R_{int}	0.048
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.699
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.028, 0.075, 1.09
No. of reflections	368
No. of parameters	16
H-atom treatment	H-atom parameters not defined
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	2.31, −1.59

Computer programs: *CrysAlis PRO* (Rigaku OD, 2024), *SHELXT* (Sheldrick, 2015*a*), *SHELXL* (Sheldrick, 2015*b*), *OLEX2* (Dolomanov *et al.*, 2009) and *publCIF* (Westrip, 2010).

References

Bernal, I. (2006). *C. R. Chim.* **9**, 1454–1466.
Clark, R. C. & Reid, J. S. (1995). *Acta Cryst.* A**51**, 887–897.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Gražulis, S., Daškevič, A., Merkys, A., Chateigner, D., Lutterotti, L., Quirós, M., Serebryanaya, N. R., Moeck, P., Downs, R. T. & Le Bail, A. (2012). *Nucleic Acids Res.* **40**, D420–D427.
Kucheriv, O. I., Haleliuk, D. A., Shova, S. & Gural'skiy, I. A. (2025). *Dalton Trans.* **54**, 1618–1624.
Kucheriv, O. I., Sirenko, V. Y., Petrosova, H. R., Pavlenko, V. A., Shova, S. & Gural'skiy, I. A. (2023). *Inorg. Chem. Front.* **10**, 6953–6963.
Kunisawa, H., Yamaura, J.-I. & Nomura, T. (2026). *IUCrData* **11**, x260790.
Liu, M., Zhao, J., Luo, Z., Sun, Z., Pan, N., Ding, H. & Wang, X. (2018). *Chem. Mater.* **30**, 5846–5852.
Llunell, M., Casanova, D., Cirera, J., Alemany, P. & Alvarez, S. (2013). *SHAPE.* Version 2.1. Universitat de Barcelona, Barcelona, Spain.
Mitzi, D. B. (2001). *J. Chem. Soc. Dalton Trans.* pp. 1–12.
Rigaku OD (2024). *CrysAlis PRO*. Rigaku Oxford Diffraction, Yarnton, England.
Sharenko, A., Mackeen, C., Jewell, L., Bridges, F. & Toney, M. F. (2017). *Chem. Mater.* **29**, 1315–1320.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.
Shimoni-Livny, L., Glusker, J. P. & Bock, C. W. (1998). *Inorg. Chem.* **37**, 1853–1867.
Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
Yuan, L., Xue, Q., Wang, F., Li, N., Waterhouse, G. I. N., Brabec, C. J., Gao, F. & Yan, K. (2025). *Chem. Rev.* **125**, 5057–5162.

supporting information

Acta Cryst. (2026). E**82** [https://doi.org/10.1107/S2056989026011291]

Synthesis and structure of poly[hydroxonium [μ_4-bromido-tetra-μ_3-bromido-diplumbate(II)]]

Danylo S. Kreiman, Olesia I. Kucheriv, Alexandru-Constantin Stoica, Sergey O. Malinkin and Il'ya A. Gural'skiy

Computing details

Poly[hydroxonium [μ_4-bromido-tetra-μ_3-bromido-diplumbate(II)]]

Crystal data

$(H_3O)[Pb_2Br_5]$
M_r = 832.95
Tetragonal, *I*4/*mcm*
a = 8.3948 (4) Å
c = 14.3392 (10) Å
V = 1010.52 (12) Å^3
Z = 4
F(000) = 1400
D_x = 5.475 Mg m^{-3}
Mo *Kα* radiation, λ = 0.71073 Å
Cell parameters from 1179 reflections
θ = 2.8–29.7°
μ = 52.98 mm^{-1}
T = 100 K
Plate, light yellow
0.20 × 0.17 × 0.06 mm

Data collection

XtaLAB Synergy, Dualflex, HyPix diffractometer
Radiation source: micro-focus sealed X-ray tube, PhotonJet (Mo) X-ray Source
Mirror monochromator
Detector resolution: 10.0000 pixels mm^{-1}
ω scans
Absorption correction: analytical [CrysAlisPro (Rigaku OD, 2024), based on expressions derived by Clark & Reid, 1995]
T_{min} = 0.011, T_{max} = 0.094
1765 measured reflections
368 independent reflections
317 reflections with $I > 2\sigma(I)$
R_{int} = 0.048
θ_{max} = 29.8°, θ_{min} = 2.8°
h = −11→11
k = −10→7
l = −18→13

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.075
S = 1.09
368 reflections
16 parameters
0 restraints
H-atom parameters not defined
$w = 1/[\sigma^2(F_o^2) + (0.037P)^2 + 12.0445P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 2.31 e Å^{-3}
$\Delta\rho_{min}$ = −1.59 e Å^{-3}
Extinction correction: SHELXL2018/3 (Sheldrick 2015b), $Fc^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.00046 (9)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Pb1	0.83338 (4)	0.33338 (4)	0.500000	0.0116 (2)
Br1	1.000000	0.000000	0.500000	0.0102 (4)
Br2	0.65560 (8)	0.15560 (8)	0.36269 (7)	0.0109 (3)
O1	0.500000	0.500000	0.250000	0.030 (4)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Pb1	0.0094 (3)	0.0094 (3)	0.0161 (4)	−0.0005 (2)	0.000	0.000
Br1	0.0078 (5)	0.0078 (5)	0.0150 (9)	0.000	0.000	0.000
Br2	0.0105 (4)	0.0105 (4)	0.0117 (5)	−0.0014 (4)	−0.0010 (3)	−0.0010 (3)
O1	0.034 (6)	0.034 (6)	0.023 (8)	0.000	0.000	0.000

Geometric parameters (Å, º)

Pb1—Br1	3.1287 (2)	Pb1—Br2^{ii}	2.8863 (10)
Pb1—Br1^{i}	3.1287 (2)	Pb1—Br2	2.8863 (10)
O1···Br1^{iii}	3.5848 (3)	O1···Br2^{iv}	3.5604 (1)
O1···Br2	3.5604 (1)	O1···Br2^{v}	3.5604 (1)
Br1—Pb1—Br1^{i}	143.113 (17)	Pb1—Br1—Pb1^{vi}	180.0
Br2^{ii}—Pb1—Br1^{i}	76.624 (9)	Pb1^{vii}—Br1—Pb1^{viii}	180.0
Br2^{ii}—Pb1—Br1	76.624 (9)	Pb1—Br1—Pb1^{vii}	90.0
Br2—Pb1—Br1	76.624 (9)	Pb1^{vii}—Br1—Pb1^{vi}	90.0
Br2—Pb1—Br1^{i}	76.624 (9)	Pb1^{viii}—Br1—Pb1^{vi}	90.0
Br2^{ii}—Pb1—Br2	86.02 (4)	Pb1—Br1—Pb1^{viii}	90.0

Symmetry codes: (i) −*x*+3/2, *y*+1/2, −*z*+1; (ii) *x*, *y*, −*z*+1; (iii) *x*−1/2, *y*+1/2, *z*−1/2; (iv) −*x*+1, *y*, −*z*+1/2; (v) *x*, −*y*+1, −*z*+1/2; (vi) −*x*+2, −*y*, −*z*+1; (vii) *y*+1, −*x*+1, −*z*+1; (viii) −*y*+1, *x*−1, *z*.