Revision 1

Crystal chemistry of layered Pb oxychloride minerals with PbO-related structures. II. Crystal structure of vladkrivovichevite, $[Pb_{32}O_{18}][Pb_4Mn_2O]Cl_{14}(BO_3)_8 \cdot 2H_2O$

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Abstract

The crystal structure of vladkrivovichevite, a new complex lead oxychloride mineral from the Kombat Mine, Grootfontein, Namibia, has been solved by direct methods and refined to $R_1 = 0.048$ for 3801 unique observed reflections. The mineral is orthorhombic, *Pmmn*, $a = 12.759(1)$, $b = 27.169(4)$, $c = 11.515(1)$ Å, $V = 3992.0(9)$ Å^3. The structure of vladkrivovichevite belongs to a novel type of layered Pb oxychloride structure. The structure contains 12 symmetrically independent Pb sites. All Pb sites have strongly asymmetric coordination. Two B atoms form slightly distorted BO_3 triangles. One symmetrically independent Mn atom forms five Mn-O bonds and one Mn-Cl bond by forming MnO_5Cl octahedra. The O1, O2, O10, O11, and O12 atoms are tetrahedrally coordinated by four Pb atoms each, forming OPb_4 oxocentered tetrahedra. The O7 site has a remarkable octahedral coordination, consisting of four Pb and two Mn atoms. The $O1Pb_4$, $O2Pb_4$, $O10Pb_4$ and $O11Pb_4$ tetrahedra share common edges to produce bands interconnected by $O12Pb_4$ tetrahedra, forming a $[O_{18}Pb_{32}]^{28+}$ layer. A $O7Pb_4Mn_2$

heterometallic oxocentered octahedron serves as the core of the $[OPb_4Mn_2Cl_2(BO_3)_8]^{16-}$ clusters that link to the $[O_{18}Pb_{32}]^{28+}$ layer via BO_3 triangles. The presence of $[OPb_4Mn_2Cl_2(BO_3)_8]^{16-}$ clusters is associated with large cross-like vacancies in the $[O_{18}Pb_{32}]^{28+}$ layer.

Keywords: vladkrivovichevite; lead oxyhalides; crystal structure; litharge derivatives; layered structures; oxocentered units; borates; complex topologies.

Introduction

Vladkrivovichevite, a new complex Pb-Mn oxychloride borate, $[Pb_{32}O_{18}][Pb_4Mn_2O]Cl_{14}(BO_3)_8 \cdot 2H_2O$, was found in a specimen from the Kombat Mine, Grootfontein, Namibia (Turner et al. 2012). The mineral occurs as pale green crystals and grains in close association with hereroite (Siidra et al. 2012). Vladkrivovichevite was named in honour of Prof. Dr. Vladimir Gerasimovich Krivovichev (b. 1946), Head of the Department of Mineralogy, Faculty of Geology, St. Petersburg State University. In the present paper, we report on the crystal structure of vladkrivovichevite and its relationships with other complex layered Pb oxyhalides.

Experimental

Chemical composition

Fourty analyses on three different grains of vladkrivovichevite were obtained using a Camscan-4DV scanning electron microscope (SEM) and AN-10000 (EDX) spectrometer at the Radium Institute, St. Petersburg (Turner et al. 2012). The empirical formula for vladkrivovichevite, calculated on the basis of Pb+Mn = 38 APFU, is $Pb_{36.32}O_{19}Mn_{1.68}Cl_{13.99}(BO_3)_8 \cdot 2H_2O$, and the ideal formula is $[Pb_{32}O_{18}][Pb_4Mn_2O]Cl_{14}(BO_3)_8 \cdot 2H_2O$.

Single crystal X-ray analysis

A transparent, equant green crystal of vladkrivovichevite was studied using the Bruker Smart Apex II diffractometer at the Department of Crystallography, St. Petersburg State University, Russia. More than a hemisphere of X-ray diffraction data ($\theta_{max} = 30.61°$) with the frame widths of 0.3º in ω, and with 55 s count time per frame were collected at room temperature using Mo$K\alpha$ radiation. The data

were integrated and corrected for absorption using an empirical ellipsoidal model and the Bruker programs *APEX* and *XPREP*. The observed systematic absences were consistent with the space group *Pmmn*. The structure was solved in this space group by direct methods and refined to $R_1 = 0.048$ on the basis of F^2 for all unique data. The *SHELX* program package was used for all structure calculations (Sheldrick, 2008). The final model included all atomic positional parameters, refinable weighting scheme of the structure factors and anisotropic-displacement parameters for all atoms except O(8)-O(12), OW(1), OW(2), B(1), B(2), Cl(1A) and Cl(1B). Attempts to refine these atoms anisotropically resulted in physically unrealistic parameters. Thermal parameters of the B(1), B(2) and O(10), O(11), O(12) sites were fixed at the final stages of refinement. The final atomic coordinates and displacement parameters are given in Table 2, selected interatomic distances are listed in Table 3. The list of observed and calculated structure factors can be provided by the authors upon request.

Results

Cation coordination

Details of the cation coordination polyhedra for the Pb atoms are shown in Figure 1 (all distances shorter than 3.5 Å are taken into account). The structure of vladkrivovichevite contains 12 symmetrically independent Pb sites. All Pb sites have strongly asymmetric coordination with three to four short Pb-O bonds in one coordination hemisphere. The coordination is complemented by several additional longer bonds that vary from site to site. The Pb1-Pb10 atoms form from 2 to 4 Pb-Cl bonds, whereas the Pb11 and Pb12 atoms are not bonded to Cl at all. Four Pb atoms (Pb2, Pb4, Pb5, Pb6) form bonds to the OW1 and OW2 water molecules. The coordination of the Pb10, Pb11 and Pb12 sites is unusual, with five short and four long Pb-O bonds. Two symmetrically independent B atoms form slightly distorted BO_3 triangles with the <B-O> bond lengths of 1.38 and 1.39 Å for B1 and B2, respectively. One symmetrically independent Mn atom forms five Mn-O bonds and one Mn-Cl bond,

87 forming MnO_5Cl octahedra. Such mixed-ligand Mn octahedra are quite rare in minerals, but have been
88 observed in synthetic Mn oxychlorides (Zalkin et al. 1964; Buisson, 1977; Knee et al. 2002).
89
90 Anion coordination
91
92 The Cl1, Cl3, Cl4, and Cl6 atoms have cubic coordination by eight Pb atoms each, which is
93 typical for layered Pb oxyhalides. The Cl2 and Cl5 sites have strongly distorted $ClPb_6Pb_2$
94 coordinations. The Cl1A and Cl1B sites have site-occupation factors (s.o.f.) of 50% and are mutually
95 incompatible. The structure of vladkrivovichevite contains 14 symmetrically independent O sites. The
96 diversity and complexity of the oxygen atom arrangements is remarkable. Two oxygen atoms (OW1,
97 OW2) belonging to H_2O molecules are half occupied (s.o.f. = 50%). The O3, O4, O5, O6, O8 and O9
98 sites belong to the BO_3 triangles. The O1, O2, O10, O11, and O12 atoms are tetrahedrally coordinated
99 by four Pb atoms forming OPb_4 oxocentered tetrahedra. The <O-Pb> bond lengths in the tetrahedra are
100 in the range 2.31-2.33 Å in agreement with the value of 2.33 Å derived by Krivovichev et al. (1998).
101 The <Pb-O-Pb> angles vary from 109.19º (O11) to 109.44º (O10), which is very close to the value of
102 109.5º for an ideal tetrahedron. The average Pb···Pb distances within the OPb_4 tetrahedra are 3.78, 3.77,
103 3.79, 3.77, and 3.79 Å for $O(1)Pb_4$, $O(2)Pb_4$, $O(10)Pb_4$, $O(11)Pb_4$ and $O(12)Pb_4$, respectively. These
104 distances are slightly larger than the average value of 3.74 Å reported by Krivovichev and Filatov
105 (1999), a result of distortion of the OPb_4 subunits due to the sharing of edges with adjacent tetrahedra.
106 The O7 site has a remarkable octahedral coordination, consisting of four Pb and two Mn atoms (Fig. 1).
107 This type of coordination is unusual for oxysalt minerals. In fact, octahedral coordination is more
108 typical for F^- anions in inverted (or anti-) perovskites (Krivovichev 2008). In synthetic compounds,
109 homometallic OPb_6 octahedra have been observed in $Pb_6O[(Si_6Al_2)O_{20}]$ (Siidra et al., 2009), whereas
110 heterometallic OPb_5Mn octahedra are present in $Pb_5Sb_2MnO_{11}$ (Abakumov et al. 2004).
111
112 Bond-valence analysis

The calculated bond-valence sums (Table 2) are in general agreement with the expected oxidation states. The bond-valence sums for the Cl2-Cl7 sites are remarkably low (0.14-0.44 valence units, v.u.), which is typical for Cl^- anions located in structure cavities (the same effect has also been observed, for instance, in the structure of leucostaurite, $Pb_2[B_5O_9]Cl{\cdot}0.5H_2O$ (Brugger et al. 2012)). It is also possible that the existing Pb^{2+}-Cl^- bond-valence parameters are not flexible enough to account properly for long Pb-Cl bonds.

Structure description

As is typical for Pb oxyhalides with layered structures, their description is more straightforward in terms of structural units based upon oxocentered tetrahedra (Siidra et al., 2008). The $O1Pb_4$, $O2Pb_4$, $O10Pb_4$ and $O11Pb_4$ tetrahedra share common edges to produce bands interconnected by the $O12Pb_4$ tetrahedra, which results in formation of a $[O_{18}Pb_{32}]^{28+}$ tetrahedral layer (Fig. 2a, b). In contrast to the $[O_{21}Pb_{32}]^{22+}$ layer in the structure of hereroite (Siidra et al., 2012), the layer in vladkrivovichevite is topologically very simple. The local environments of the $O(1)Pb_4$, $O(2)Pb_4$, $O(10)Pb_4$, $O(11)Pb_4$ and $O(12)Pb_4$ oxocentered tetrahedra is different already at the first-corona level (Fig. 3), which means that all tetrahedra have different topological functions in the layer architecture. The OPb_4Mn_2 heterometallic oxocentered octahedron serves as a core of unusually complex $[OPb_4Mn_2Cl_2(BO_3)_8]^{16-}$ clusters (Fig. 4) located in the halogen interlayer (Fig. 5d) and linked to the $[O_{18}Pb_{32}]^{28+}$ tetrahedral layer via BO_3 triangles. The cavities or micelles around the clusters are most probably filled by lone electron pairs on Pb^{2+} cations (Fig. 5d) which is typical for the structures containing Tl^+, Pb^{2+} and Bi^{3+} (Makovicky 1997; Siidra et al. 2009). $[OPb_4Mn_2Cl_2(BO_3)_8]^{16-}$ cluster is associated with the large cross-like vacancy in the $[O_{18}Pb_{32}]^{28+}$ layer (Fig. 4). The Cl1B atom that forms strong bonds with Mn atoms at the centre of the vacancy (Fig. 2a). A similar feature occurs in the structure of synthetic $Pb_{31}O_{22}Br_{10}Cl_8$ (Krivovichev *et al*. 2006), where the $[PbX_6]^{4-}$ (X = Cl, Br) octahedra are located

between the Pb-O layers in such a way that square vacancies in the PbO matrix are exactly above and below these units. Figure 5d shows the structure of the Pb-Cl-H_2O sheet, a planar arrangement of isolated OPb_4 squares (which are equatorial to the $O7Pb_4Mn_2$ octahedra), Cl^- anions, and H_2O molecules. In general, the structure of vladkrivovichevite belongs to the 1:1 type (Siidra et al. 2012) and consists of alternating Pb-O layers and Pb-Cl-H_2O sheets oriented parallel to the (100) plane (Fig. 6).

Discussion

The structure of vladkrivovichevite belongs to a new type of layered Pb oxychloride structure. Its unique character involves the incorporation of complex Pb-Mn-Cl-borate clusters into the interlayer space between the PbO-derived layers. Welch et al. (2000) observed that interlayer Cl in layered Pb oxychlorides can be replaced by water molecules, whereas the interlayer space in the structures of $Pb_{31}O_{22}Br_{10}Cl_8$ (Krivovichev et al. 2006) (Fig. 5b) and mereheadite (Krivovichev et al. 2009) (Fig. 5c) accommodates additional Pb sites coordinated solely by Cl^- anions.

Vladkrivovichevite is the fifth mineral known to date that contains both Pb^{2+} cations and borate groups. The other four are hyalotekite, $PbBa_3Ca_2[B_2(Si,Be)_2Si_8O_{28}]F$ (Moore et al. 1982), britvinite, $[Pb_7(OH)_3F(BO_3)_2(CO_3)][Mg_{4.5}(OH)_3(Si_5O_{14})]$ (Chukanov et al. 2008; Yakubovich et al. 2008), mereheadite, $Pb_{47}O_{24}(OH)_{13}Cl_{25}(BO_3)_2(CO_3)$ (Krivovichev et al. 2009), and leucostaurite, $Pb_2[B_5O_9]Cl{\cdot}0.5H_2O$ (Brugger et al. 2012). Among minerals and synthetic compounds, only mereheadite, leucostaurite and $Pb_4O[Pb_2(BO_3)_3Cl]$ (Behm, 1983) contain Pb, B, and Cl.

The interaction of the $[OPb_4Mn_2Cl_2(BO_3)_8]^{16-}$ clusters with the halogen layer (Fig. 5d) is limited to very weak electrostatic forces. In this sense, $[OPb_4Mn_2Cl_2(BO_3)_8]^{16-}$ oxocentered clusters in the structure of vladkrivovichevite can be considered as complex anionic guests accommodated within the halogen and PbO-like host matrix. It is possible that octahedral clusters of the type observed in

vladkrivovichevite were present in the crystallization solutions as pre-nucleation building blocks absorbed by the growing Pb oxychloride structure to form a complex fascinating architecture.

Acknowledgements

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References Cited

Abakumov, A.M., Rozova, M.G., Chizhov, P.S., Antipov, E.V., Hadermann, J., and Van Tendeloo, G. (2004) Synthesis and crystal structure of the novel $Pb_5Sb_2MnO_{11}$compound. Journal of Solid State Chemistry, 177, 2855-2861.

Behm, H. (1983) Hexalead chloride triorthoborate oxide, $Pb_4O(Pb_2(BO_3)_3Cl)$. Acta Crystallographica, C39, 1317-1319.

Brown, I.D., and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. Acta Crystallographica, B41, 244-247.

Brugger, J., Meisser, N., Ansermet, S., Krivovichev, S., Kahlenberg, V., Belton, D., and Ryan, C.G. (2012) Leucostaurite, $Pb_2[B_5O_9]Cl{\cdot}0.5H_2O$, from the Atacama Desert: the first Pb-dominant member of the hilgardite group, and micro-determination of boron in minerals by PIGE. American Mineralogist, in press.

Buisson, G. (1977) Structure cristalline d'un oxychlorure de manganese, $Mn_8O_{10}Cl_3$. Acta Crystallographica, B33, 1031-1034.

Chukanov, N.V., Yakubovich, O.V., Pekov, I.V., Belakovsky, D.I., and Massa, W. (2008) Britvinite, $Pb_{15}Mg_9(Si_{10}O_{28})(BO_3)_4(CO_3)_2(OH)_{12}O_2$, a new mineral species from Långban, Sweden. Geology of Ore Deposits, 50, 713-719.

Knee, C.S., Zhukov, A.A., and Weller, M.T. (2002) Crystal structures and magnetic properties of the manganese oxide chlorides Sr_2MnO_3Cl and $Sr_4Mn_3O_{8-y}Cl_2$. Chemistry of Materials, 14, 4249-4255.

Krivovichev, S.V. (2008) Minerals with antiperovskite structure: a review. Zeitschrift für Kristallographie, 223, 109-113.

Krivovichev, S.V. and Brown, I.D. (2001) Are the compressive effects of encapsulation an artifact of the bond valence parameters? Zeitschrift für Kristallographie, 216, 245-247.

Krivovichev, S.V., Siidra, O.I., Nazarchuk, E.V., Burns, P.C., Depmeier, W. (2006) Exceptional topological complexity of lead oxide blocks in $Pb_{31}O_{22}X_{18}$ (X = Br, Cl). Inorganic Chemistry. 45, 3846-3848.

Makovicky, E. (1997) Modular crystal chemistry of sulphosalts and other complex sulphides. In: Merlino, S. (ed.) Modular Aspects of Minerals. EMU Notes in Mineralogy, Vol. 1. Eötvös University Press, Budapest 1997, pp. 237-271.

Moore, P.B., Araki, T., and Ghose, S. (1982) Hyalotekite, a complex lead borosilicate: its crystal structure and the lone-pair effect of Pb(II). American Mineralogist, 67, 1012-1020.

Sheldrick, G.M. (2008) A short history of SHELX. Acta Crystallographica, A64, 112-122.

Siidra, O.I., Krivovichev, S.V. and Filatov, S.K. (2008) Minerals and synthetic Pb(II) compounds with oxocentered tetrahedra: review and classification. Zeitschrift für Kristallographie, 223, 114-126.

Siidra, O.I., Krivovichev, S.V., and Depmeier, W. (2009) Crystal structure of $Pb_6O[(Si_6Al_2)O_{20}]$. Glass Physics and Chemistry, 35, 406-410.

Siidra, O. I., Britvin, S.N., Krivovichev, S.V., Depmeier, W. (2009) Hydroxocentered $[(OH)Tl_3]^{2+}$ triangle as a building unit in thallium compounds: synthesis and crystal structure of $Tl_4(OH)_2CO_3$. Zeitschrift für Kristallographie, 224, 563-567.

Siidra, O. I., Krivovichev, S.V., Turner, R., and Rumsey, M. (2012) Crystal chemistry of layered Pb oxychloride minerals with PbO-related structures. I. Crystal structure of hereroite, $[Pb_{32}O_{21-x+y}](AsO_4)_2((Si_x(As,V)_{1-x-y}Mo_y)O_4)_2Cl_{10}$. American Mineralogist, submitted.

Turner, R., Siidra, O.I., Krivovichev, S.V., Stanley, C.J., Spratt, J. (2012b) Rumseyite, $[Pb_2OF]Cl$, the first naturally occurring fluoroxychloride mineral with the parent crystal structure for layered lead oxychlorides. Mineralogical Magazine, submitted.

Turner, R., Siidra, O.I., Rumsey, M.S., Krivovichev, S.V., Stanley, C.J., Spratt, J. (2012) Hereroite and vladkrivovichevite - two novel lead oxychlorides from the Kombat mine, Namibia. Mineralogical Magazine, submitted.

Welch, M.D., Cooper, M.A., Hawthorne, F.C., and Criddle, A.J. (2000) Symesite, $Pb_{10}(SO_4)O_7Cl_4(H_2O)$, a new PbO-related sheet mineral: description and crystal structure. American Mineralogist, 85, 1526-1533.

Yakubovich, O.V., Massa, W., and Chukanov, N.V. (2008) Crystal structure of britvinite $[Pb_7(OH)_3F(BO_3)_2(CO_3)][Mg_{4.5}(OH)_3(Si_5O_{14})]$: a new layered silicate with an original type of silicon-oxygen networks. Crystallography Reports, 53, 206-215.

Zalkin, A., Forrester, J.D., Templeton, D.H. (1964) The crystal structure of manganese dichloride tetrahydrate. Inorganic Chemistry, 3, 529-533.

Figure Captions

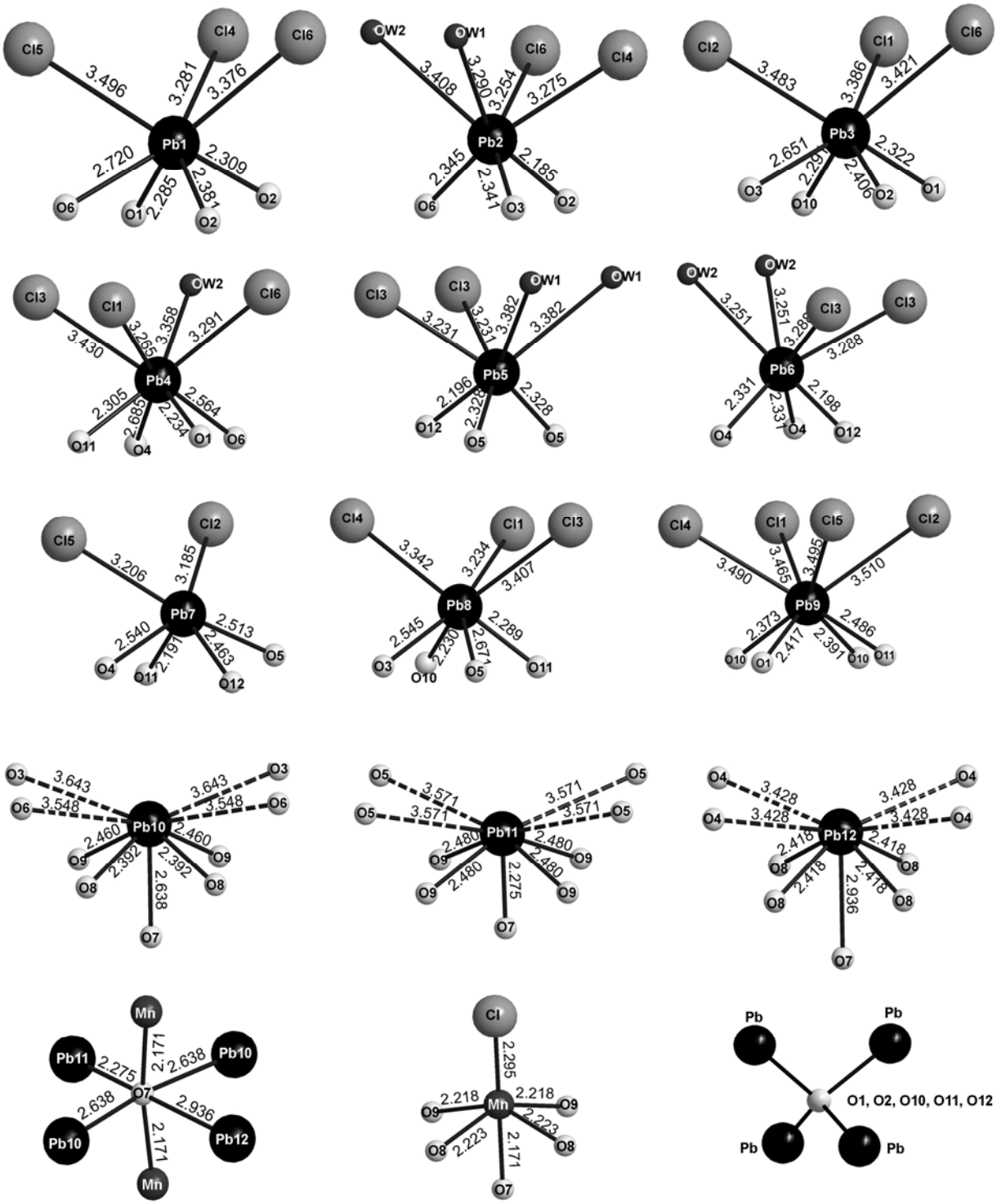


Figure 1. Cation and anion coordination in the structure of vladkrivovichevite.

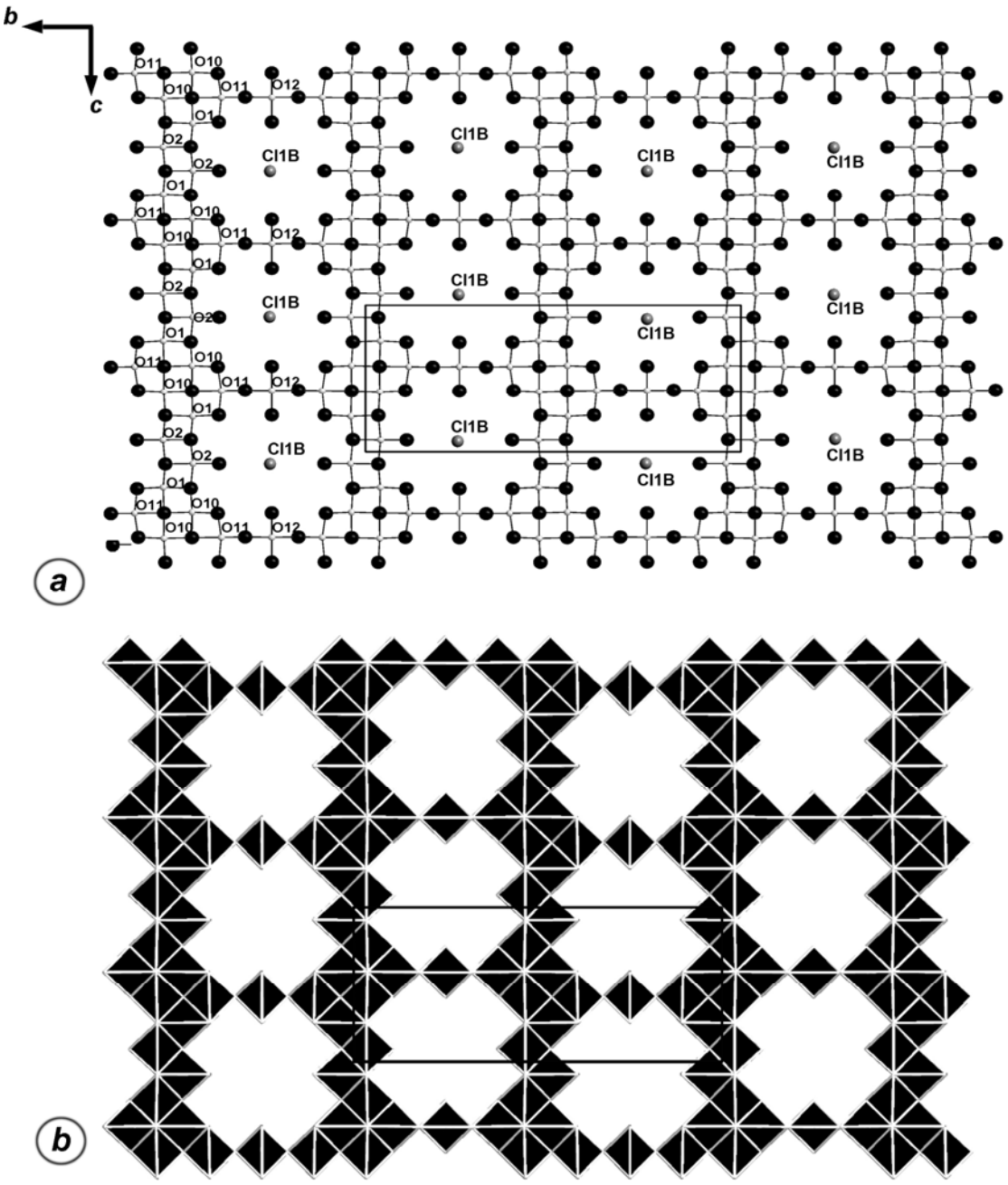
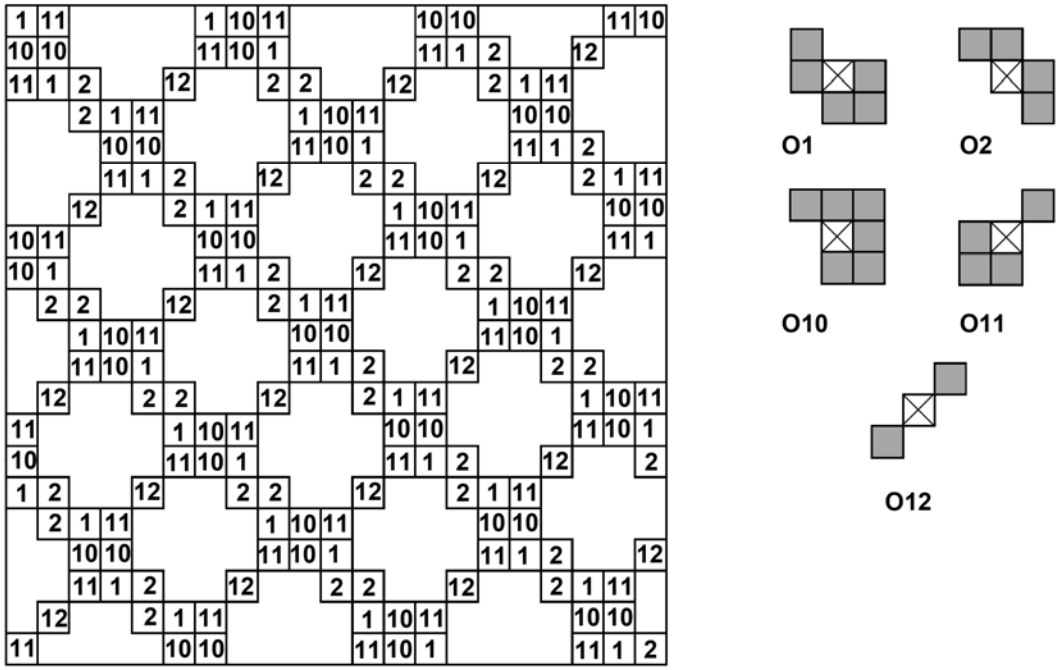


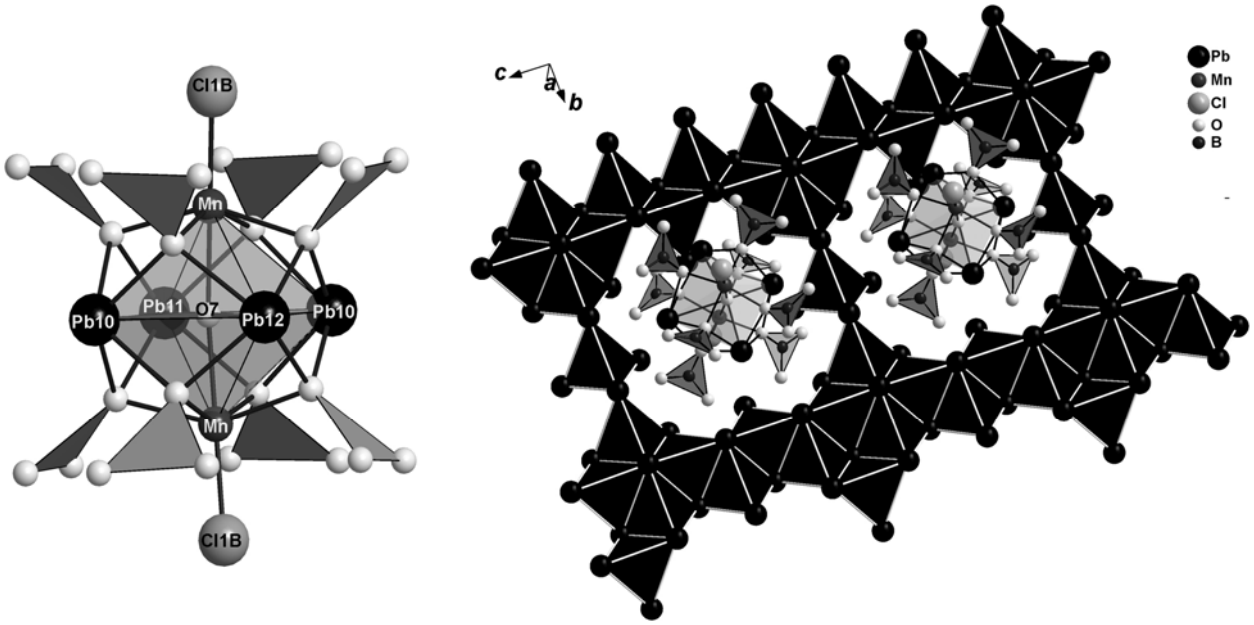
Figure 2. General projection of the $[O_{18}Pb_{32}]^{28+}$ layer along the *a* axis in the structure of vladkrivovichevite.



243

244

245 Figure 3. Topological structure of the $[O_{18}Pb_{32}]^{28+}$ layer in vladkrivovichevite, examined using
246 the method of square lattices (left). First coronas of the OPb_4 tetrahedra (central tetrahedra
247 are shown as crossed squares) are shown by grey shading (right).



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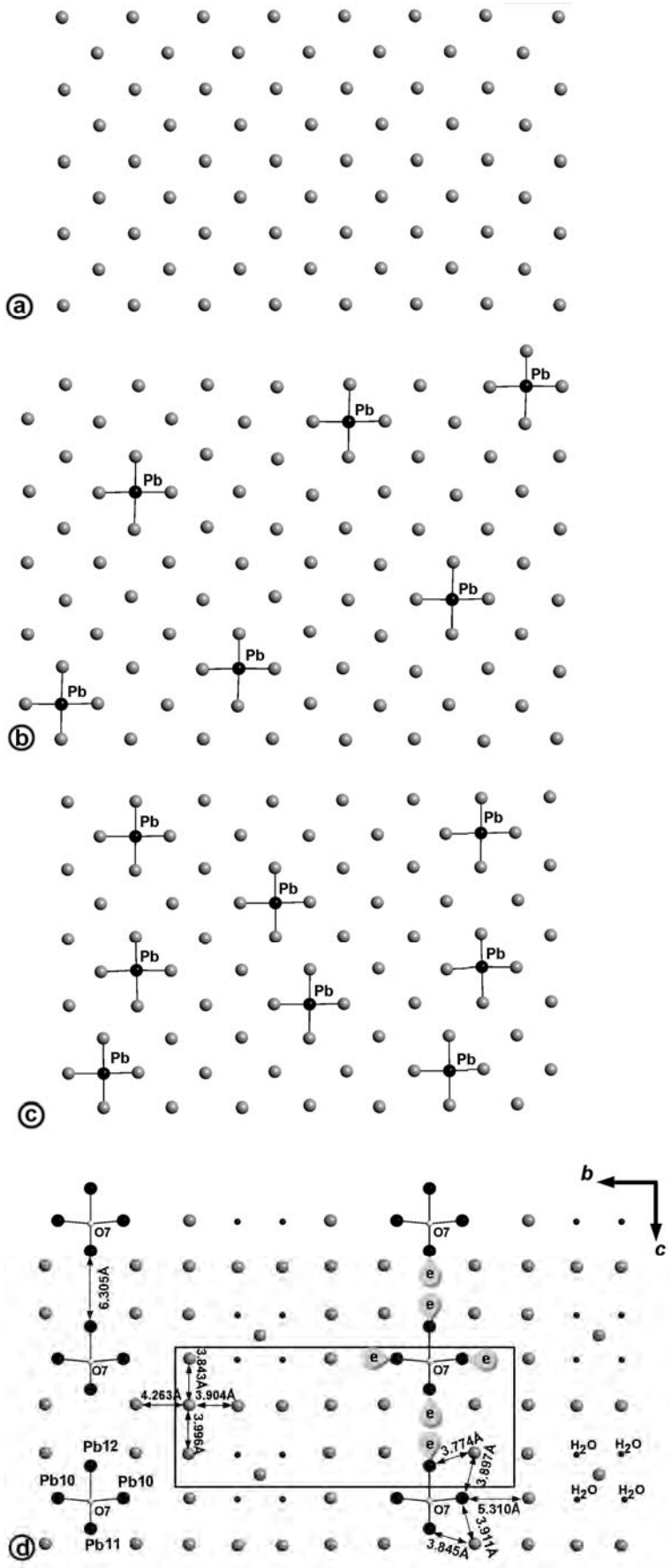
249 Figure 4. $[OPb_4Mn_2Cl_2(BO_3)_8]^{16-}$ oxocentered clusters (left) cause the presence of cross-like vacancies
250 in the $[O_{18}Pb_{32}]^{28+}$ layer (right) in the structure of vladkrivovichevite.


a
b
Pb
c
d
b
c
O7
6.305Å
e
3.843Å
4.263Å
3.904Å
3.996Å
3.774Å
3.897Å
5.310Å
3.911Å
3.845Å
Pb12
Pb10
Pb10
Pb11
H2O

251

Figure 5. The structures of halogen layers in lead oxyhalides. The defect-free Cl tetragonal layer in rumseyite (a). Additional Pb sites are located within the sheets of Cl^- anions in the structures of $Pb_{31}O_{22}Br_{10}Cl_8$ (b) and mereheadite (c). OPb_4 planar groups are intruded into the Cl-H_2O layer in vladkrivovichevite (lone pairs on Pb^{2+} cations are shown schematically as “e”).

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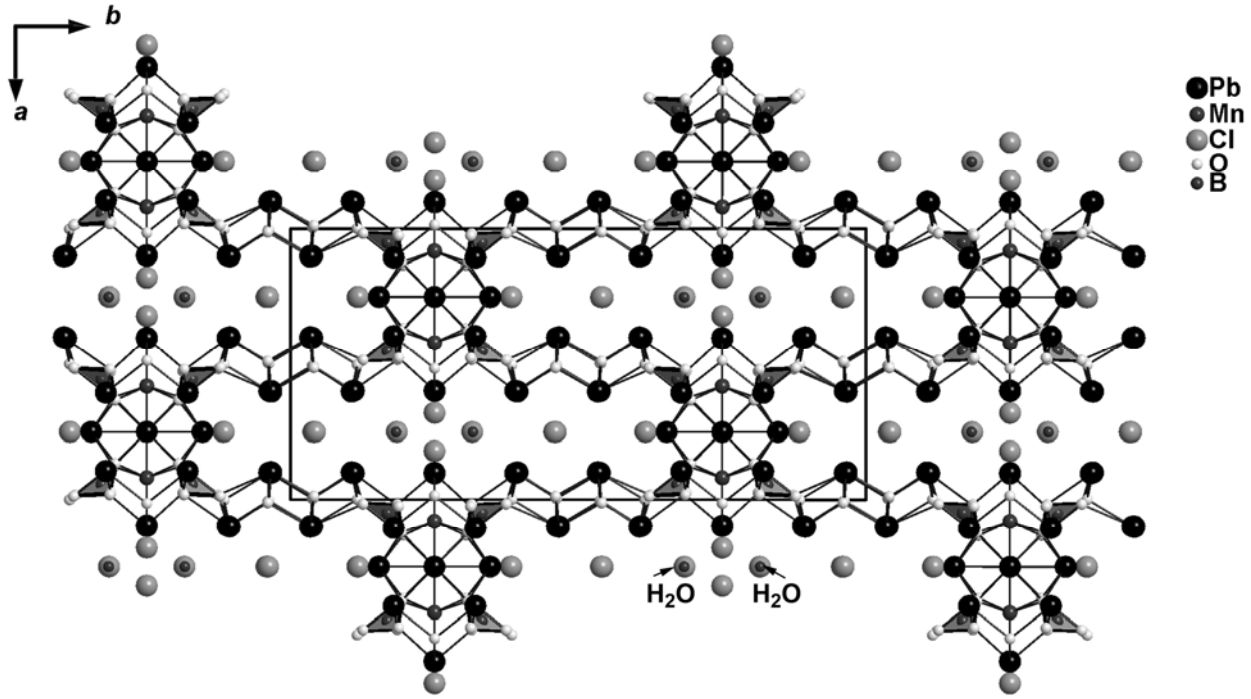


Figure 6. The structure of vladkrivovichevite along the *c* axis.

TABLE 1. CRYSTALLOGRAPHIC DATA AND REFINEMENT PARAMETERS FOR VLADKRIVOVICHEVITE

a (Å)	12.759(1)
b (Å)	27.169(4)
c (Å)	11.515(1)
V (Å^3)	3992.0(9)
Space group	*Pmmn*
Z	2
D_{calc}(g/cm^3)	7.380
μ (mm^{-1})	76.425
F_{000}	7280
Crystal size (mm)	0.10×0.09×0.10
Radiation	Mo*K*α
h_{min}, h_{max}	-18, 18
k_{min}, k_{max}	-37, 38
l_{min}, l_{max}	-16, 16
θ_{min}, θ_{max}	1.50, 30.61
Total Ref.	54194
Unique Ref.	6512
Unique $\|F_o\| \geq 4\sigma_F$	3801
R_1	0.048
wR_2	0.113
S	1.048

268 **Table 2**. Atomic coordinates, displacement parameters (Å^2), bond-valence sums* (BVS; valence units), and site-occupancy factors (SOFs) for
269 vladkrivovichevite
270

Atom	BVS	*x*	*y*	*z*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb1	1.74	0.60145(4)	-0.03386(1)	0.08290(6)	0.0061(1)	0.0014(2)	0.0063(2)	0.0106(2)	0.0001(2)	0.0011(3)	0.0018(1)
Pb2	1.75	0.40209(4)	-0.10963(1)	0.91911(6)	0.0080(1)	0.0050(2)	0.0066(2)	0.0125(3)	0.0002(3)	-0.0004(3)	-0.0025(1)
Pb3	1.72	0.59916(5)	-0.03388(1)	0.75152(5)	0.0063(1)	0.0021(3)	0.0061(3)	0.0109(3)	-0.0001(2)	0.0000(2)	0.0015(2)
Pb4	2.00	0.59906(5)	0.10875(2)	0.74916(5)	0.0064(1)	0.0034(2)	0.0047(2)	0.0113(3)	0.0003(2)	-0.0016(2)	-0.0016(2)
Pb5	1.76	0.59914(6)	¼	0.41533(8)	0.0081(1)	0.0046(3)	0.0071(3)	0.0129(4)	0	0.0033(4)	0
Pb6	1.78	0.59687(7)	¼	0.74897(7)	0.0077(1)	0.0041(4)	0.0060(4)	0.0129(4)	0	-0.0026(3)	0
Pb7	1.71	0.39464(4)	0.17892(1)	0.57936(5)	0.0077(1)	0.0026(2)	0.0041(2)	0.0165(3)	-0.0002(2)	0.0000(2)	0.0019(1)
Pb8	1.73	0.60101(4)	0.10589(1)	0.41831(6)	0.0070(1)	0.0041(2)	0.0052(2)	0.0119(3)	-0.0013(2)	0.0016(3)	-0.0015(1)
Pb9	1.67	0.59948(4)	-0.03728(1)	0.41594(6)	0.0062(1)	0.0018(2)	0.0050(2)	0.0119(3)	-0.0005(2)	0.0006(3)	0.0002(1)
Pb10	1.81	¼	0.15335(4)	0.0814(1)	0.0229(2)	0.0138(4)	0.0225(5)	0.0324(5)	0.0027(5)	0	0
Pb11	1.93	¼	¼	0.3013(1)	0.0194(3)	0.0153(7)	0.0255(8)	0.0173(6)	0	0	0
Pb12	1.74	¼	¼	-0.1511(1)	0.0192(3)	0.0113(6)	0.0242(8)	0.0220(7)	0	0	0
Mn	1.86	0.0809(3)	¼	0.0831(3)	0.0080(6)	0.019(1)	0.000(1)	0.004(1)	0	0	0
Cl1	0.70	¾	0.0408(2)	0.5857(6)	0.016(1)	0.014(3)	0.012(2)	0.024(3)	0.005(3)	0	0
Cl2	0.14	¼	0.1161(2)	0.4095(6)	0.021(1)	0.013(3)	0.017(3)	0.033(4)	-0.014(3)	0	0
Cl3	0.44	¾	0.1845(2)	0.5793(6)	0.019(1)	0.021(3)	0.009(2)	0.028(3)	0.000(3)	0	0
Cl4	0.34	¾	0.0393(2)	0.2387(6)	0.015(1)	0.019(3)	0.012(3)	0.015(3)	-0.001(2)	0	0
Cl5	0.16	¼	0.1170(2)	0.7540(5)	0.016(1)	0.007(2)	0.019(3)	0.024(3)	-0.002(3)	0	0
Cl6	0.26	¼	-0.0421(2)	0.0806(6)	0.018(1)	0.012(2)	0.018(3)	0.027(3)	0.008(3)	0	0
Cl7A#	-	-0.1794(11)	¼	0.087(1)	0.028(3)						
Cl7B#	-	-0.0977(12)	¼	0.059(1)	0.028(3)						
O1	2.01	0.5056(8)	0.0393(4)	0.758(1)	0.007(2)	0.005(5)	0.009(5)	0.009(5)	-0.006(4)	-0.003(4)	0.000(4)
O2	1.96	0.4878(8)	-0.0400(3)	0.919(1)	0.007(1)	0.006(5)	0.006(5)	0.009(5)	-0.002(5)	-0.001(5)	0.003(4)
O3	1.89	0.5123(11)	-0.1224(4)	0.759(1)	0.019(3)	0.032(8)	0.008(6)	0.018(6)	0.002(5)	0.002(6)	-0.001(5)
O4	2.09	0.4750(10)	0.1875(4)	0.780(1)	0.014(2)	0.022(7)	0.008(6)	0.014(6)	-0.002(4)	-0.001(5)	-0.004(5)
O5	2.15	0.4821(10)	0.1856(4)	0.384(1)	0.018(3)	0.027(7)	0.021(7)	0.007(5)	-0.009(5)	0.006(5)	-0.014(6)
O6	1.97	0.5169(9)	-0.1257(4)	0.073(1)	0.012(2)	0.013(5)	0.007(5)	0.017(6)	0.006(5)	-0.003(5)	0.002(4)
O7	1.75	¼	¼	0.104(3)	0.036(8)	0.029(17)	0.05(2)	0.02(1)	0	0	0
O8	2.03	0.6334(9)	-0.1952(4)	0.0479(9)	0.013(2)						
O9	1.97	0.1223(11)	0.3075(5)	0.212(1)	0.022(3)						
O10	1.75	0.5041(9)	0.0377(4)	0.411(1)	0.010$^{\$}$						
O11	2.03	0.5011(8)	0.1156(4)	0.581(1)	0.010$^{\$}$						
O12	1.96	0.5145(12)	¼	0.581(1)	0.010$^{\$}$						

OW1#	0.26	-¼	0.3162(14)	0.231(3)	0.025(9)
OW2#	0.36	-¼	0.3167(19)	-0.089(5)	0.057(9)
B1	2.94	0.4501(15)	0.1684(7)	0.282(1)	0.010[$]
B2	2.85	0.5554(15)	-0.1718(7)	0.115(1)	0.010[$]

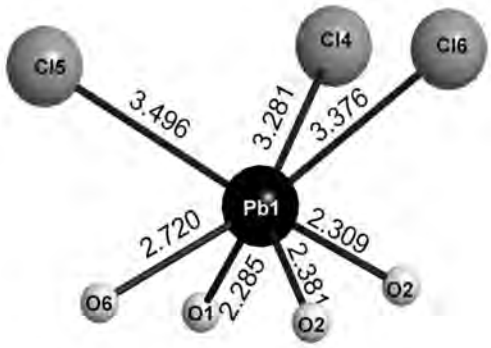
* calculated using bond-valence parameters from Krivovichev and Brown (2001) for the Pb^{2+}-O bonds and from Brown and Altermatt (1985) for other bonds

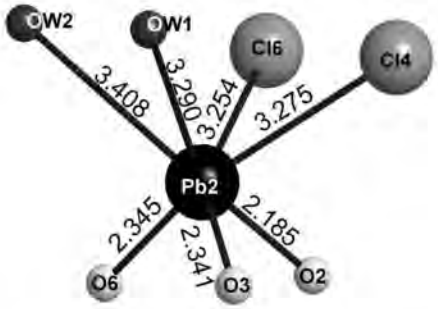
- S.O.F. = 0.50

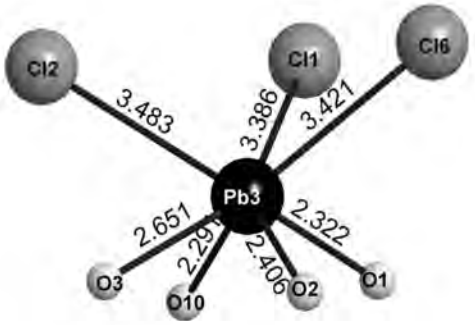
[$] fixed during refinement

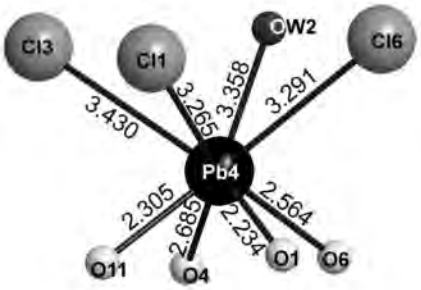
Table 3. Selected bond lengths (Å) in the structure of vladkrivovichevite

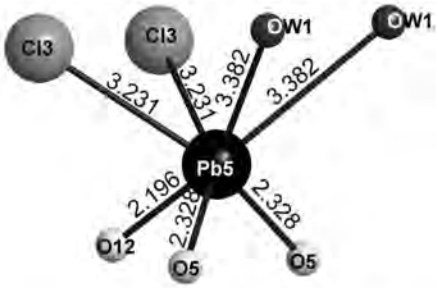
Pb1-O1	2.285(11)	Pb5-O12	2.196(16)	Pb10-O8	2.392(11)×2
Pb1-O2	2.309(9)	Pb5-O5	2.328(12)×2	Pb10-O9	2.460(13)×2
Pb1-O2	2.381(1)	Pb5-Cl3	3.231(5)×2	Pb10-O7	2.638(3)
Pb1-O6	2.720(11)	Pb5-OW1	3.38(3)×2		
Pb1-Cl4	3.280(5)			Pb11-O7	2.27(3)
Pb1-Cl6	3.376(5)	Pb6-O12	2.198(16)	Pb11-O9	2.480(13)×4
Pb1-Cl5	3.496(3)	Pb6-O4	2.331(11)×2		
		Pb6-OW2	3.25(4)×2	Pb12-O8	2.418(12)×4
Pb2-O2	2.185(10)	Pb6-Cl3	3.288(5)×2	Pb12-O7	2.94(3)
Pb2-O3	2.341(13)				
Pb2-O6	2.345(11)	Pb7-O11	2.191(10)	Mn-O7	2.171(5)
Pb2-Cl6	3.254(6)	Pb7-O12	2.463(9)	Mn-O9	2.218(13)×2
Pb2-Cl4	3.275(5)	Pb7-O5	2.513(11)	Mn-O8	2.223(11)×2
Pb2-OW1	3.29(3)	Pb7-O4	2.540(11)	Mn-Cl1B	2.295(16)
Pb2-OW2	3.41(4)	Pb7-Cl2	3.185(5)		
		Pb7-Cl5	3.206(5)	B1-O5	1.332(2)
Pb3-O10	2.291(11)			B1-O9	1.390(2)
Pb3-O1	2.322(10)	Pb8-O10	2.230(10)	B1-O3	1.419(3)
Pb3-O2	2.406(11)	Pb8-O11	2.289(11)		
Pb3-O3	2.651(12)	Pb8-O3	2.545(13)	B1-O4	1.337(2)
Pb3-Cl1	3.386(5)	Pb8-O5	2.671(14)	B1-O8	1.410(2)
Pb3-Cl6	3.421(6)	Pb8-Cl1	3.234(5)	B1-O6	1.428(1)
Pb3-Cl2	3.483(5)	Pb8-Cl4	3.342(5)		
		Pb8-Cl3	3.407(5)		
Pb4-O1	2.207(11)				
Pb4-O11	2.292(10)	Pb9-O10	2.373(10)		
Pb4-O6	2.388(9)	Pb9-O10	2.391(11)		
Pb4-O4	2.721(19)	Pb9-O1	2.417(11)		
Pb4-Cl1	2.798(13)	Pb9-O11	2.486(10)		
Pb4-Cl6	3.291(5)	Pb9-Cl1	3.465(5)		
Pb4-OW2	3.36(4)	Pb9-Cl4	3.490(5)		
Pb4-Cl3	3.430(5)	Pb9-Cl5	3.495(5)		
		Pb9-Cl2	3.510(5)		

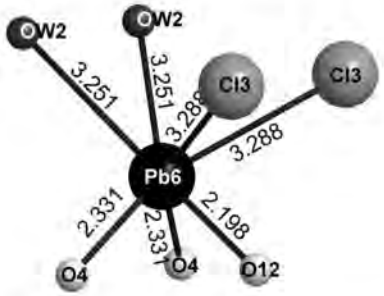

Cl5
Cl4
Cl6
3.496
3.281
3.376
Pb1
2.720
2.309
2.285
2.381
O6
O1
O2
O2

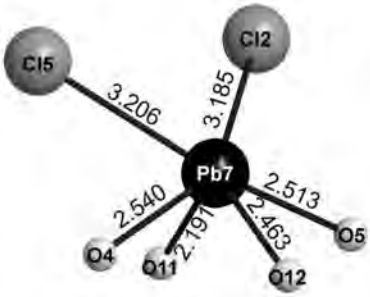

OW2
OW1
Cl6
Cl4
3.408
3.290
3.254
3.275
Pb2
2.345
2.341
2.185
O6
O3
O2

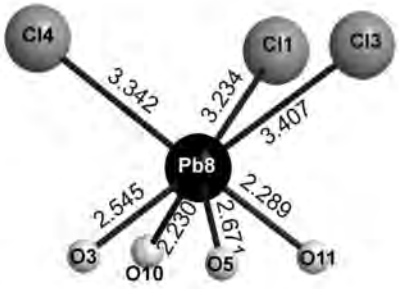

Cl2
Cl1
Cl6
3.483
3.386
3.421
Pb3
2.651
2.322
O3
O10
O2
O1

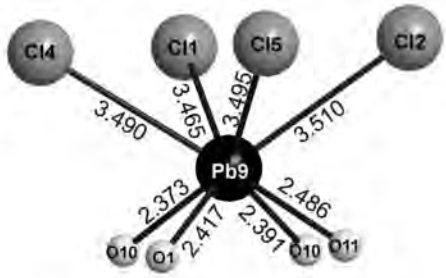

Cl3
Cl1
OW2
Cl6
3.430
3.265
3.358
3.291
Pb4
2.305
2.685
2.234
2.564
O11
O4
O1
O6

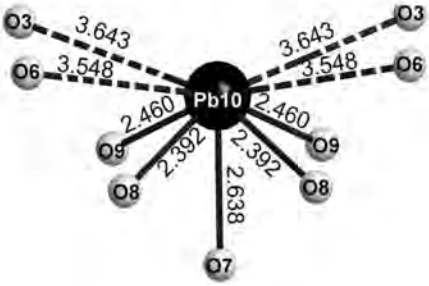

Cl3
Cl3
OW1
OW1
3.231
3.231
3.382
3.382
Pb5
2.196
2.328
2.328
O12
O5
O5


OW2
OW2
3.251
3.251
Cl3
Cl3
3.288
3.288
Pb6
2.331
2.331
2.198
O4
O4
O12

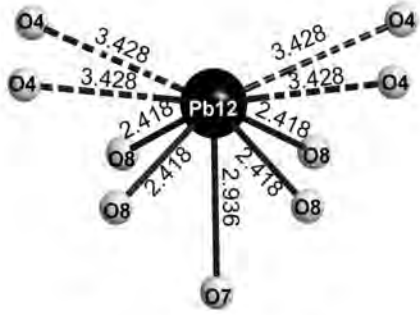

Cl5
Cl2
3.206
3.185
Pb7
2.540
2.513
2.191
2.463
O4
O11
O5
O12

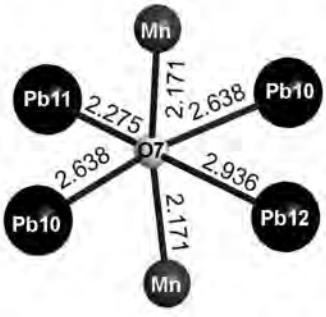

Cl4
Cl1
Cl3
3.342
3.234
3.407
Pb8
2.545
2.289
2.230
2.671
O3
O10
O5
O11

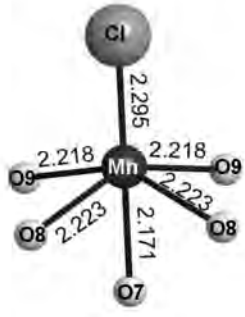

Cl4
Cl1
Cl5
Cl2
3.490
3.465
3.495
3.510
Pb9
2.373
2.486
2.417
2.391
O10
O1
O10
O11

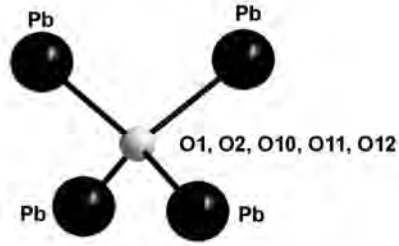

O3
3.643
3.643
O3
O6
3.548
3.548
O6
Pb10
2.460
2.460
O9
O9
2.392
2.392
O8
O8
2.638
O7

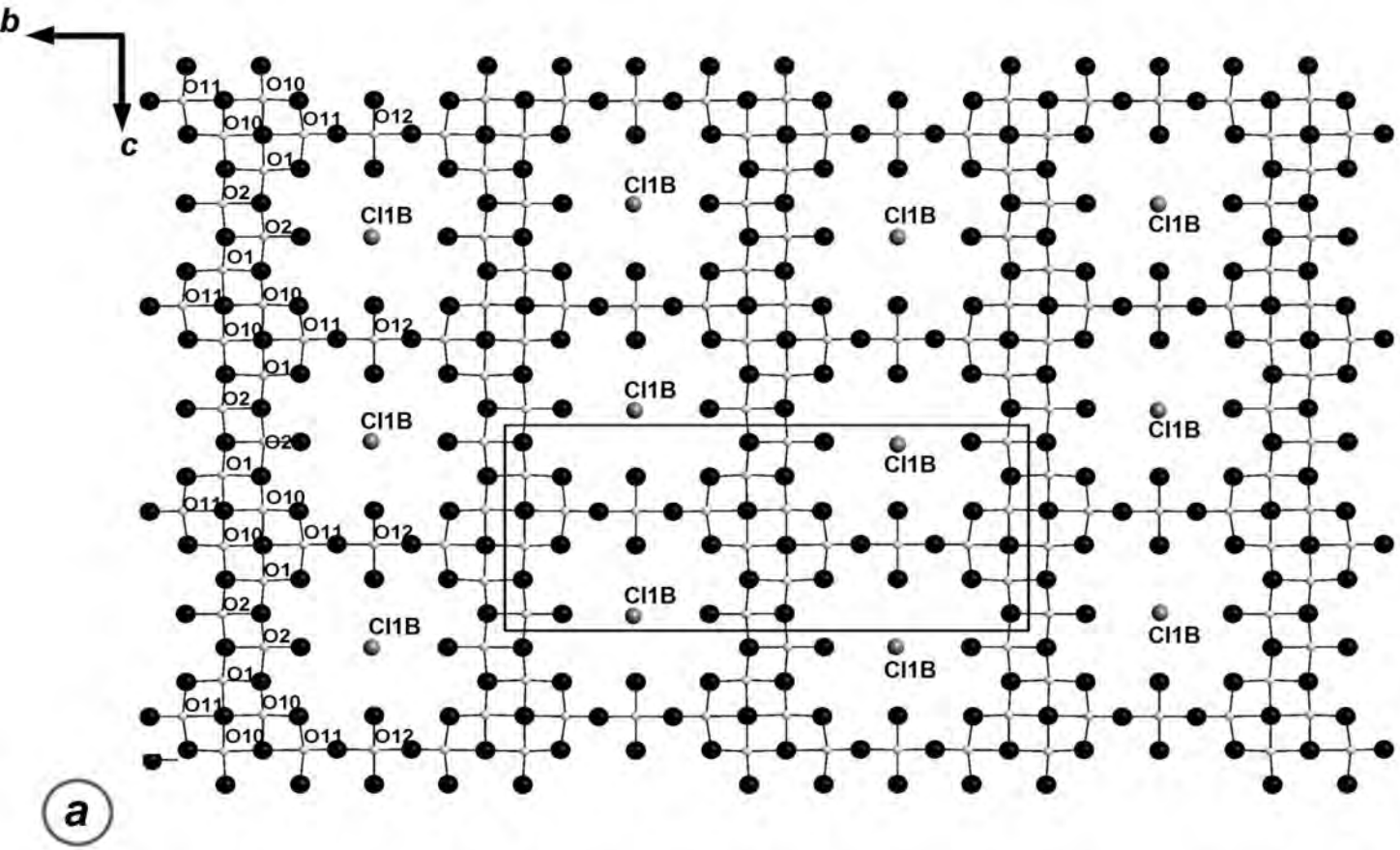

O5
3.571
3.571
O5
O5
3.571
3.571
O5
Pb11
2.480
2.480
O9
O9
2.480
2.480
O9
O9
2.275
O7

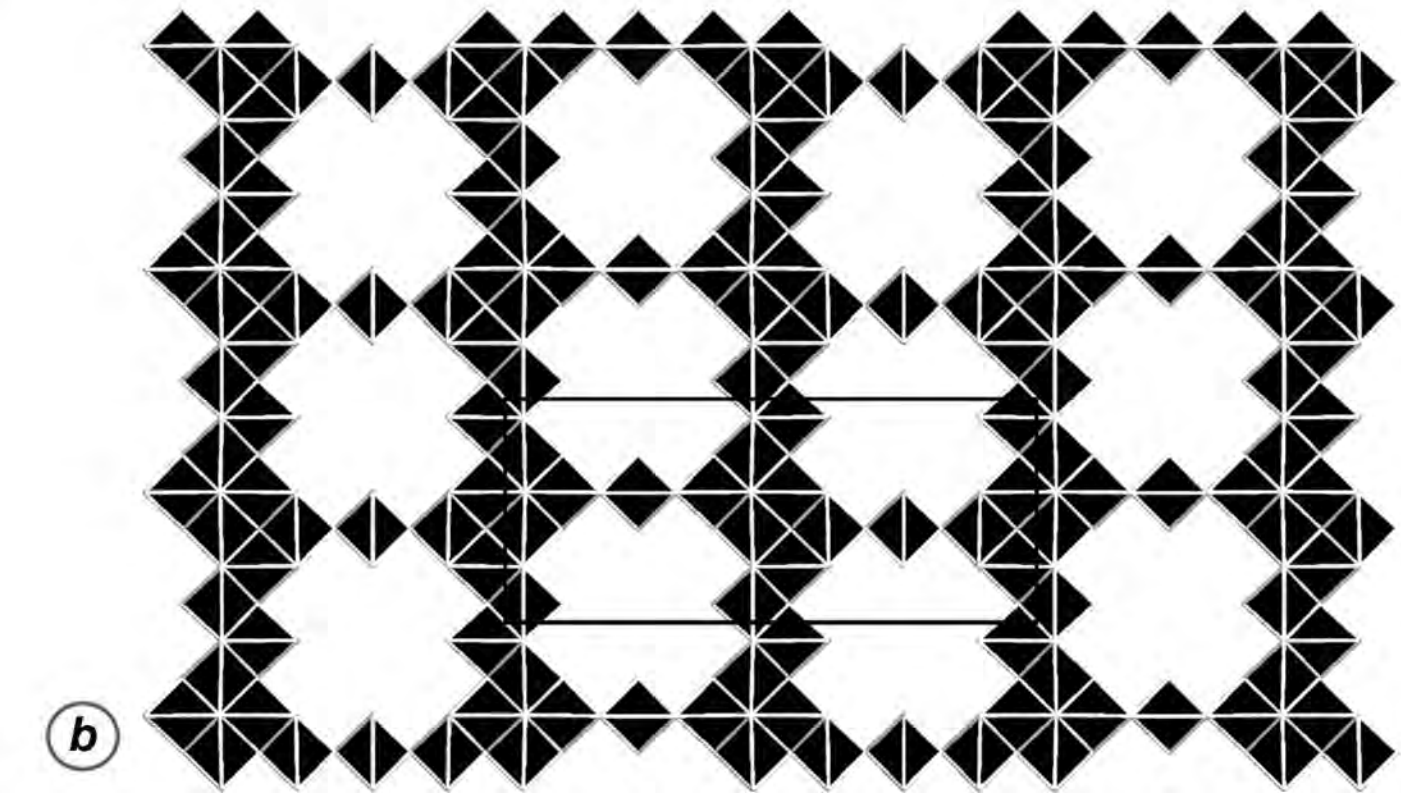

O4
3.428
3.428
O4
O4
3.428
3.428
O4
Pb12
2.418
2.418
O8
O8
2.418
2.418
O8
O8
2.936
O7

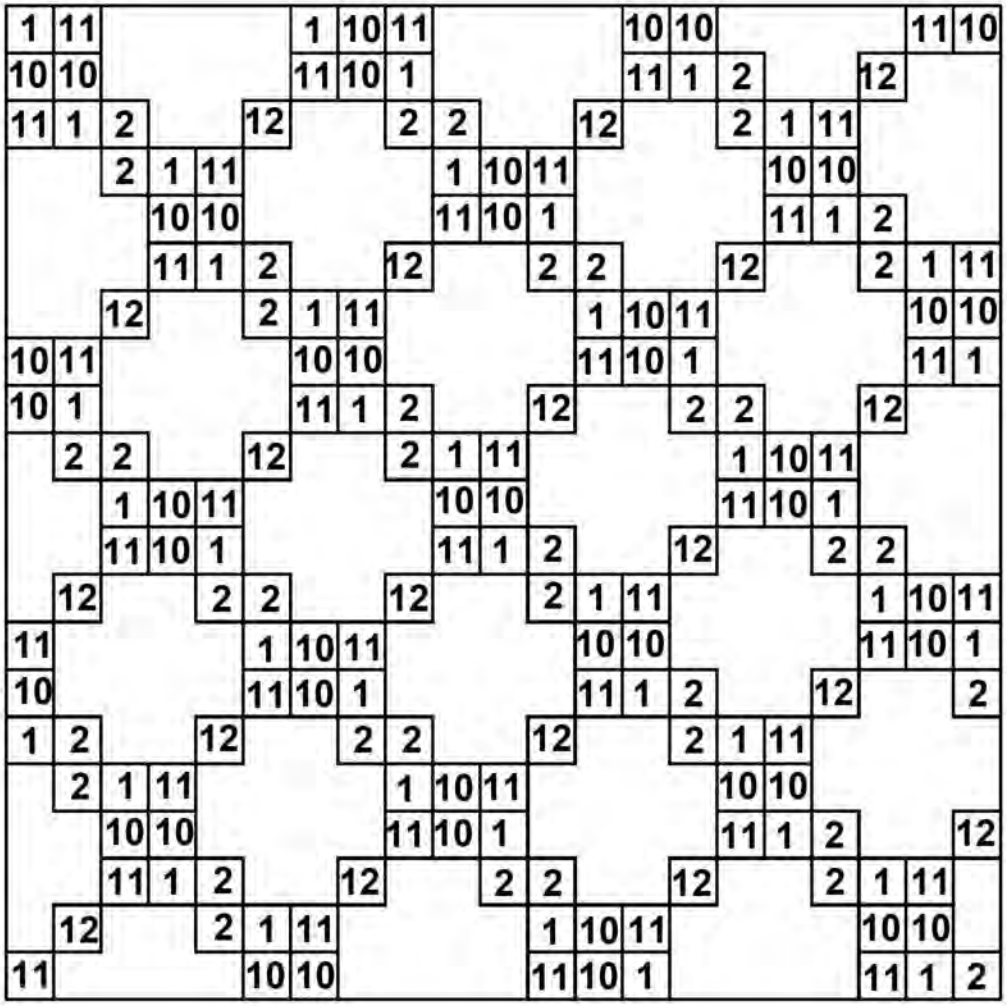

Mn
Pb11
2.275
2.171
2.638
Pb10
O7
2.638
2.936
Pb10
Pb12
2.171
Mn

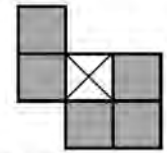

Cl
2.295
2.218
2.218
O9
Mn
O9
2.223
2.223
O8
O8
2.171
O7


Pb
Pb
O1, O2, O10, O11, O12
Pb
Pb

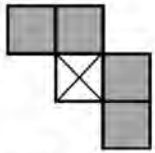

b
c
O11
O10
O12
O1
O2
Cl1B
a


b

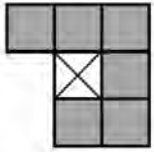




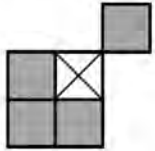
O1



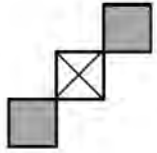
O2



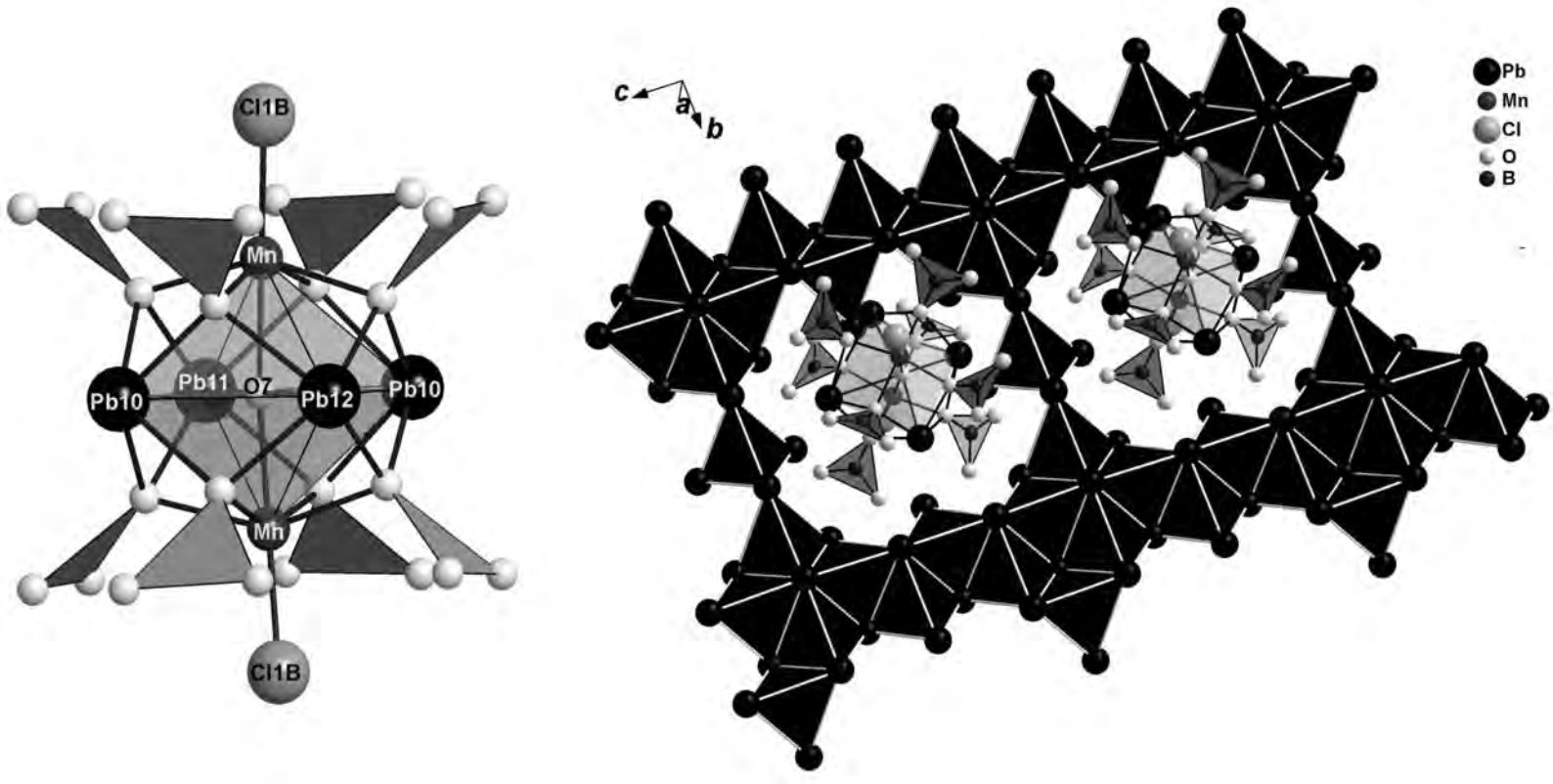
O10

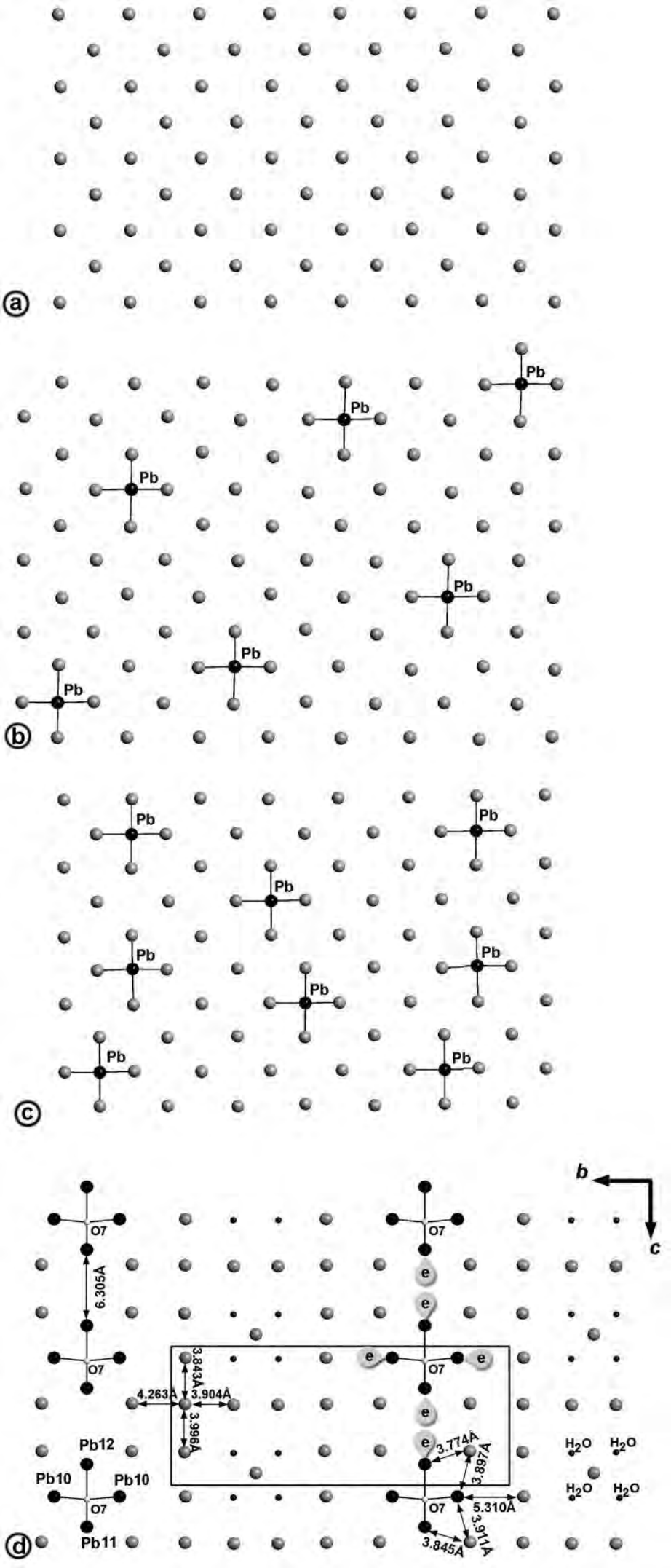


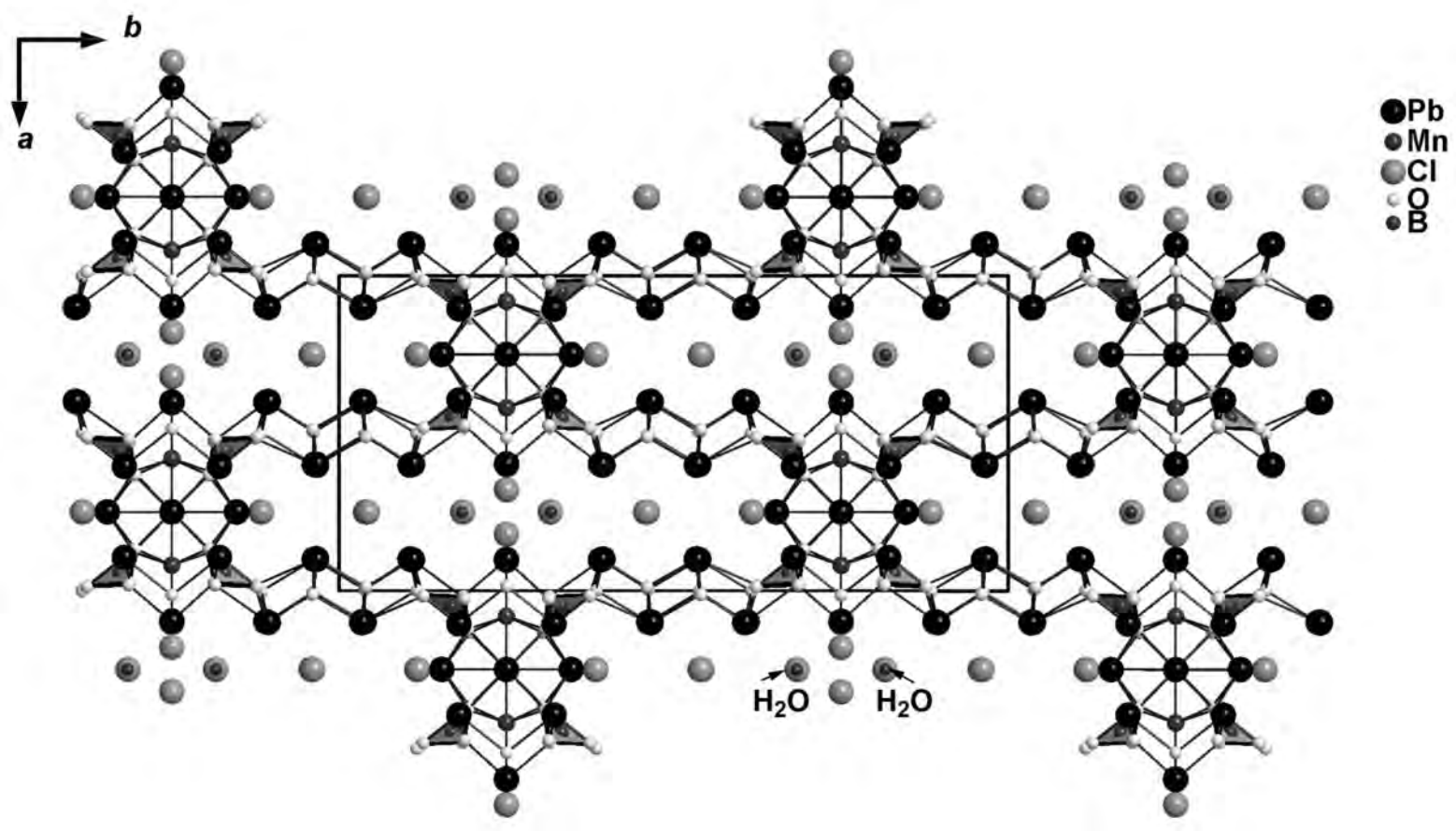
O11



O12


Cl1B
Mn
Pb10
Pb11
O7
Pb12
Pb10
Mn
Cl1B
c
a
b
Pb
Mn
Cl
O
B


a
Pb
b
Pb
c
O7
6.305Å
3.843Å
4.263Å
3.904Å
3.996Å
Pb12
Pb10
Pb10
O7
Pb11
e
3.774Å
3.897Å
5.310Å
3.911Å
3.845Å
H2O
b
c
d


b
a
Pb
Mn
Cl
O
B
H2O
H2O