

THE CRYSTAL STRUCTURE OF VASILYEVITE, $(\text{Hg}_2)^{2+}_{10} \text{O}_6 \text{I}_3 (\text{Br}, \text{Cl})_3 (\text{CO}_3)$

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ABSTRACT

The crystal structure of vasilyevite, ideally $(\text{Hg}_2)^{2+}_{10} \text{O}_6 \text{I}_3 \text{Br}_2 \text{Cl} (\text{CO}_3)$, triclinic, a 9.344(2), b 10.653(2), c 18.265(4) Å, α 93.262(5), β 90.548(4), γ 115.422(4)°, V 1638.3(9) Å³, space group $P\bar{1}$, $Z = 2$, $D(\text{calc}) = 9.57 \text{ g cm}^{-3}$, has been solved by direct methods and refined to an R_1 index of 8.9% for 3400 unique reflections measured with MoK α X-radiation on a four-circle diffractometer equipped with a CCD detector. There are twenty unique Hg sites that are associated as pairs of sites with pair separations of 2.533 to 2.593 Å; this association of Hg atoms is typical of Hg⁺ cations pairing to form $(\text{Hg}_2)^{2+}$ dimers. Each $(\text{Hg}_2)^{2+}$ dimer is extended at each end by bonding to axial O atoms with Hg–O distances in the range 2.00 to 2.32 Å, with one dimer showing a terminal I atom with a very short Hg–I distance of 2.75 Å. These $[\phi\text{--Hg--Hg--}\phi]$ tetramers form near-linear arrangements that are surrounded by several meridional anions, O atoms at distances from 2.44 to 2.85 Å, mixed (Cl,Br) sites at distances from 2.89 to 3.78 Å, and I atoms at distances from 3.11 to 4.02 Å. Bonds to axial anions make angles of <23° with the Hg–Hg axis, involving the Hg atoms to which they are bonded; bonds to meridional anions make angles of <31° with the perpendicular to the Hg–Hg axis, involving the Hg atoms to which they are bonded. There is one site, labeled C,S, that is surrounded by a triangle of O atoms at a mean distance of 1.25 Å; the presence of S in the chemical composition and the refined scattering at the C,S site indicates that this site is occupied by both (CO_3) and S^{2-} in the ratio 0.85 : 0.15. There are three distinct I sites occupied solely by I[−] anions that are [8]- or [9]-coordinated by Hg cations. There are three X sites that are occupied by 0.73 Br + 0.27 Cl, 0.69 Br + 0.31 Cl, and 0.22 Br + 0.78 Cl and are [7]- and [8]-coordinated by Hg cations. The fundamental building block of the vasilyevite structure is the strongly bonded $[\phi\text{--Hg--Hg--}\phi]$ tetramer. These groups link together at their anion vertices to form a complex interpenetrating framework of two discrete three- and four-connected nets. The halogen atoms and the (CO_3) and S^{2-} anions occur in the interstices of the two nets and serve to stabilize the nets *via* additional weak linkages to Hg atoms.

Keywords: vasilyevite, crystal structure, Hg–Hg dumbbells, electron-microprobe analysis, mercurous oxide iodide bromide-chloride carbonate mineral.

SOMMAIRE

Nous avons résolu la structure cristalline de la vasilyevite, dont la composition idéale est $(\text{Hg}_2)^{2+}_{10} \text{O}_6 \text{I}_3 \text{Br}_2 \text{Cl} (\text{CO}_3)$, triclinique, a 9.344(2), b 10.653(2), c 18.265(4) Å, α 93.262(5), β 90.548(4), γ 115.422(4)°, V 1638.3(9) Å³, groupe spatial $P\bar{1}$, $Z = 2$, $D(\text{calculée}) = 9.57 \text{ g cm}^{-3}$, par méthodes directes, et nous l'avons affinée jusqu'à un résidu R_1 de 8.9% avec 3400 réflexions uniques mesurées avec rayonnement MoK α sur un diffractomètre à quatre cercles muni d'un détecteur de type CCD. Il y a vingt sites Hg distincts qui sont associés en paires, avec une séparation entre membres d'une paire de 2.533 à 2.593 Å. Cette association est typique d'atomes de Hg monovalents en paires, formant un dimère, $(\text{Hg}_2)^{2+}$. Chacun de ces dimères est allongé à chaque bout par liaisons à des atomes d'oxygène axiaux, avec des distances Hg–O dans l'intervalle de 2.00 à 2.32 Å, un de ces dimères montrant un atome de I terminal avec une liaison Hg–I très courte de 2.75 Å. Ces tétramères $[\phi\text{--Hg--Hg--}\phi]$ forment des agencements quasi-linéaires entourés de plusieurs anions méridionaux, des atomes de O situés entre 2.44 et 2.85 Å, des sites mixtes (Cl,Br) à une distance entre 2.89 et 3.78 Å, et des atomes de I à une distance entre 3.11 et 4.02 Å. Les liaisons aux anions axiaux définissent un angle de <23° avec l'axe Hg–Hg, impliquant les atomes Hg auxquels ils sont liés; les liaisons avec les anions méridionaux font un angle de <31° avec la perpendiculaire à l'axe Hg–Hg, impliquant les atomes de Hg auxquels ils sont liés. Il y a un site nommé C,S, qui est entouré d'un triangle d'atomes O à une distance moyenne de 1.25 Å; la présence de S dans la composition chimique et le pouvoir de dispersion affiné du site C,S indiquent que ce site est occupé à la fois par le (CO_3) et le S^{2-} dans un rapport 0.85 : 0.15. Il y a trois sites I distincts remplis uniquement d'anions I[−], qui ont une coordinence de [8] ou [9] avec les cations Hg. Il y a trois sites X qui sont remplis par 0.73 Br + 0.27 Cl, 0.69 Br + 0.31 Cl, et 0.22 Br + 0.78 Cl, et qui ont une coordinence [7] et [8] aux cations Hg. Le bloc structural fondamental de la structure de la vasilyevite est le tétramère $[\phi\text{--Hg--Hg--}\phi]$, à fortes liaisons. Ces groupes sont liés ensemble à leurs extrémités anioniques pour former une trame complexe interpénétrante de deux réseaux séparés à trois ou quatre connexions. Les atomes d'halogènes et les anions (CO_3) et S^{2-} sont situés dans les interstices des deux réseaux et servent à les stabiliser grâce à de faibles liaisons additionnelles avec des atomes Hg.

(Traduit par la Rédaction)

Mots-clés: vasilyevite, structure cristalline, Hg–Hg en forme d'haltères, analyses à la microsonde électronique, minéral, oxyde mercureux à iodure, bromure, chlorure et carbonate.

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INTRODUCTION

Vasilyevite is a new mercury oxycarbonate mineral containing essential iodine, bromine and chlorine, described recently by Roberts *et al.* (2003) from the claim of the Clear Creek mercury mine, New Idria district, San Benito County, California, U.S.A. (Dunning *et al.* 2004). Three other mercury carbonate minerals, peterbaylissite, $\text{Hg}^{1+}_3(\text{CO}_3)(\text{OH})(\text{H}_2\text{O})_2$ (Roberts *et al.* 1995), clearcreekite, $\text{Hg}^{1+}_3(\text{CO}_3)(\text{OH})(\text{H}_2\text{O})_2$ (Roberts *et al.* 2001), and szymańskiite, $\text{Hg}^{1+}_{16}(\text{Ni,Mg})_6(\text{CO}_3)_{12}(\text{OH})_{12}(\text{H}_2\text{O})^{1+}_8(\text{H}_2\text{O})_3$ (Roberts *et al.* 1990, Szymański & Roberts 1990), have been described from this locality. Mercury minerals can be particularly difficult to characterize with regard to their correct chemical formula because of (1) the uncertainties in the valence state(s) of mercury, and (2) the difficulty in accurately analyzing the sample for any additional elements in the structure in the presence of such a heavy element. Crystal-structure analysis can play an important role in (1) deriving the valence states of mercury, (2) in detecting light elements (relative to mercury) in the structure, and (3) evaluating the degree of anion order within the structure. Here, we report on the crystal structure of vasilyevite, with its particularly complex atomic arrangement.

EXPERIMENTAL

An irregular fragment (Table 1) was cut from the crystal used for the precession study of Roberts *et al.* (2003) and mounted on a Bruker four-circle diffractometer equipped with a 1K CCD detector at a crystal-to-detector distance of 4 cm. In excess of a hemisphere of intensity data was collected to $60^\circ 2\theta$ using a frame width of 0.3° and frame time of 120 s (Cooper & Hawthorne 2001). Frame sequences uniformly distributed through the entire dataset were sampled to give intense reflections (~ 1000) for least-squares refinement of the cell parameters and orientation matrix. The resulting orientation matrix was then used for three-

dimensional integration of the intensity data, and standard corrections (for Lorentz, polarization and background effects) were applied. The final unit-cell parameters (Table 1) are based on least-squares refinement of 3,229 reflections ($>10\sigma I$). The SADABS program was then used to apply an empirical absorption correction to all 27,768 reflections. Identical reflections (at different Ψ angles) were combined to give a total of 16,896 reflections in the Ewald sphere. In the space group $P\bar{1}$, this gives 9,452 unique data with a Laue ($\bar{1}$) merging of 3.7%.

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms were taken from the *International Tables for X-ray Crystallography* (1992); R indices are of the form in Table 1, and are expressed as percentages. The Bruker SHELXTL PLUS (PC version) system of programs was used for this work. The structure was solved by direct methods in space group $P\bar{1}$. Twenty Hg sites were identified, in which all Hg atoms are spatially paired, with an Hg–Hg separation of ~ 2.5 Å, a characteristic feature of the mercurous ion $[\text{Hg}_2]^{2+}$. Successive cycles of difference-Fourier synthesis and refinement gave the halogen and oxygen [O(1) $\rightarrow$ O(6)] sites. Of the six halogen sites, three had site occupancies consistent with occupancy by I and are denoted as $I(1) \rightarrow I(3)$; the other three sites are denoted as $X(1) \rightarrow X(3)$, and have scattering values between that of Cl and that of Br; site-occupancy refinement gave the following compositions: $X(1) = 0.73 \text{ Br} + 0.27 \text{ Cl}$; $X(2) = 0.69 \text{ Br} + 0.31 \text{ Cl}$; $X(3) = 0.22 \text{ Br} + 0.78 \text{ Cl}$. At this stage, the formula derived from the structure $[(\text{Hg}_2)^{2+}_{10} \text{O}_6 (\text{I,Br,Cl})_6]$ is deficient by two negative charges. Careful examination of the residual electron-density contained in the difference-Fourier map revealed four weak peaks in close proximity to each other; their relative positions are consistent with a planar triangular group, and this scattering was incorporated into the refinement as a carbonate group. During refinement, two unusual features of the carbonate group became apparent: (1) scattering at the C site was greater than 6 electrons, and (2) scattering at the associated O sites [O(7) $\rightarrow$ O(9)] was less than 8 electrons. This result suggested a possible isomorphous substitution involving C and another “heavier” element at the C site. The simplest homovalent solution would involve coupled substitution between $(\text{CO}_3)^{2-}$ and S^{2-} or $(\text{SO}_4)^{2-}$, providing the necessary two negative charges required for electro-neutrality. The occupancy of the C site was therefore allowed to refine in terms of coupled C and S occupancies, and the three O atoms associated with the (CO_3) group had their occupancies constrained to be equal to the C occupancy factor; this model gave 0.80(5) $(\text{CO}_3) + 0.20(5) \text{ S}$. We did not observe any peaks in the difference-Fourier map that were consistent with the O atoms of an (SO_4) group. However, given the amount of S in the structure, each O atom would correspond to $\sim 1 e$

TABLE 1. MISCELLANEOUS INFORMATION FOR VASILYEVITE

a (Å)	9.344(2)	crystal size (mm)	$0.03 \times 0.08 \times 0.10$
b	10.653(2)	radiation	MoK α /Gr
c	18.265(4)	No. of reflections	27768
α ($^\circ$)	93.262(5)	No. in Ewald sphere	16896
β	90.548(4)	No. unique reflections	9452
γ	115.422(4)	No. $ F_o > 5\sigma$	3400
V (Å 3)	1638.3(9)	R_{merge} %	3.7
Sp. Gr.	$P\bar{1}$	R_{obs} %	8.9
Z	2	wR_{obs} %	10.5
μ (mm $^{-1}$)	98.2		
D_{calc} (g/cm 3)	9.57		
Cell content	$2 [(\text{Hg}_2)^{2+}_{10} \text{O}_6 \text{I}_3 (\text{Br}_{1.6} \text{Cl}_{1.4})_{\Sigma=3} \{(\text{CO}_3)_{0.8} \text{S}^{2-}_{0.2}\}_{\Sigma=1}]$		
$R = \Sigma(F_o - F_c) / \Sigma F_o $			
$wR = [\Sigma w(F_o - F_c)^2 / \Sigma F_o^2]^{1/2}$, $w = 1$			

TABLE 2. FINAL ATOM PARAMETERS FOR VASILYEVITE

	x	y	z	U
Hg(1)	0.4508(5)	0.3267(4)	0.4759(2)	0.027(2)
Hg(2)	0.2648(5)	0.1059(4)	0.4020(2)	0.028(2)
Hg(3)	0.5351(5)	0.2824(4)	0.7804(2)	0.025(2)
Hg(4)	0.5985(5)	0.4122(5)	0.6605(2)	0.028(2)
Hg(5)	0.8273(5)	-0.1104(4)	0.9045(2)	0.023(1)
Hg(6)	0.1287(5)	0.0098(4)	0.2213(2)	0.026(2)
Hg(7)	0.9750(5)	0.2052(4)	0.9605(2)	0.025(2)
Hg(8)	0.7029(5)	0.1959(4)	0.9281(2)	0.026(2)
Hg(9)	0.2223(5)	0.0437(4)	0.9077(2)	0.026(2)
Hg(10)	0.2081(5)	-0.1672(4)	0.8309(2)	0.030(2)
Hg(11)	0.8386(5)	0.2521(4)	0.6604(3)	0.026(2)
Hg(12)	0.0431(5)	0.4739(5)	0.7262(3)	0.035(2)
Hg(13)	0.6969(6)	0.1718(5)	0.4778(2)	0.031(2)
Hg(14)	0.6993(5)	0.2321(5)	0.3448(2)	0.030(2)
Hg(15)	0.5510(5)	0.3552(5)	0.2057(3)	0.032(2)
Hg(16)	0.6970(6)	0.6043(5)	0.8167(3)	0.041(2)
Hg(17)	-0.1367(5)	-0.0950(5)	0.3689(3)	0.029(2)
Hg(18)	0.4120(5)	0.1058(5)	0.6110(3)	0.032(2)
Hg(19)	0.4805(5)	0.3880(4)	0.9638(2)	0.028(2)
Hg(20)	0.8710(5)	0.5119(5)	0.5151(3)	0.028(2)
Cl/S	0.549(5)	0.997(5)	0.745(3)	0.004(6)
O(1)	0.916(7)	0.062(6)	0.670(3)	0.009(4)*
O(2)	-0.194(6)	-0.193(6)	0.015(3)	0.009(4)*
O(3)	0.506(7)	0.236(6)	0.892(3)	0.009(4)*
O(4)	0.620(6)	0.096(6)	0.590(3)	0.009(4)*
O(5)	0.618(6)	0.450(6)	0.550(3)	0.009(4)*
O(6)	0.752(7)	0.311(6)	0.241(3)	0.009(4)*
O(7)	0.326(7)	-0.107(6)	0.219(3)	0.004(6)**
O(8)	0.427(7)	0.009(6)	0.742(3)	0.004(6)**
O(9)	0.430(7)	0.102(6)	0.272(3)	0.004(6)**
I(1)	0.078(1)	0.2800(8)	0.3117(4)	0.034(2)
I(2)	0.085(1)	0.4491(8)	0.1046(4)	0.034(2)
I(3)	0.195(1)	0.3017(9)	0.8173(5)	0.040(2)
X(1)	0.483(1)	0.838(1)	0.9311(7)	0.025(4)
X(2)	0.315(2)	0.469(1)	0.6301(8)	0.035(5)
X(3)	0.003(2)	0.175(2)	0.505(1)	0.026(7)

*, ** constrained to be equal during refinement.

TABLE 3. ANISOTROPIC DISPLACEMENT PARAMETERS FOR Hg ATOMS IN VASILYEVITE

	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₂	U ₁₃
Hg(1)	0.027(2)	0.022(2)	0.024(2)	-0.008(2)	-0.004(2)	0.005(2)
Hg(2)	0.027(2)	0.022(2)	0.024(2)	-0.007(2)	-0.004(2)	0.001(2)
Hg(3)	0.029(2)	0.020(2)	0.022(2)	-0.000(2)	0.004(2)	0.007(2)
Hg(4)	0.033(2)	0.033(2)	0.015(2)	-0.003(2)	0.002(2)	0.012(2)
Hg(5)	0.025(2)	0.021(2)	0.018(2)	-0.002(2)	-0.001(2)	0.005(2)
Hg(6)	0.026(2)	0.034(2)	0.015(2)	0.006(2)	0.002(2)	0.009(2)
Hg(7)	0.019(2)	0.026(2)	0.030(2)	-0.002(2)	0.000(2)	0.011(2)
Hg(8)	0.016(2)	0.028(2)	0.033(2)	0.002(2)	0.001(2)	0.010(2)
Hg(9)	0.026(2)	0.023(2)	0.026(2)	-0.008(2)	0.000(2)	0.009(2)
Hg(10)	0.029(2)	0.028(2)	0.030(2)	-0.011(2)	0.003(2)	0.010(2)
Hg(11)	0.020(2)	0.018(2)	0.037(2)	-0.004(2)	0.001(2)	0.004(2)
Hg(12)	0.024(2)	0.028(2)	0.044(3)	-0.007(2)	-0.008(2)	0.004(2)
Hg(13)	0.035(2)	0.031(2)	0.025(2)	0.001(2)	-0.000(2)	0.013(2)
Hg(14)	0.034(2)	0.031(2)	0.023(2)	-0.000(2)	0.000(2)	0.011(2)
Hg(15)	0.023(2)	0.035(2)	0.040(3)	0.002(2)	-0.003(2)	0.013(2)
Hg(16)	0.032(2)	0.029(2)	0.060(3)	-0.013(2)	-0.015(2)	0.014(2)
Hg(17)	0.016(2)	0.035(2)	0.034(2)	-0.003(2)	0.001(2)	0.009(2)
Hg(18)	0.024(2)	0.032(2)	0.039(3)	-0.003(2)	0.003(2)	0.011(2)
Hg(19)	0.034(2)	0.022(2)	0.027(2)	-0.006(2)	0.003(2)	0.011(2)
Hg(20)	0.018(2)	0.034(2)	0.032(2)	-0.002(2)	0.005(2)	0.011(2)

scattering power, a value that lies within the background fluctuations. Hence we cannot distinguish between S^{2-} and $(SO_4)^{2-}$ from the structure solution and refinement. Full-matrix least-squares refinement of all variable parameters for a model involving anisotropic displacement of the Hg atoms and isotropic displacement of the remaining atoms converged to an R index of 8.9% for 3400 observed ($|Fo| > 5\sigma F$) unique reflections. The high R value is the result of an inadequate absorption-correction owing to the very irregular shape and extreme X-ray absorption ($\mu = 98.2 \text{ mm}^{-1}$) by the crystal. Final atom parameters are listed in Tables 2 and 3, selected interatomic distances and angles are given in Table 4, a bond-valence analysis is given in Table 5, and results of a chemical analysis is given in Table 6. A table of structures factors is available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2, Canada.

STRUCTURE DESCRIPTION

Mercurous ions $[Hg_2]^{2+}$

There are 20 Hg sites that form 11 unique $[Hg-Hg]^{2+}$ dimers (Fig. 1), with Hg-Hg separations between 2.533 and 2.593 Å. The $[Hg-Hg]^{2+}$ dimers have strong covalent bonds to O atoms at each end of the dimer, except for Hg(16), which forms a strong bond to an I atom at the I(2) site (lower left of Fig. 1). These approximately linear $[\phi-Hg-Hg-\phi]$ groups ($\phi: O, I$) are characteristic of compounds containing mercurous ions ($[Hg_2]^{2+}$), where each Hg^{1+} forms two nearly collinear sp bonds. In Figure 2, we have summarized the stereochemical variations present for the 11 unique $[Hg-Hg]^{2+}$ dimers in the vasilyevite structure. Strong covalent bonds to anions at the ends of the dimers fall inside the orange-shaded region, within 23° of the dimer axis ($157^\circ < Hg-Hg-\phi < 176^\circ$); the deviation from linearity in the $[\phi-Hg-Hg-\phi]$ groups is therefore appreciable. Short axial bonds to O atoms [O(1) $\rightarrow$ O(6)] fall between 2.00 and 2.32 Å, and to I atoms [I(2)] at 2.75 Å. Situated at a high angle to the dimer axis are longer bonds from Hg to: (i) O atoms [O(1) $\rightarrow$ O(9)] between 2.44 and 2.85 Å, (ii) Cl and Br atoms [X(1) $\rightarrow$ X(3)] between 2.89 and 3.78 Å, and (iii) I atoms [I(1) $\rightarrow$ I(3)] between 3.11 and 4.02 Å. These weaker bonds to more distant meridional anions fall inside the blue-shaded region (Fig. 2) within 31° of the perpendicular to the dimer axis ($79^\circ < Hg-Hg-\phi < 121^\circ$).

Connectivity

The fundamental building block of the vasilyevite structure is the strongly bonded $[\phi-Hg-Hg-\phi]$ group, and these groups join together at their anion vertices to form a very complex interpenetrating framework (Fig. 3). The approximately linear $[\phi-Hg-Hg-\phi]$ groups are aligned along two principal directions: (1)

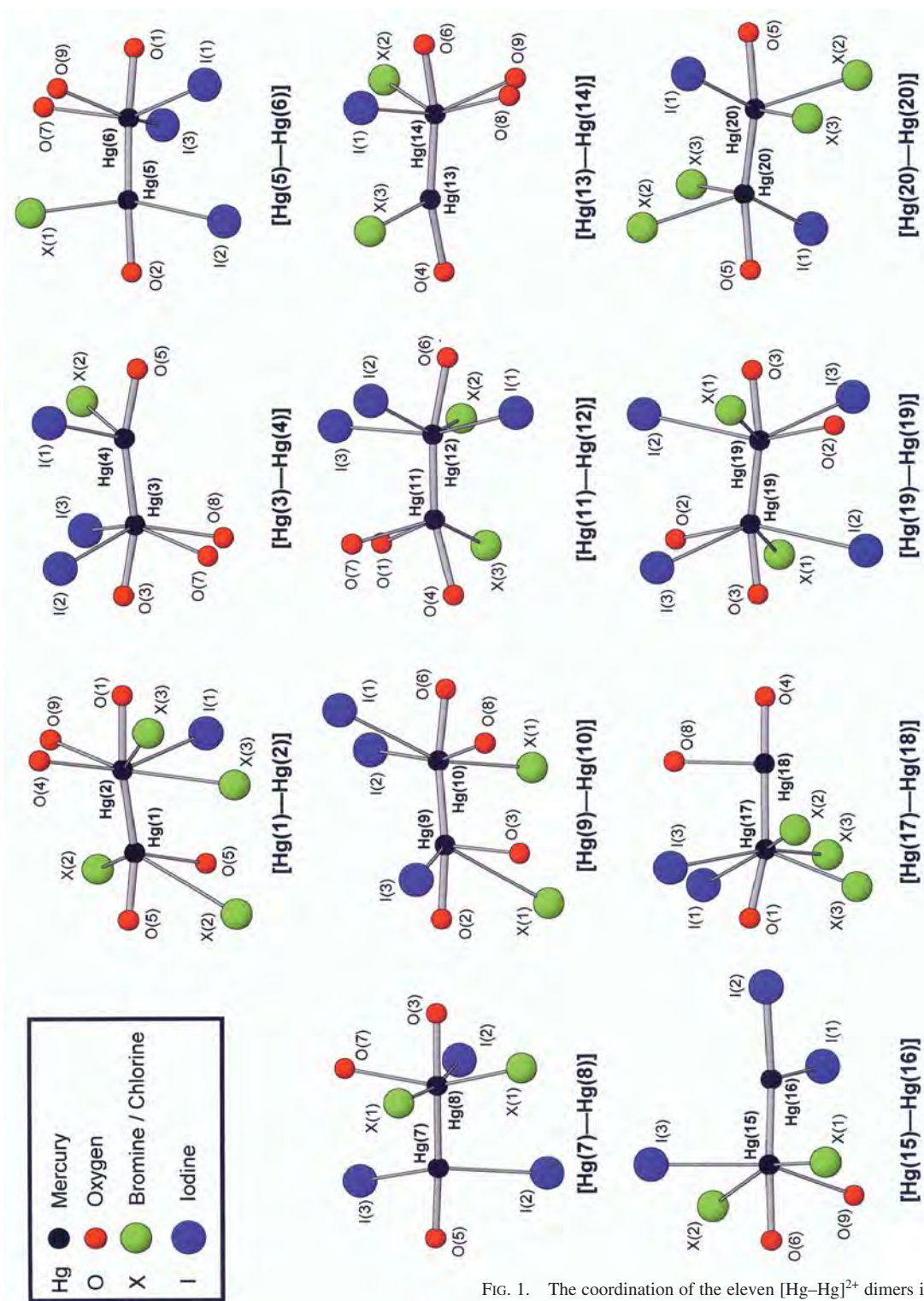


FIG. 1. The coordination of the eleven $[\text{Hg-Hg}]^{2+}$ dimers in vasilyevite; thick lines: strong axial bonds, thin lines: weak meridional bonds.

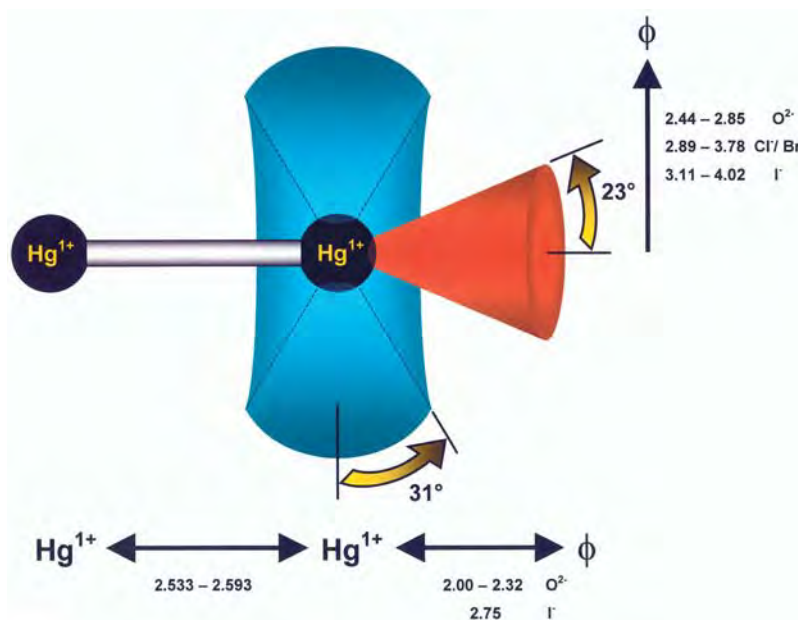


FIG. 2. Stereochemical variation for the eleven $[\text{Hg}-\text{Hg}]^{2+}$ dimers in vasilyevite; orange: axial-bond region, blue: meridional-bond region.

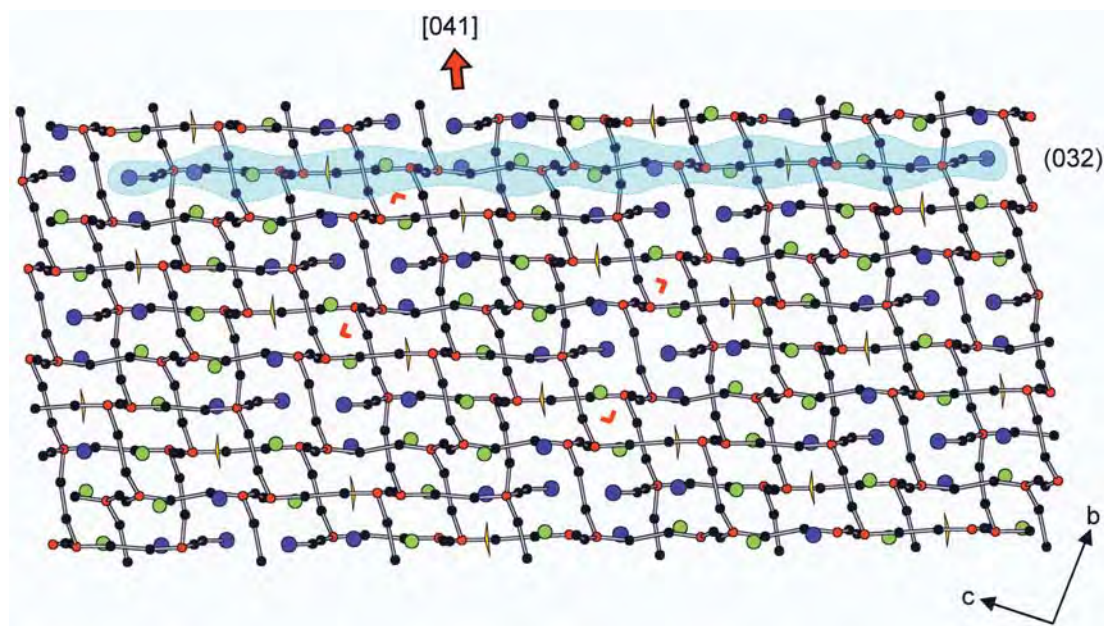


FIG. 3. The crystal structure of vasilyevite viewed down the a axis. Legend as in Figure 1; carbonate groups: yellow triangles, grey lines: strong axial bonds of the $[\phi-\text{Hg}-\text{Hg}-\phi]$ groups. Four red right-angle markers: corners of the unit cell.

along (032) as well-defined horizontal rows (Fig. 3), and (2) as somewhat staggered tilted columns along [041]. The result is a rhombic pattern with disruptions in the connectivity occurring at the *I*(2) site. A contiguous segment oriented within (032) is highlighted by faint blue back-shading in Figure 3. There are two interesting features of this pattern: (1) The halogen and C,S sites all lie approximately *within* the (032) plane of strong bonding, and *between* the staggered [–φ–Hg–Hg–φ–] bonding along [041]. (2) Adjacent rows of [–φ–Hg–Hg–φ–] bonding within (032) are not linked to each other *via* strong bonding along [041]. Instead, the bonds along [041] extend past the adjacent row and connect to the next row. Two adjacent (032) rows of [–φ–Hg–Hg–φ–] bonds are shown in Figure 4a, looking down onto (032). The bonds on the upper layer are shown as black solid lines, and the bonds on the lower layer are shown as orange lines. Thin black-outlined hollow bonds extend down from the upper layer, and up from the lower layer. Note that the upper and lower layers do not connect, but interpenetrate. In the upper layer, continuous strings of atoms in which strong bonding ends at the *I*(2) anion are shown in their entirety: they have a crankshaft appearance and are comprised of six alternating folds (concave – convex – concave – *etc.*). Similar strings of atoms in the lower net are displaced by: (i) $\sim 1/3$ left or right on the page, and (ii) $\sim 1/2$ up or down on the page, relative to strings in the upper net. An entire crankshaft from the upper net is shown in Figure 4b, with all linkages to neighboring crankshafts above and below. The O atoms at the O(1) → O(5) sites are coordinated by three Hg atoms, whereas the O(6) site is coordinated by four Hg atoms. Inspection of the bond-valence table (Table 5) shows that the O(1) → O(5) sites are coordinated by an additional fourth (more distant) Hg atom.

In terms of the network of stronger [–φ–Hg–Hg–φ–] bonds, the structure of vasilyevite consists of two interpenetrating three- and four-connected nets, where net interruption occurs at the *I*(2) site. The halogens and (CO₃) groups – S^{2–} anions (see below) are situated in the interstices of the nets and serve to stabilize the nets *via* additional weak linkages to Hg atoms.

(CO₃) – S^{2–} anions

Bonding to the (CO₃) group and S^{2–} anion (see below) is shown in Figures 5a and 5b, respectively. Each of the three atoms of oxygen [O(7) → O(9)] belonging to the (CO₃) group receives four weak bonds (2.60–2.85 Å) from nearby Hg atoms (Table 4, Fig. 5a). The S^{2–} anion is coordinated by nine Hg atoms (2.94–3.77 Å) in a distorted tri-augmented trigonal prismatic coordination (Table 4, Fig. 5b).

TABLE 4. SELECTED BOND DISTANCES (Å) AND ANGLES (°) IN VASILYEVITE

Hg(1)–Hg(2)	2.541(5)	Hg(3)–Hg(4)	2.593(6)		
–Hg(1)–O(5)	2.00(2)	159(2)	–Hg(3)–O(3)	2.12(6)	163(2)
–Hg(2)–O(1)c	2.21(5)	170(2)	–Hg(4)–O(5)	2.07(6)	162(2)
–Hg(1)–O(5)a	2.78(7)	112(1)	–Hg(3)–O(7)c	2.69(8)	110(1)
–Hg(1)–X(2)a	3.12(1)	108.9(3)	–Hg(3)–O(8)	2.69(6)	107(1)
–Hg(1)–X(2)	3.62(2)	121.4(3)	–Hg(3)–I(2)a	3.95(1)	96.3(2)
–Hg(2)–O(4)c	2.80(7)	109(1)	–Hg(3)–I(3)	3.34(1)	98.9(3)
–Hg(2)–O(9)	2.85(7)	105(1)	Hg(4)–X(2)	3.02(2)	104.6(3)
–Hg(2)–X(3)	3.39(2)	79.1(3)	Hg(4)–I(1)a	3.36(1)	110.1(2)
–Hg(2)–X(3)f	3.51(2)	119.0(3)			
–Hg(2)–I(1)	3.50(1)	92.5(2)			
Hg(5)–Hg(6)c	2.554(6)	Hg(7)–Hg(8)	2.563(7)		
–Hg(5)–O(2)j	2.23(6)	176(2)	–Hg(7)–O(2)c	2.15(7)	175(1)
–Hg(6)–O(1)c	2.15(6)	175(2)	–Hg(8)–O(3)	2.16(7)	167(1)
–Hg(5)–X(1)k	3.07(1)	101.9(3)	–Hg(7)–I(2)j	3.41(1)	99.1(2)
–Hg(5)–I(2)c	4.02(1)	108.9(2)	–Hg(7)–I(3)e	3.27(1)	108.1(2)
–Hg(6)–O(7)	2.63(8)	101(1)	–Hg(8)–O(7)c	2.77(6)	100(2)
–Hg(6)–O(9)	2.69(6)	101(1)	–Hg(8)–X(1)g	3.07(1)	108.6(3)
–Hg(6)–I(1)	3.45(1)	98.1(2)	–Hg(8)–X(1)k	3.47(1)	97.7(3)
–Hg(6)–I(3)f	3.43(1)	100.9(2)	–Hg(8)–I(2)a	3.53(1)	85.4(2)
Hg(9)–Hg(10)	2.533(7)	Hg(11)–Hg(12)e	2.537(5)		
–Hg(9)–O(2)f	2.17(6)	168(1)	–Hg(11)–O(4)	2.32(5)	162(2)
–Hg(10)–O(6)c	2.12(6)	167(1)	–Hg(12)–O(6)a	2.31(5)	167(1)
–Hg(9)–O(3)	2.60(5)	105(1)	–Hg(11)–O(1)	2.44(7)	111(1)
–Hg(9)–X(1)g	3.78(1)	115.2(3)	–Hg(11)–O(7)c	2.83(6)	101(1)
–Hg(9)–I(3)	3.39(1)	117.1(2)	–Hg(11)–X(3)e	3.47(2)	108.8(3)
–Hg(10)–O(8)	2.73(6)	89(2)	–Hg(12)–X(2)	3.12(2)	92.4(3)
–Hg(10)–X(1)k	3.12(2)	87.9(3)	–Hg(12)–I(1)i	3.37(1)	104.5(2)
–Hg(10)–I(1)f	3.48(1)	114.1(3)	–Hg(12)–I(2)j	3.51(1)	112.4(2)
–Hg(10)–I(2)f	3.37(1)	107.2(2)	–Hg(12)–I(3)	3.27(1)	92.1(2)
Hg(13)–Hg(14)	2.545(6)	Hg(15)–Hg(16)a	2.566(8)		
–Hg(13)–O(4)	2.26(6)	164(2)	–Hg(15)–O(6)	2.23(7)	172(2)
–Hg(14)–O(6)	2.09(6)	168(1)	–Hg(16)–I(2)a	2.75(1)	157.1(3)
–Hg(13)–X(3)e	2.89(2)	104.7(4)	–Hg(15)–O(9)	2.80(6)	103(2)
–Hg(14)–O(8)c	2.72(6)	109(1)	–Hg(15)–X(1)a	3.07(1)	98.6(3)
–Hg(14)–O(9)	2.60(6)	115(1)	–Hg(15)–X(2)a	3.37(1)	101.1(4)
–Hg(14)–X(2)a	3.25(2)	99.4(3)	–Hg(15)–I(3)a	3.45(1)	93.0(3)
–Hg(14)–I(1)e	3.42(1)	97.1(2)	–Hg(16)–I(1)a	3.11(1)	108.3(3)
Hg(17)–Hg(18)f	2.557(7)	Hg(19)–Hg(19)g	2.543(9)		
–Hg(17)–O(1)c	2.08(6)	166(2)	–Hg(19)–O(3)	2.12(6)	165(1)
–Hg(18)–O(4)	2.03(7)	175(2)	–Hg(19)–O(2)f	2.64(5)	109(1)
–Hg(17)–X(2)f	3.61(2)	87.8(3)	–Hg(19)–X(1)g	3.29(2)	112.1(3)
–Hg(17)–X(3)f	2.94(2)	113.9(5)	–Hg(19)–I(2)a	3.92(1)	92.7(2)
–Hg(17)–X(3)	3.47(2)	87.0(4)	–Hg(19)–I(3)	3.55(1)	111.9(3)
–Hg(17)–I(1)	3.83(1)	99.5(2)			
–Hg(17)–I(3)f	3.85(1)	102.4(2)			
–Hg(18)–O(8)	2.69(7)	93(2)			
Hg(20)–Hg(20)h	2.59(1)				
–Hg(20)–O(5)	2.28(6)	159(2)			
–Hg(20)–X(2)a	3.22(2)	112.2(4)			
–Hg(20)–X(3)a	3.08(2)	97.4(5)			
–Hg(20)–I(1)a	3.66(1)	110.7(3)			
C–O(7)a	1.37(7)	O(7)a–C–O(8)b	116(6)		
C–O(8)b	1.20(9)	O(7)a–C–O(9)a	116(6)		
C–O(9)a	1.18(9)	O(8)b–C–O(9)a	128(5)		
O(7)–Hg(3)c	2.69(8)	O(8)–Hg(3)	2.69(6)		
O(7)–Hg(6)	2.63(8)	O(8)–Hg(10)	2.73(6)		
O(7)–Hg(8)c	2.77(6)	O(8)–Hg(14)c	2.72(6)		
O(7)–Hg(11)c	2.83(6)	O(8)–Hg(18)	2.69(7)		
O(9)–Hg(2)	2.85(7)	S–Hg(2)a	3.59(5)		
O(9)–Hg(6)	2.69(6)	S–Hg(3)b	3.13(5)		
O(9)–Hg(14)	2.60(6)	S–Hg(6)a	3.10(6)		
O(9)–Hg(15)	2.80(6)	S–Hg(8)b	3.77(4)		
		S–Hg(10)b	3.36(4)		
		S–Hg(11)b	3.37(4)		
		S–Hg(14)a	2.94(4)		
		S–Hg(15)a	3.62(5)		
		S–Hg(18)b	3.25(5)		

symmetry operators: a: $\bar{x}+1, \bar{y}+1, \bar{z}+1$; b: $x, y+1, z$; c: $\bar{x}+1, \bar{y}, \bar{z}+1$; d: $x-1, y, z$; e: $x+1, y, z$; f: $\bar{x}, \bar{y}, \bar{z}+1$; g: $\bar{x}+1, \bar{y}+1, \bar{z}+2$; h: $\bar{x}+2, \bar{y}+1, \bar{z}+1$; i: $\bar{x}, \bar{y}+1, \bar{z}+1$; j: $x+1, y, z+1$; k: $x, y-1, z$

TABLE 5. BOND-VALENCE (ν) TABLE FOR VASILYEVITE

	Hg(1)	Hg(2)	Hg(3)	Hg(4)	Hg(5)	Hg(6)	Hg(7)	Hg(8)	Hg(9)	Hg(10)	Hg(11)	Hg(12)	Hg(13)	Hg(14)	Hg(15)	Hg(16)	Hg(17)	Hg(18)	Hg(19)	Hg(20)	C	Σ	
O(1)		0.43				0.51						0.23					0.61					1.78	
O(2)					0.41		0.51		0.48										0.14			1.54	
O(3)			0.55					0.50	0.15										0.55			1.75	
O(4)		0.09									0.32		0.38					0.70				1.49	
O(5)	0.76 0.09			0.63																0.36		1.84	
O(6)										0.55		0.33		0.60	0.41							1.89	
I(1)		0.09		0.12		0.10				0.09		0.12		0.11		0.25	0.04			0.06		0.98	
I(2)			0.03		0.02		0.11	0.08		0.12		0.08				0.65			0.03			1.12	
I(3)			0.13			0.10	0.16		0.12			0.16				0.10		0.03		0.07		0.87	
X(1)					0.15			0.15 0.05	0.02	0.13						0.15			0.08			0.73	
X(2)	0.13 0.03			0.17								0.13		0.09	0.07		0.03			0.10		0.75	
X(3)		0.05 0.04									0.04		0.21				0.18 0.04			0.12		0.68	
Σ	1.01	0.70	0.71	0.92	0.58	0.71	0.78	0.78	0.77	0.89	0.59	0.82	0.59	0.80	0.73	0.90	0.93	0.70	0.87	0.64			
O(7)			0.12			0.14		0.10			0.08										1.06	1.50	
O(8)			0.12							0.11				0.11				0.12				1.67	2.13
O(9)		0.08				0.12								0.15	0.09							1.67	2.11
Σ	1.01	0.78	0.95	0.92	0.58	0.97	0.78	0.88	0.77	1.00	0.67	0.82	0.59	1.06	0.82	0.90	0.93	0.82	0.87	0.64			
S		0.03	0.11			0.12		0.02		0.06	0.06			0.19	0.03			0.08				0.70	
Σ	1.01	0.73	0.82	0.92	0.58	0.83	0.78	0.80	0.77	0.95	0.65	0.82	0.59	0.99	0.76	0.90	0.93	0.78	0.87	0.64	4.40		

CHEMICAL FORMULA

During electron-microprobe analysis (Roberts *et al.* 2003), a minor quantity of S was measured (0.1 wt.%), which gives 0.15 S^{2-} atoms *pfu* (per formula unit). The presence of a (CO_3) group is clearly indicated in the infrared spectrum by the absorptions at 1336, 1024, 837 and 678 cm^{-1} . On the other hand, there is no absorption at $\sim 1100\text{ cm}^{-1}$ typical of an $(SO_4)^{2-}$ group (Myneni 2000) in vasilyevite (Roberts *et al.* 2003), and hence the presence of S^{2-} rather than $(SO_4)^{2-}$ is indicated by the infrared spectrum. The electron-microprobe data (Table 6) were normalized on an anion basis (14.7 anions): $(O + I + Br + Cl) = 12$ and $[1 - x](CO_3)^{2-} + x(S^{2-}) = 1$, where x was set at 0.15 *apfu* from the electron-microprobe data. The chemical composition gives the following simplified formula: $(Hg_2)^{2+}_{10} O_6 I_3 (Br_{1.9} Cl_{1.1})_{\Sigma 3} [(CO_3)_{0.85} S^{2-}_{0.15}]_{\Sigma 1}$. The formula resulting from crystal-structure analysis is in close agreement: $(Hg_2)^{2+}_{10} O_6 I_3 (Br_{1.6} Cl_{1.4})_{\Sigma 3} [(CO_3)_{0.8} S^{2-}_{0.2}]_{\Sigma 1}$. The X(1) and X(2) sites are occupied mainly by Br, whereas the X(3) site contains mainly Cl; an ideal end-member composition involving complete order of anions can be written as $(Hg_2)^{2+}_{10} O_6 I_3 Br_2 Cl (CO_3)$, where the X(1) and X(2) sites are occupied by Br, and the X(3) site is occupied by Cl.

RELATED STRUCTURES

Mercury shows a strong tendency to form poly-cations (*e.g.*, Volkova & Magarill 1999). The $[Hg-$

$Hg]^{2+}$ “dumbbell” is a prominent feature of the crystal chemistry of low-valence-Hg minerals and synthetic compounds (Pervukhina *et al.* 1999a, Borisov *et al.* 1999), and also occurs as a complex in aqueous solutions [*e.g.*, in aqueous $Hg_2(ClO_4)(H_2O)_4$, Johansson 1966]. The bond topology and crystal chemistry of Hg minerals and synthetic Hg compounds have been very thoroughly examined by Pervukhina *et al.* (1999a, b) and Magarill *et al.* (2000). Thus here we will examine the relations between vasilyevite and only the most similar of the Hg minerals.

The $[Hg-Hg]^{2+}$ dumbbell is generally linked strongly to two anions to form a quasi-linear $[\phi-Hg-Hg-\phi]$ group. This group may occur as isolated groups (*e.g.*, in calomel, $[Hg_2]Cl_2$), as clusters (*e.g.*, in shakovite, $[Hg_2]_2Sb(OH)_3O_3$), and as highly polymerized motifs in other minerals (Pervukhina *et al.* 1999b). The structure of vasilyevite consists of two interpenetrating three-dimensional frameworks of $[\phi-Hg-Hg-\phi]$ groups (Figs. 3, 4). The minerals most resembling vasilyevite are poyarkovite, $[Hg_2]OCl$, the structure of which was reported by Vasil'ev *et al.* (1999), and eglestonite, $[Hg_2]_3Cl_3O_2H$ (Mereiter & Zemann 1976, Mereiter *et al.* 1992). In poyarkovite, $[\phi-Hg-Hg-\phi]$ groups polymerize to form two interpenetrating three-dimensional frameworks, and in eglestonite, $[\phi-Hg-Hg-\phi]$ groups polymerize to form four interpenetrating three-dimensional frameworks. The additional topological complexity of vasilyevite arises from the fact that polymerization in the *c* direction involves a crankshaft (Fig. 4b) rather than a linear motif.

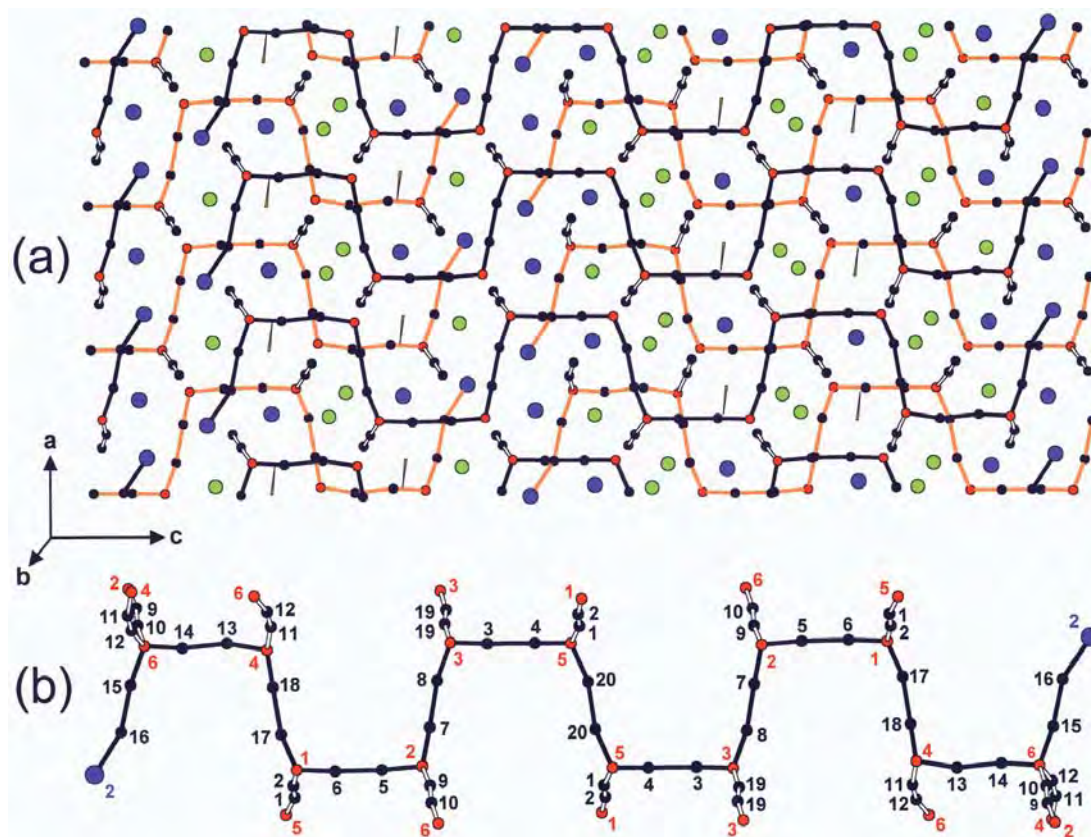


FIG. 4. The crystal structure of vasilyevite projected onto (032). Legend as in Figure 1. (a) Thick black lines: bonds in the upper net, thick orange lines: bonds in the lower net, hollow lines: connections extending through the central cavity. (b) A single contiguous string of $[-\phi\text{-Hg-Hg-}\phi-]$ groups from the upper net (a similar string is highlighted in blue in Fig. 3).

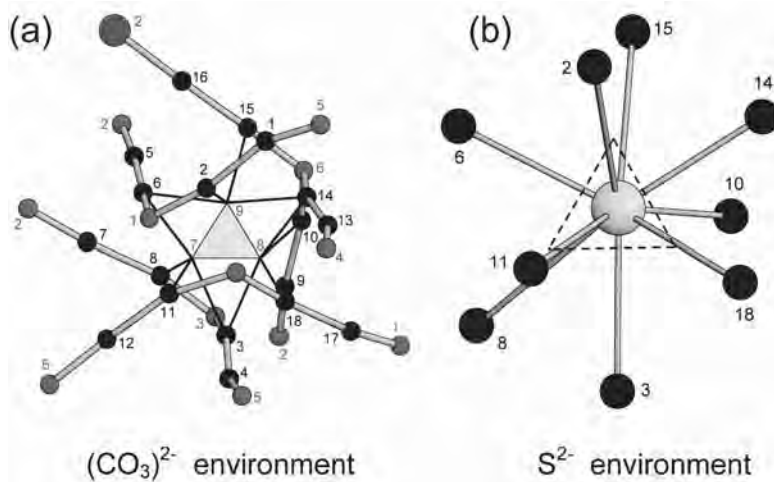


FIG. 5. The environments of the (CO_3) group (a) and the S^{2-} anion (b) in vasilyevite. Legend as in Figures 1, 3. Thin black lines: weak bonds from Hg atoms to O atoms of the (CO_3) group, yellow circle: S^{2-} atom, dashed triangle: outline of unoccupied (CO_3) triangle.

TABLE 6. CHEMICAL COMPOSITION (wt %) AND UNIT FORMULA (*apfu*) FOR VASILYEVITE

Hg	89.1	Hg ¹⁺	20.93
I	7		
Br	2.5	I ⁻	2.70
Cl	0.6		
S	0.1	Br ⁻	1.53
CO ₂ *	0.8	Cl ⁻	0.83
	100.1	Σ	2.36
-(O = I, Br, Cl, S)	-0.9		
Sum	99.2	(CO ₂) ²⁺	0.85
		S ²⁺	0.15
		Σ	1.00

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REFERENCES

- BORISOV, V., MAGARILL, S.A., ROMANENKO, G.V. & PERVUKHINA, N.V. (1999): Crystal chemistry peculiarities in rare mercury minerals of supergene origin: possible sources of mercury in surface water-air watersheds. *Chemistry for the Benefit of Stable Development* 7, 497-503.
- COOPER, M.A. & HAWTHORNE, F.C. (2001): Structure topology and hydrogen bonding in marthozite, Cu²⁺[(UO₂)₃(SeO₃)₂O₂](H₂O)₈, a comparison with guilleminite, Ba[(UO₂)₃(SeO₃)₂O₂](H₂O)₃. *Can. Mineral.* 39, 797-807.
- DUNNING, G.E., HADLEY, T.A., CHRISTY, A.G., MAGNASCO, J. & COOPER, J.F., JR. (2004): The Clear Creek mine, San Benito County, California; a unique mercury locality. *Mineral Rec.* (in press).
- INTERNATIONAL TABLES FOR X-RAY CRYSTALLOGRAPHY (vol. C) (1992): Kluwer Academic Publishers, Dordrecht, The Netherlands.
- JOHANSSON, G. (1966): An X-ray investigation of the structure of the Hg²⁺ ion in solution. *Acta Chem. Scand.* 20, 553-562.
- MAGARILL, S.A., ROMANENKO, G.V., PERVUKHINA, N.V., BORISOV, S.V. & PALCHIK, N.A. (2000): Oxocentered polycationic complexes – an alternative approach to crystal-chemical investigation of the structure of natural and synthetic mercury oxosalts. *J. Struct. Chem.* 41, 96-105.
- MEREITER, K. & ZEMANN, J. (1976): Neubearbeitung des Quecksilberminerals Eglestonit: Kristallstruktur, chemische Zusammensetzung und Synthese. *Tschermaks Mineral. Petrogr. Mitt.* 23, 105-115.
- _____, _____ & HEWAT, A.W. (1992): Eglestonite, [Hg₂]₃Cl₃O₂H: confirmation of the chemical formula by neutron powder diffraction. *Am. Mineral.* 77, 839-842.
- MYNENI, S.C.B. (2000): X-ray and vibrational spectroscopy of sulfate in Earth materials. *Rev. Mineral. Geochem.* 40, 113-172.
- PERVUKHINA, N.V., MAGARILL, S.A., BORISOV, S.V., ROMANENKO, G.V. & PALCHIK, N.A. (1999a): Crystal chemistry of compounds containing mercury in low oxidation states. *Russ. Chem. Rev.* 68, 615-636.
- _____, ROMANENKO, G.V., BORISOV, S.V., MAGARILL, S.A. & PALCHIK, N.A. (1999b): Crystal chemistry of mercury(I) and mercury (I,II) minerals. *J. Struct. Chem.* 40, 461-476.
- ROBERTS, A.C., COOPER, M.A., HAWTHORNE, F.C., STIRLING, J.A.R., PAAR, W.H., STANLEY, C.J., DUNNING, G.E. & BURNS, P.C. (2003): Vasilyevite, (Hg₂)²⁺₁₀O₆I₃BrCl(CO₃), a new mineral species from the Clear Creek Claim, San Benito County, California. *Can. Mineral.* 41, 1167-1172.
- _____, ERCIT, T.S., ERD, R.C. & OSCARSON, R.L. (1990): Szymańskiite, Hg¹⁺₁₆(Ni,Mg)₆(CO₃)₁₂(OH)₁₂(H₃O)₁₊₈•3H₂O, a new mineral species from the Clear Creek Claim, San Benito County, California. *Can. Mineral.* 28, 703-707.
- _____, _____, GROAT, L.A., CRIDDLE, A.J., ERD, R.C. & WILLIAMS, R.S. (1995): Peterbaylissite, Hg¹⁺₃(CO₃)(OH)•2H₂O, a new mineral species from the Clear Creek Claim, San Benito County, California. *Can. Mineral.* 33, 47-53.
- _____, GROAT, L.A., RAUDSEPP, M., ERCIT, T.S., ERD, R.C., MOFFATT, E.A. & STIRLING, J.A.R. (2001): Clearcreekite, a new polymorph of Hg¹⁺₃(CO₃)(OH)•2H₂O, from the Clear Creek Claim, San Benito County, California. *Can. Mineral.* 39, 779-784.
- SZYMAŃSKI, J.T. & ROBERTS, A.C. (1990): The crystal structure of szymańskiite, a partly disordered, (Hg–Hg)²⁺, (Ni,Mg)²⁺ hydronium-carbonate-hydroxide-hydrate. *Can. Mineral.* 28, 709-718.
- VASIL'EV, V.I., PERVUKHINA, N.V., ROMANENKO, G.V., MAGARILL, S.A. & BORISOV, S.V. (1999): New data on the mercury oxide-chloride mineral poyarkovite: the second find, and crystal-structure determination. *Can. Mineral.* 37, 119-126.
- VOLKOVA, L.M. & MAGARILL, S.A. (1999): On formation of polyatomic mercury cations. *J. Struct. Chem.* 40, 262-269.

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