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THE STRUCTURE OF EDOYLERITE DETERMINED FROM A MICROCRYSTAL

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ABSTRACT

The structure of edoylerite, $Hg^{2+}_3Cr^{6+}O_4S_2$, $Z = 4$, monoclinic, a 7.5283(4), b 14.8325(8), c 7.4629(4) Å, β 118.746(1)°, V 730.6(1) Å^3, space group $P2_1/c$, has been solved by direct methods and refined by full-matrix least-squares techniques to an agreement factor (R) of 7.9% and a goodness-of-fit (S) of 1.31 using 1193 unique observed reflections ($|F_o| > 4\sigma_F$) collected for a microcrystal with a volume of 400 μm^3 using Mo$K\alpha$ X-radiation and a CCD (charge-coupled device) area detector. The structure contains three symmetrically distinct Hg^{2+} sites, each of which is strongly bonded to two S anions to form approximately linear S–Hg–S clusters. The S–Hg–S clusters link to form crankshaft-type chains composed of eight-membered rings of alternating Hg^{2+} and S that are parallel to [101]. The Hg^{2+} cations are weakly bonded to additional anions, resulting in distorted-octahedral coordinations in two cases and a pentagonal bipyramidal coordination in the other case. The Hg^{2+} polyhedra link to each other and to CrO_4 tetrahedra by the sharing of polyhedron edges and corners, resulting in a heteropolyhedral framework structure.

Keywords: edoylerite, mercury mineral, microcrystal, structure determination.

SOMMAIRE

La structure de la edoylerite, $Hg^{2+}_3Cr^{6+}O_4S_2$, $Z = 4$, monoclinique, a 7.5283(4), b 14.8325(8), c 7.4629(4) Å, β 118.746(1)°, V 730.6(1) Å^3, groupe spatial $P2_1/c$, a été résolue par méthodes directes et affinée par moindres carrés sur matrice entière jusqu'à un résidu R de 7.9% et un facteur de concordance S de 1.31 en utilisant 1193 réflexions uniques observées ($|F_o| > 4\sigma_F$). L'expérience a porté sur un microcristal avec un volume de 400 μm^3, étudié avec un rayonnement Mo$K\alpha$ et un détecteur à aire CCD à couplage de charges. La structure contient trois sites Hg^{2+} symétriquement distincts. Chacun de ceux-ci est fortement lié à deux anions de soufre S dans un agencement S–Hg–S approximativement linéaire. Les agencements S–Hg–S sont liés et forment des chaînes en vilebrequin faites d'anneaux à huit membres, avec une alternance de Hg^{2+} et S, qui sont parallèles à [101]. Les cations Hg^{2+} sont faiblement liés à d'autres anions, pour donner une coordinence octaédrique difforme dans deux cas et une coordinence pentagonale bipyramidale dans l'autre cas. Les polyèdres Hg^{2+} sont connectés entre eux et à des tétraèdres CrO_4 par partage d'arêtes et de coins des polyèdres, ce qui mène à une trame hétéropolyédrique.

(Traduit par la Rédaction)

Mots-clés: edoylerite, minéral de mercure, microcristal, détermination de la structure.

INTRODUCTION

Edoylerite, $Hg^{2+}_3Cr^{6+}O_4S_2$, was described from the Clear Creek claim, San Benito County, California (Erd *et al.* 1993). The mercury mineralization at the Clear Creek claim is in hydrothermally altered serpentinite, and the list of identified mercury minerals includes cinnabar, elemental mercury, edgarbaileyite, metacinnabar, montroydite, eglestonite, calomel, edoylerite, wattersite, gianellaite, mosesite, deanesmithite, and szymańskiite (Erd *et al.* 1993). The structure of edoylerite has been determined using data collected from a microcrystal using a CCD area detector, and the results are presented herein.

EXPERIMENTAL

An acicular crystal of edoylerite with a maximum dimension of ~0.2 mm was obtained for study, but preliminary examination of the crystal revealed the presence of multiple orientations. Therefore, a very small crystal, with approximate dimensions 0.04 × 0.005 × 0.002 mm, was selected for study. The crystal was mounted on a Bruker PLATFORM three-circle goniom-

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eter equipped with a 1K SMART CCD (charge-coupled device) detector with a crystal-to-detector distance of 5 cm.

The data were collected using graphite-monochromated Mo$K\alpha$ X-radiation and framewidths of 0.15° in ω, with 120 s used to acquire each frame. More than a hemisphere of three-dimensional data was collected, and the data were analyzed to locate peaks for the determination of the unit-cell dimensions. These were refined with 1705 reflections using least-squares techniques (Table 1). Data were collected for $3° \leq 2\theta \leq 55°$ in approximately 90 hours, and the intensities of equivalent reflections collected at various times throughout the data collection showed no decay. The three-dimensional data were reduced and filtered for statistical outliers using the Bruker program SAINT. An absorption correction was applied using Gaussian quadrature integration, and the data were corrected for Lorentz, polarization, and background effects. A total of 3760 reflections was collected, of which there were 1470 unique reflections (R_{INT} = 6.8%) with 1193 classed as observed ($|F_o| \geq 4\sigma_F$).

STRUCTURE SOLUTION AND REFINEMENT

Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from *International Tables for X-Ray Crystallography, Vol. IV* (Ibers & Hamilton 1974). The Bruker SHELXTL Version 5 system of programs was used for the determination and refinement of the crystal structure.

Systematic absences and reflection statistics indicated the space group $P2_1/c$, as given by Erd *et al.* (1993), and verified by the successful solution of the structure by direct methods. Refinement of all atomic position parameters, allowing for isotropic atomic-displacement, gave a model with an agreement index (R) of 10.0%. Conversion of the displacement parameters for Hg, Cr, and S to an anisotropic form, together with the inclusion of a refinable weighting-scheme of the structure factors, provided a final model with an agreement index of 7.9% for 1193 observed reflections ($|F_o| \geq 4\sigma_F$) and a goodness-of-fit (S) of 1.31. A model with anisotropic-displacement parameters for the O atoms was tried, but the parameters were found to be unstable. In the final cycle of refinement, the average parameter shift/esd was 0.000, and the maximum peaks in the final difference-Fourier maps were 2.96 and –2.77 $e/\text{Å}^3$, respectively. The final atomic position parameters and anisotropic-displacement parameters are given in Table 2, selected interatomic distances and angles are given in Table 3, and a bond-valence analysis is presented in Table 4. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2.

TABLE 1. MISCELLANEOUS INFORMATION CONCERNING EDOYLERITE

a (Å)	7.5283(4)	Crystal size (mm)	0.04x0.005
b (Å)	14.8325(8)		x0.002
c (Å)	7.4629(4)	Total ref.	3760
β (°)	118.746(1)	Unique ref.	1470
V (Å^3)	730.6(1)	R_{int}	6.8%
Space group	$P2_1/c$	Unique $\lvert F_o\rvert \geq 4\sigma_F$	1193
F(000)	1312	Final R	7.9%
μ (mm^{-1})	64.8	S	1.31
D_{calc}	7.11 g/cm^3		

Unit cell contents: $4[\mathrm{Hg^{2+}_3Cr^{6+}O_4S_2}]$

$R = \Sigma(|F_o|-|F_c|)/\Sigma|F_o|$

$S = [\Sigma w(|F_o|-|F_c|)^2/(m-n)]^{½}$, for m observations and n parameters

RESULTS

Cation coordination

The structure of edoylerite contains three symmetrically unique $\mathrm{Hg^{2+}}$ cations, each of which is located on a general position. All three $\mathrm{Hg^{2+}}$ cations are strongly bonded to two S anions each, with Hg–S bond-lengths of ~2.4 Å and individual bond-valences of ~0.7 valence units (*vu*) (Tables 3, 4). The S–Hg–S bond-angles are 173.9(3), 173.5(3), and 163.7(3) for the Hg(1), Hg(2) and Hg(3) cations, respectively. The remaining bond-valence requirements of the $\mathrm{Hg^{2+}}$ cations are met by additional interactions with O and S anions, with the additional bonds oriented roughly perpendicular to the strong Hg–S bonds (Fig. 1). These additional bonds have bond valences ranging from 0.06 to 0.27 *vu*, indicating that they are substantially weaker than the strong

TABLE 2. ATOMIC PARAMETERS FOR THE STRUCTURE OF EDOYLERITE

	x	Y	z	*U_{eq}	**U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Hg(1)	0.1673(2)	0.0432(1)	0.3681(2)	265(4)	228(7)	268(9)	268(8)	-41(6)	95(6)	34(6)
Hg(2)	0.1033(2)	0.1437(1)	-0.0814(2)	256(4)	226(7)	318(9)	195(7)	-44(7)	77(6)	-20(6)
Hg(3)	0.5952(2)	0.1633(1)	0.3976(2)	244(4)	147(7)	303(9)	258(8)	12(6)	78(6)	28(6)
Cr	0.6200(8)	0.0959(4)	0.8917(8)	163(12)	118(25)	228(31)	153(26)	25(23)	73(21)	42(23)
S(1)	0.240(1)	0.1865(6)	0.268(1)	178(18)	150(40)	168(46)	183(41)	17(34)	55(34)	-44(34)
S(2)	-0.069(1)	0.1034(7)	-0.431(1)	212(20)	120(40)	334(55)	190(42)	-35(38)	80(34)	-78(38)
O(1)	0.491(5)	0.123(2)	0.007(5)	430(76)						
O(2)	0.693(5)	0.191(2)	0.820(5)	438(78)						
O(3)	0.487(5)	0.033(2)	0.698(5)	533(90)						
O(4)	0.824(4)	0.036(2)	0.037(4)	371(70)						

*U_{eq} = U_{eq} Å^2 x 10^4
**Uij = U_{ij} Å^2 x 10^4

TABLE 3. EDOYLERITE: SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°)

Hg(1)-S(1)	2.402(9)	Hg(3)-S(2)h	2.386(9)
Hg(1)-S(2)a	2.41(1)	Hg(3)-S(1)	2.391(8)
Hg(1)-O(3)	2.49(3)	Hg(3)-O(2)g	2.43(3)
Hg(1)-O(4)b	2.58(3)	Hg(3)-O(1)	2.70(3)
Hg(1)-S(2)c	2.964(8)	Hg(3)-O(2)	2.90(3)
Hg(1)-O(3)d	3.08(3)	Hg(3)-O(3)d	2.99(4)
Hg(2)-S(2)	2.366(9)	Cr-O(3)	1.60(3)
Hg(2)-S(1)	2.381(8)	Cr-O(1)c	1.63(3)
Hg(2)-O(1)	2.68(3)	Cr-O(4)c	1.65(3)
Hg(2)-O(4)e	2.71(3)	Cr-O(2)	1.69(3)
Hg(2)-O(2)f	2.90(3)	<Cr-O>	1.64
Hg(2)-O(4)b	3.08(3)		
Hg(2)-S(1)g	3.129(9)		
S(1)-Hg(1)-S(2)a	173.9(3)	S(2)-Hg(2)-S(1)	173.5(3)
S(1)-Hg(1)-O(3)	96.1(9)	S(2)-Hg(2)-O(1)	101.4(7)
S(1)-Hg(1)-O(4)b	90.5(7)	S(2)-Hg(2)-O(4)e	81.8(6)
S(1)-Hg(1)-S(2)c	100.0(3)	S(2)-Hg(2)-O(2)f	80.2(7)
S(1)-Hg(1)-O(3)d	86.4(7)	S(2)-Hg(2)-O(4)b	95.6(6)
S(2)a-Hg(1)-O(3)	89.5(9)	S(2)-Hg(2)-S(1)g	84.7(3)
S(2)a-Hg(1)-O(4)b	83.8(7)	S(1)-Hg(2)-O(1)	85.1(7)
S(2)a-Hg(1)-S(2)c	81.8(3)	S(1)-Hg(2)-O(4)e	99.9(6)
S(2)a-Hg(1)-O(3)d	93.6(7)	S(1)-Hg(2)-O(2)f	93.4(6)
O(3)-Hg(1)-O(4)b	173(1)	S(1)-Hg(2)-O(4)b	79.6(6)
O(3)-Hg(1)-S(2)c	92.9(8)	S(1)-Hg(2)-S(1)g	97.8(2)
O(3)-Hg(1)-O(3)d	69(1)	O(1)-Hg(2)-O(4)e	74.1(9)
O(4)b-Hg(1)-S(2)c	85.8(7)	O(1)-Hg(2)-O(2)f	172(1)
O(4)b-Hg(1)-O(3)d	111.5(9)	O(1)-Hg(2)-O(4)b	132.9(9)
S(2)c-Hg(1)-O(3)d	161.6(7)	O(1)-Hg(2)-S(1)g	70.9(7)
		O(4)e-Hg(2)-O(2)f	113.4(9)
S(2)h-Hg(3)-S(1)	163.7(3)	O(4)e-Hg(2)-O(4)b	65(1)
S(2)h-Hg(3)-O(2)g	95.4(8)	O(4)e-Hg(2)-S(1)g	139.0(6)
S(2)h-Hg(3)-O(1)	100.4(7)	O(2)f-Hg(2)-O(4)b	53.7(9)
S(2)h-Hg(3)-O(2)	79.8(7)	O(2)f-Hg(2)-S(1)g	102.0(7)
S(2)h-Hg(3)-O(3)d	79.1(7)	O(4)b-Hg(2)-S(1)g	154.9(6)
S(1)-Hg(3)-O(2)g	100.5(8)		
S(1)-Hg(3)-O(1)	84.5(7)		
S(1)-Hg(3)-O(2)	93.9(6)		
S(1)-Hg(3)-O(3)d	88.8(7)		
O(2)g-Hg(3)-O(1)	85(1)		
O(2)g-Hg(3)-O(2)	100.5(8)		
O(2)g-Hg(3)-O(3)d	149(1)		
O(1)-Hg(3)-O(2)	175(1)		
O(1)-Hg(3)-O(3)d	67(1)		
O(2)-Hg(3)-O(3)d	108.2(9)		

a = -x, -y, -z; b = x-1, y, z; c = x, y, z+1; d = 1-x, -y, 1-z; e = 1-x, -y, -z; f = x-1, y, z-1; g = x, ½-y, z-½; h = x+1, y, z+1

TABLE 4. BOND-VALENCE* (*vu*) ANALYSIS FOR EDOYLERITE

	Hg(1)	Hg(2)	Hg(3)	Cr	Σ
S(1)	0.67	0.71 0.18	0.69		2.25
S(2)	0.67 0.24	0.73	0.70		2.34
O(1)		0.14	0.13	1.60	1.87
O(2)		0.08	0.27 0.08	1.34	1.77
O(3)	0.23 0.06		0.07	1.75	2.11
O(4)	0.18	0.13 0.06		1.51	1.88
Σ	2.05	2.03	1.94	6.20	

*Bond-valence parameters from Brown (1981)

Hg–S bonds, with valences ~0.7 *vu*. However, without these additional weak bonds, the Hg^{2+} cations would be substantially underbonded. These weak bonds result in overbonding at the S anion positions, as was also observed for the structure of deanesmithite (Szymański & Groat 1997). In the case of Hg(1), there are weak bonds to one S and three O anions, resulting in a distorted octahedral coordination. The Hg(2) cation is weakly bonded to one S and four O anions, giving a distorted-pentagonal-bipyramidal coordination. The Hg(3) cation is weakly bonded to four O anions, giving a distorted-octahedral coordination.

The structure contains one unique Cr^{6+} cation, located on a general position, which is coordinated by four O anions in a tetrahedral arrangement. The <Cr–O> bond-length of 1.64 Å, the bond-valence sum of 6.20 *vu* at the cation site, and the observed site-scattering are consistent with complete occupancy of this site by Cr^{6+}.

Structure connectivity

The structure of edoylerite, and the relations between the physical properties and the structure, are best un-

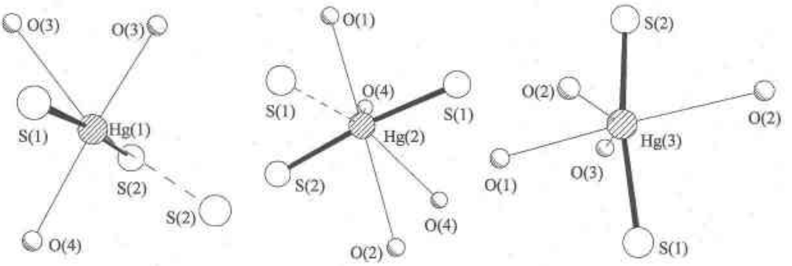

FIG. 1. The coordination polyhedra about the Hg^{2+}cations. Strong bonds to S (~0.7 *vu*) are shown as heavy lines, and weaker bonds to O and S are shown as light lines and broken lines, respectively. The Hg(1) and Hg(3) cations are in distorted octahedral coordination, and the Hg(2) cation is in pentagonal-bipyramidal coordination.

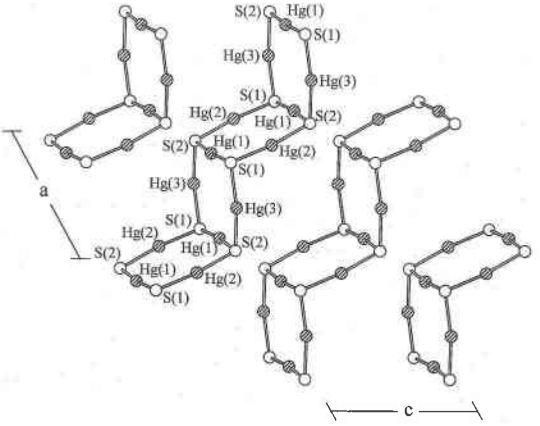

FIG. 2. The structure of edoylerite projected along [010]. Only the Hg^{2+} cations and S anions and the strong (~0.7 *vu*) bonds between them are shown.

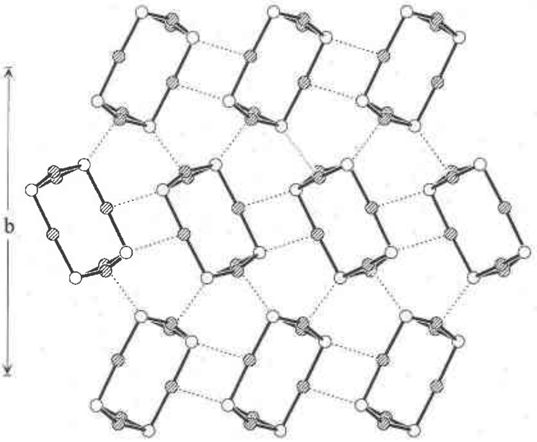

FIG. 3. Projection of the structure of edoylerite along [101]. Only the Hg^{2+} cations and S anions are shown. Strong (~0.7 *vu*) bonds and weaker bonds are shown as heavy and broken lines, respectively. Hg^{2+} cations are shown as circles shaded with parallel lines, and S anions are displayed as open circles.

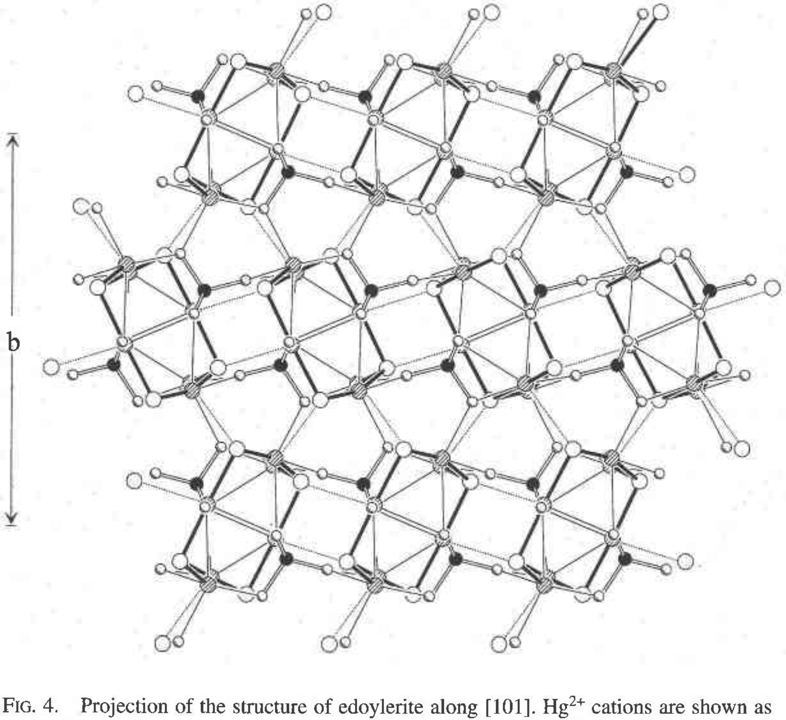

FIG. 4. Projection of the structure of edoylerite along [101]. Hg^{2+} cations are shown as circles shaded with parallel lines, S anions are shown as open circles, Cr^{6+} cations are shown as black circles, and O anions are shown as small circles that are shaded in the lower-left corners. Strong (~0.7 *vu*) and weak Hg–S bonds are shown as heavy and broken lines, respectively. The Cr–O bonds are illustrated with double lines, and Hg–O bonds are shown as light lines.

derstood by first considering only the Hg^{2+} and S ions, as well as the strong (~0.7 *vu*) bonds that occur between them. The approximately linear S–Hg–S units link to form crankshaft-type chains that are parallel to [101], as can be seen in Figure 2. There are two symmetrically distinct eight-membered rings of alternating Hg^{2+} and S ions in the crankshaft chain, one contains Hg(1) and Hg(2) cations, the other contains Hg(1) and Hg(3) cations. The eight-membered rings alternate along the crankshaft chain, and adjacent rings are inclined to each other by ~110° (Fig. 2).

Projection of the structure along [101] shows the arrangement of the crankshaft chains (Fig. 3). Linkages between adjacent chains are provided by weak Hg–S interactions over distances of ~3 Å, as illustrated in Figure 3. Each crankshaft chain is linked to six surrounding chains by these weak Hg–S interactions, resulting in an open framework. The CrO_4 tetrahedra are located in cavities within the Hg–S framework, and additional linkages between as well as within the crankshaft chains are provided by Hg–O bonds (Fig. 4). Note that the structure contains planes of weakness parallel to (010), along which breakage requires only the disruption of relatively weak Hg–O and Hg–S bonds, resulting in very good cleavage on {010} (Erd *et al.* 1993). Breakage along (101) can also occur without the disruption of the strong Hg–S bonds, resulting in a fair {101} cleavage (Erd *et al.* 1993).

Polyhedral representations of the structure are shown in Figure 5. The Hg polyhedra are drawn such that they include all anions that are bonded to the central cation. The structure contains symmetrically equivalent layers of polyhedra that are parallel to (001) at $z \approx 0$ and ½ (Figs. 5a, b). The layers are formed by $Hg\phi_n$ (ϕ: unspecified anion) and CrO_4 polyhedra that link by sharing corners and edges, and the layers are in turn linked by the sharing of polyhedron elements to create a framework structure (Fig. 5d).

Related species

Wattersite, $Hg^{1+}{}_4Hg^{2+}Cr^{6+}O_6$, and deanesmithite, $Hg^{1+}{}_2Hg^{2+}{}_3Cr^{6+}O_5S_2$, are chemically similar to edoylerite, although both species contain both Hg^{1+} and

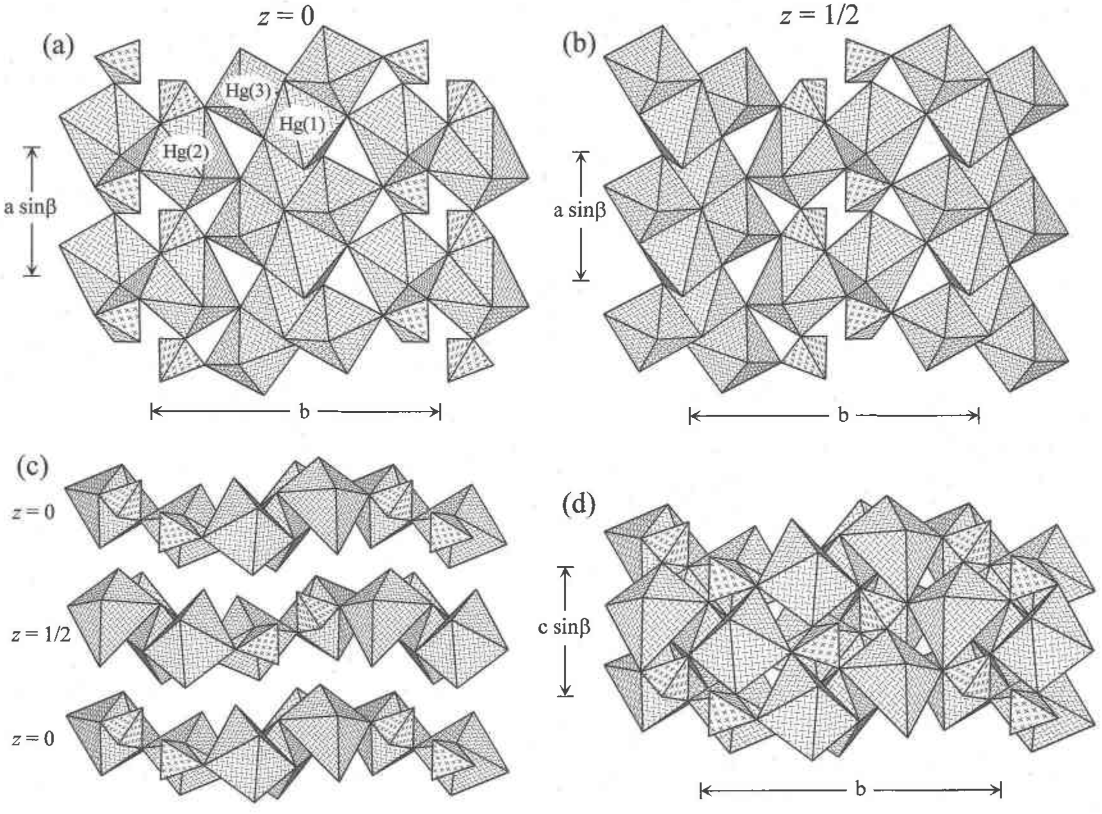

FIG. 5. Polyhedral representations of the structure of edoylerite. (a) The layer of polyhedra at $z \approx 0$ projected along [001]. (b) The later of polyhedra at $z \approx$ ½ projected along [001]. (c) The layers of polyhedra at $z \approx 0$ and ½ projected along [100]. (d) Projection of the structure along [100]. The $Hg^{2+}\phi_n$ polyhedra are shaded with a herring-bone pattern, and the CrO_4 tetrahedra are shaded with crosses.

Hg^{2+}. The structure of wattersite contains chains of edge-sharing $Hg^{2+}\phi_6$ octahedra that link to CrO_4 tetrahedra by corner sharing, with the heteropolyhedral chains linked though bonds to a Hg^{1+}–Hg^{1+} dimer (Groat *et al.* 1995).

The structure of deanesmithite contains four symmetrically distinct Hg^{2+} cations; three are in distorted octahedral coordination, and the other is in a planar rhombic coordination (Szymański & Groat 1997). As in the structure of edoylerite, each of the $Hg^{2+}\phi_6$ octahedra in deanesmithite include two strong Hg–S bonds with bond valences of ~0.7 *vu*, whereas the other octahedral ligands are more weakly bonded to the Hg^{2+} cation. The structure of deanesmithite contains sheets of edge-sharing $Hg^{2+}\phi_6$ octahedra that are parallel to (010), with CrO_4 tetrahedra attached on either side by corner-sharing. Linkages between the heteropolyhedral sheets are accomplished by the sharing of polyhedral corners between the $Hg^{2+}\phi_6$ octahedra and CrO_4 tetrahedra with the interlayer $Hg^{2+}\phi_4$ planar rhombic polyhedron, as well as by bonds to an interlayer Hg^{1+}–Hg^{1+} cluster. If only the strong Hg–S bonds within the sheet of octahedra are considered, chains parallel to [001] are revealed (Fig. 6). These chains contain twelve-membered rings of alternating Hg^{2+} and S ions, which can be compared to the eight-membered rings of alternating Hg^{2+} and S ions in the chains found in the structure of edoylerite (Fig. 2).

CCD DETECTORS FOR STUDYING MICROCRYSTALS

The structure determination reported herein was done for a crystal with an estimated volume of only 400 μm³ and an average edge-length of 7.4 μm. Prior to the introduction of CCD X-ray area detectors, synchrotron radiation was required to obtain structures of such small crystals. However, the CCD detector is very sensitive to X-rays, permitting structure determinations for microcrystals using lab-source X-rays. In the case of Hg minerals and other highly absorbing crystals, the use of a CCD detector permits the study of very small crystals, which helps alleviate the effects of the high absorption on the data. Burns (1998) discussed the application of CCD X-ray detectors to the analysis of mineral structures.

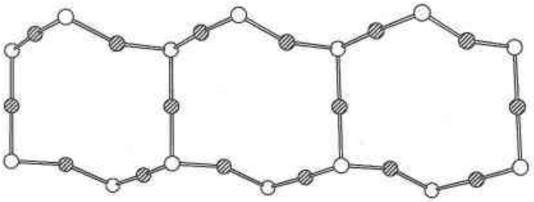

FIG. 6. The Hg–S chains that occur in the structure of deanesmithite. Only the Hg^{2+} cations and S anions and the strong (~0.7 *vu*) bonds between them are shown. The chains are parallel to [001] and are linked by weaker bonds to form sheets that are parallel to (010). Legend as in Figure 3.

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