The Canadian Mineralogist
Vol. 35, pp. 765-772 (1997)

THE CRYSTAL STRUCTURE OF DEANESMITHITE, $Hg^{1+}_2Hg^{2+}_3Cr^{6+}O_5S_2$

JAN T. SZYMAŃSKI[1]

CANMET, Natural Resources Canada, 555 Booth Street, Ottawa, Ontario K1A 0G1

LEE A. GROAT[1]

Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia V6T 1Z4

ABSTRACT

The crystal structure of deanesmithite, $Hg^{1+}_2Hg^{2+}_3Cr^{6+}O_5S_2$, a 8.1287(8), b 9.4916(7), c 6.8940(4) Å, α 100.356(6), β 110.163(7), γ 82.981(8)°, V 490.13(7) Å^3, space group $P\bar{1}$, $Z = 2$, has been solved by direct methods and refined to an R index of 2.9% on the basis of 2808 unique reflections measured with Mo$K\alpha$ radiation. There are six distinct Hg sites; two are at special positions on centers of symmetry. Hg(1) and Hg(2) form a diatomic Hg^{1+}–Hg^{1+} bond and are coordinated to additional S and O atoms. Hg(3) is in planar rhomb coordination with two S and two O atoms. The remaining three Hg sites are each coordinated to six anions, forming distorted octahedra. The octahedra share edges to form corrugated sheets parallel to (010), with one vacancy for every five occupied octahedrally coordinated sites. The sheets are decorated on both sides by CrO_4 tetrahedra that share faces with the vacant polyhedra and project in (approximately) the (010) direction. The heteropolyhedral sheets are held together by four-coördinated Hg(4) atoms and the Hg(1)–Hg(2) dimers. There are numerous similarities between the structures of deanesmithite and wattersite, another Hg-bearing mineral from the Clear Creek claim.

Keywords: deanesmithite, crystal structure, mercury, chromate, Clear Creek claim, San Benito County, California.

SOMMAIRE

Nous avons affiné la structure cristalline de la deanesmithite, $Hg^{1+}_2Hg^{2+}_3Cr^{6+}O_5S_2$, a 8.1287(8), b 9.4916(7), c 6.8940(4) Å, α 100.356(6), β 110.163(7), γ 82.981(8)°, V 490.13(7) Å^3, groupe spatial $P\bar{1}$, $Z = 2$, par méthodes directes jusqu'à un résidu R de 2.9%; l'affinement a porté sur 2808 réflexions mesurées avec rayonnement Mo$K\alpha$. La structure contient six sites distincts occupés par le Hg; deux de ces sites occupent une position spéciale, sur centres de symétrie. Hg(1) et Hg(2) forment une liaison diatomique Hg^{1+}–Hg^{1+}, et sont de plus coordonnés à des atomes S et O. Hg(3) est en liaison avec deux atomes S et deux atomes O en plan rhombique. Les trois autres sites Hg sont entourés de six anions en coordinence octaédrique difforme. Les octaèdres partagent des arêtes, ce qui donne des feuillets ondulants parallèles à (010), qui contiennent une lacune pour chaque cinq sites octaédriques occupés. Les feuillets sont décorés de chaque côté par des tétraèdres CrO_4 partageant des faces avec des polyèdres vides, et qui sont orientés sensiblement dans la direction (010). Les feuillets de hétéropolyèdres sont interliés par des atomes Hg(4) à coordinence 4 et par les dimères Hg(1)–Hg(2). Il y a de nombreux points communs entre la structure de la deanesmithite et celle de la wattersite, autre minéral de mercure du claim Clear Creek.

(Traduit par la Rédaction)

Mots-clés: deanesmithite, structure cristalline, mercure, chromate, claim de Clear Creek, comté de San Benito, Californie.

INTRODUCTION

Deanesmithite was described by Roberts *et al.* (1993). It is a rare constituent in a small prospect pit near the abandoned Clear Creek mercury mine, San Benito County, California. Deanesmithite is most closely associated with cinnabar and edoylerite (Erd *et al.* 1993) in a host rock composed principally of quartz and magnesite. Other mercury-bearing minerals identified from the Clear Creek claim include calomel, edgarbaileyite (Roberts *et al.* 1990a, Angel *et al.* 1990), eglestonite, gianellaite, hanawaltite (Roberts *et al.* 1996), native mercury, metacinnabar, montroydite, mosesite, peterbaylissite (Roberts *et al.* 1995), schuetteite, szymańskiite (Roberts *et al.* 1990b, Szymański & Roberts 1990), terlinguaite, wattersite (Roberts *et al.* 1991, Groat *et al.* 1995) and eight identified mercury-bearing phases that are currently under investigation. Deanesmithite is most likely formed as a result of the reaction between a Cr-rich hydrothermal solution and pre-existing mercury-bearing

---

[1] *E-mail address*: jan_szymanski@cc2smtp.nrcan.gc.ca, groat@eos.ubc.ca

minerals such as cinnabar (Roberts *et al.* 1993). As part of a general study of the crystal chemistry of the mercury oxysalt minerals, the crystal structure of deanesmithite was determined. Preliminary details of the crystal structure were reported in Roberts *et al.* (1993).

EXPERIMENTAL

The crystal studied was taken from the sample described by Roberts *et al.* (1993). A large tablet was examined under polarized light and was found to consist of at least four areas which extinguish individually. The tablet was cut into the individual optically homogeneous domains with a scalpel. The crystal used for the structure is a small flake, tabular (010), 0.08 mm across and 0.014 mm thick. X-ray-diffraction data were collected on an Enraf–Nonius CAD–4 single-crystal diffractometer with graphite-monochromated Mo*K*α X-radiation using the NRC-modified data-collection software with capabilities for line-profile analysis. The cell dimensions quoted in Table 1 were obtained from the least-squares fit of 50 reflections in the range 45° < 2θ < 60° using the routine TRUANG, which measures and averages the angles of the four equivalences of each reflection (+**H**, +2θ; +**H**, –2θ; –**H**, +2θ; –**H**, –2θ; where **H** represents the *h,k,l* indices, and 2θ indicates the positive or negative side of 2θ–zero). Data were collected for the whole sphere of reflection to a limit of 2θ = 60° at a speed of 1°(2θ)/minute. Three standard reflections were measured every 100 reflections, and the minor variation in these was used in scaling the data. An empirical Ψ-scan absorption correction (North *et al.* 1968) was applied to the intensity data, in conjunction with an average correction for the mean thickness of the crystal. The maximum: minimum variation in the Ψ-scan correction was 5:1. The software for the processing of all raw data was the NRCVAX system of programs (Gabe *et al.* 1989). Of the 2802 unique reflections measured, 1748 were classified as "observed" on the criterion that $I_{obs} > 2.5\sigma(I_{obs})$. The atomic scattering curves in this software are calculated from the coefficients given by Cromer & Mann (1968), and use the anomalous scattering components given by Cromer & Liberman (1970).

TABLE 1. CRYSTAL DATA: DEANESMITHITE

a (Å)	8.1287(8)	*Z*	2
b	9.4916(7)	Crystal size (mm)	0.014 × 0.08 × 0.08
c	6.8940(4)	μ (Mo*K*α; cm^{-1})	794.6
α (°)	100.356(6)	Rad/mono	Mo*K*α/graphite
β	110.163(7)	Total |*F*$_o$|	2808
γ	82.981(8)	[I ≥ 2.5σ(I)]	1748
V (Å^3)	490.13(7)	*R* (observed) %	2.92
Space group	$P\bar{1}$	*R*$_w$ (observed) %	3.08

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

$R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{0.5}, w = [\sigma^2(F_o)]^{-1}$

Anisotropic thermal parameters were used for Hg, Cr and S atoms; O atoms were refined isotropically as anisotropic refinements were unstable. The two S atoms were identified by having a scattering factor about double that of oxygen. Preliminary electron-microprobe analyses at the Geological Survey of Canada had failed

TABLE 2. ATOMIC PARAMETERS FOR DEANESMITHITE

Atom	*x*	*y*	*z*	U_{11}*	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Hg(1)	0.55957(8)	0.08546(7)	0.85556(10)	191(3)	301(3)	279(3)	83(2)	-8(2)	-72(2)	270(4)
Hg(2)	0.27861(9)	0.97327(8)	0.61713(11)	203(3)	443(4)	310(4)	5(3)	-6(3)	-96(3)	343(4)
Hg(3)	0	0	0	185(4)	223(4)	190(4)	37(3)	12(3)	1(3)	213(4)
Hg(4)	1/2	1/2	0	160(4)	352(5)	391(6)	41(4)	58(4)	1(4)	313(5)
Hg(5)	0.16981(8)	0.65337(7)	0.18197(10)	238(3)	296(3)	211(3)	21(2)	71(2)	-53(2)	248(4)
Hg(6)	0.11631(10)	0.66011(7)	0.66080(10)	357(4)	333(4)	176(3)	35(2)	35(3)	-37(3)	301(4)
Cr	0.37608(32)	0.29969(26)	0.40189(38)	140(11)	190(11)	194(12)	36(9)	-2(9)	-15(9)	189(11)
S(1)	0.04370(50)	0.81653(43)	0.40826(61)	146(18)	267(19)	208(18)	14(14)	13(14)	-46(14)	219(19)
S(2)	0.19375(53)	0.48557(44)	0.88688(65)	175(18)	267(20)	262(20)	37(15)	55(15)	-44(15)	237(19)
O(1)	0.49763(177)	0.30035(140)	0.25609(207)							336(29)
O(2)	0.51029(143)	0.30784(112)	0.65049(168)							198(21)
O(3)	0.26885(164)	0.14737(130)	0.33021(195)							287(25)
O(4)	0.81307(137)	0.15391(108)	0.03067(160)							174(20)
O(5)	0.23193(173)	0.44113(139)	0.38588(205)							325(28)

*U_{ij} and *U* values are listed × 10^4. Displacement factors = $-2\pi^2\{U_{11}h^2(a^*)^2 + \ldots + 2U_{12}hka^*b^* + \ldots\}$

to reveal the presence of sulfur, and the crystal was submitted for X-ray analysis as a "mixed mercury–chromium oxide". It was during site-occupancy refinement of the light atom sites that two ligands were shown to be twice as heavy as the remaining atoms of oxygen. These sites were interpreted as S atoms; the presence of S was later confirmed by more accurate electron-microprobe analyses. The S peak had been nearly buried under the Hg peak in the energy-dispersion spectra. A secondary extinction parameter was used in the final stages of the full-matrix least-squares refinement, which converged to an *R* index of 2.9% (defined in Table 1). The maximum final fractional shift (Δ/σ) was about 0.1%. Positional coordinates and anisotropic and isotropic displacement factors are given in Table 2. Selected interatomic distances and angles are given in Table 3. Structure factors may be obtained from the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Canada K1A 0S2.

DESCRIPTION OF THE STRUCTURE

Coordination polyhedra of cations in the deanesmithite structure are shown in Figure 1. There are six distinct Hg positions in the structure. Hg(1) and Hg(2), both in the general 2*i* position, form a diatomic Hg^{1+}–Hg^{1+} bond typical of mercurous compounds. The bond length (2.536 Å) is similar to those reported for hanawaltite (2.526 and 2.56 Å, Roberts *et al.* 1996), wattersite (2.526 Å, Groat *et al.* 1995), eglestonite (2.516 Å, Mereiter *et al.* 1992), kuznetsovite (2.64 Å, Solov'eva *et al.* 1991), edgarbaileyite (2.522 and 2.524 Å, Angel *et al.* 1990), szymańskiite (2.494 and 2.513 Å, Szymański & Roberts 1990), terlinguaite (2.703 Å, Brodersen *et al.* 1989), magnolite (2.53 Å, Grice 1989), shakhovite (2.543 Å, Tillmans *et al.* 1982), synthetic chursinite (2.535 Å, Kamenar & Kaitner 1973), calomel (2.53 Å, Wyckoff 1965), synthetic mosesite (2.54 Å, Wyckoff 1965), and other synthetic compounds (see list in Liao & Zhang 1995). Hg(1) is also coordinated by three O atoms at distances of 2.11, 2.66 and 2.82 Å. The one Hg and three O atoms form an extremely distorted tetrahedral coordination polyhedron around Hg(1). Bond-valence analysis (Table 4) shows that Hg(1) is underbonded (0.78 *vu:* valence units) with this arrangement. There is an additional O(1) atom 3.27 Å from Hg(1), which may bond to the Hg atom, contributing 0.025 *vu.* However, this is unlikely, as there is an Hg atom even closer to Hg(1) (at 3.227 Å). Two additional O atoms, at distances of 3.66 and 3.68 Å from Hg(1), are unlikely to form bonds with the Hg atom.

The Hg(2) position is coordinated by Hg(1), one S and two O atoms. The Hg(2)–S(1), –O(1), and –O(3) distances are 2.442, 3.06 and 2.77 Å, respectively. There is an additional S(1) atom 3.067 Å from Hg(2). Does this atom form a bond with the Hg atom? Most of the Hg–S bonds in the structure are considerably shorter, with an average length of 2.38(3) Å (based on seven distances). However, this S(1) atom contributes 0.133 *vu* to Hg(2), without which the Hg(2) position

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) FOR DEANESMITHITE

Hg(1)–Hg(2)a		2.536(1)	O(3)–Hg(3)–O(4)g	× 2	92.8(4)
–O(2)		2.66(1)	O(3)–Hg(3)–O(4)k	× 2	87.2(4)
–O(3)b		2.82(1)	O–Hg(3)–O		90.0
–O(4)c		2.11(1)			
			S(2)h–Hg(4)–O(1)	× 2	83.1(3)
Hg(2)–Hg(1)d		2.536(1)	S(2)h–Hg(4)–O(1)j	× 2	96.9(3)
–S(1)		2.442(4)	S(2)h–Hg(4)–O(2)h	× 2	89.0(3)
–S(1)e		3.067(4)	S(2)h–Hg(4)–O(2)f	× 2	91.0(3)
–O(1)f		3.06(1)	O(1)–Hg(4)–O(2)f	× 2	81.7(4)
–O(3)d		2.77(1)	O(1)–Hg(4)–O(2)h	× 2	98.3(4)
–O(4)f		3.23(1)	<O–Hg(4)–O>		90.0
Hg(3)–O(3)	× 2	2.84(1)	S(1)–Hg(5)–S(2)i		76.7(1)
–O(4)g	× 2	2.01(1)	S(1)–Hg(5)–O(2)f		102.2(3)
<Hg(3)–O>		2.43	S(1)–Hg(5)–O(4)j		94.6(3)
			S(1)–Hg(5)–O(5)		96.5(3)
Hg(4)–S(2)h	× 2	2.352(4)	S(2)h–Hg(5)–S(2)i		87.2(1)
–O(1)	× 2	2.82(1)	S(2)h–Hg(5)–O(2)f		96.9(3)
–O(2)h	× 2	2.77(1)	S(2)h–Hg(5)–O(4)j		84.8(3)
<Hg(4)–φ>		2.65	S(2)i–Hg(5)–O(4)j		122.3(2)
			S(2)h–Hg(5)–O(5)		87.9(3)
Hg(5)–S(1)		2.393(4)	S(2)i–Hg(5)–O(5)		70.1(3)
–S(2)h		2.397(4)	O(2)f–Hg(5)–O(4)j		81.9(3)
–S(2)i		3.234(4)	O(2)f–Hg(5)–O(5)		86.0(4)
–O(2)f		2.50(1)	<O–Hg(5)–O>		90.6
–O(4)j		2.58(1)			
–O(5)		2.56(1)	S(1)–Hg(6)–O(1)f		88.3(3)
<Hg(5)–φ>		2.61	S(1)–Hg(6)–O(4)f		96.8(3)
			S(1)–Hg(6)–O(5)		89.9(3)
Hg(6)–S(1)		2.364(4)	S(1)–Hg(6)–O(5)i		103.2(3)
–S(2)		2.359(4)	S(2)–Hg(6)–O(1)f		90.8(3)
–O(1)f		3.05(1)	S(2)–Hg(6)–O(4)f		88.6(3)
–O(4)f		2.45(1)	S(2)–Hg(6)–O(5)i		77.1(3)
–O(5)		2.85(1)	S(2)–Hg(6)–O(5)		84.4(3)
–O(5)i		2.99(1)	O(1)f–Hg(6)–O(4)f		77.3(4)
<Hg(6)–φ>		2.68	O(1)f–Hg(6)–O(5)		73.0(4)
			O(4)f–Hg(6)–O(5)i		106.4(4)
Cr–O(1)		1.64(1)	O(5)–Hg(6)–O(5)i		101.1(4)
–O(2)		1.68(1)	<O–Hg(6)–O>		89.7
–O(3)		1.69(1)			
–O(5)		1.66(1)	O(1)–Cr–O(2)		107.6(6)
<Cr–O>		1.67	O(1)–Cr–O(3)		110.0(7)
			O(1)–Cr–O(5)		111.6(7)
			O(2)–Cr–O(3)		109.8(6)
			O(2)–Cr–O(5)		108.2(6)
			O(3)–Cr–O(5)		109.6(6)
			<O–Cr–O>		109.5

Note: <M–φ> denotes the mean metal-ligand distance (Å). Equivalent positions: a = x $y - 1$, z; b = $1 - x$, $\bar{y}$, $1 - z$; c = x, y, $1 + z$; d = x, $1 + y$, z; e = $\bar{x}$, $1 - y + 1$, $1 - z$; f = $1 - x$, $1 - y$, $1 - z$; g = $x - 1$, y, z; h = x, y, $z - 1$; i = $\bar{x}$, $1 - y$, $1 - z$; j = $1 - x$, $1 - y$, $\bar{z}$; k = $1 - x$, $\bar{y}$, $\bar{z}$.

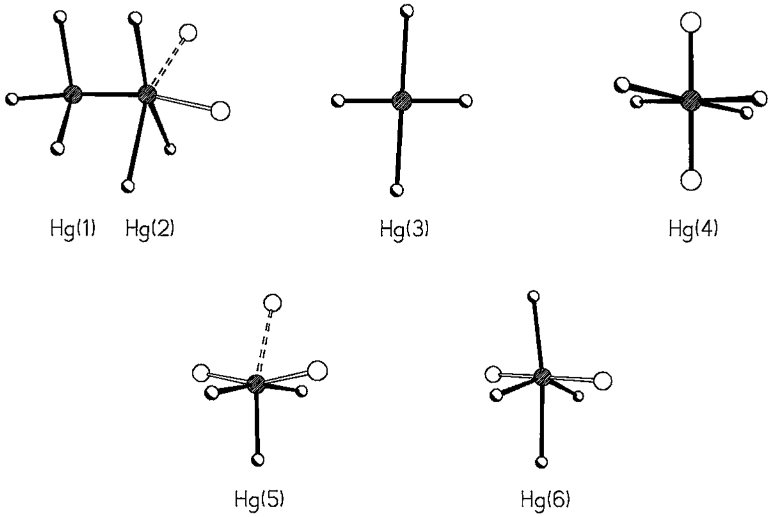

FIG. 1. Coordination polyhedra of Hg positions in the structure of deanesmithite. Hg atoms are shaded, O atoms are shadowed spheres, and S atoms are open larger spheres. Hg–O bonds are solid lines, Hg–S bonds are open lines, and Hg–S bonds over 3.0 Å are broken open lines. In this and succeeding figures, the assumption is made that there are Hg(2)–S(1)e and Hg(2)–O(4) bonds, but no Hg(3)–S bonds (see text).

TABLE 4. BOND-VALENCE* ARRANGEMENT IN DEANESMITHITE

	Hg(1)	Hg(2)	Hg(3)	Hg(4)	Hg(5)	Hg(6)	Cr	Total
S(1)		0.719(8) 0.133(1)			0.692(6)	0.735(6)		2.28(1)
S(2)				0.754(6)$^{\times 2\downarrow}$	0.686(6) 0.1535(9)	0.743(6)		2.34(1)
O(1)		0.044(1)		0.101(2)$^{\times 2\downarrow}$		0.061(1)	1.49(5)	1.70(5)
O(2)	0.128(3)			0.114(3)$^{\times 2\downarrow}$	0.222(6)		1.31(4)	1.77(4)
O(3)	0.083(2)	0.095(3)	0.097(2)$^{\times 2\downarrow}$				1.27(4)	1.55(4)
O(4)	0.57(2)	0.0267(7)	0.92(3)$^{\times 2\downarrow}$		0.181(5)	0.253(7)		1.98(4)
O(5)					0.190(5)	0.095(2) 0.069(2)	1.40(4)	1.75(4)
Total	0.78(2)	1.018(9)	2.03(4)	1.94(1)	2.13(1)	1.96(1)	5.47(9)	

*Calculated from the curves of Brese & O'Keeffe (1991) and Brown (1981); values in *vu*.

would be underbonded. Although this contributes to the overbonding at S(1) (2.28 *vu*), the assumption is made that there is a weak bond between these two atoms.

There is also an O(4) atom 3.23 Å from Hg(2), which may form a bond with the Hg atom. If O(4) is included, the coordination polyhedron around Hg(2) becomes a distorted octahedron. In addition, the closest non-bonded cation to Hg(2) is an Hg atom at a distance of 3.496 Å. However, the bond-valence contribution is only 0.027 *vu*, and each O(4) atom is already bonded to four Hg atoms. Despite this, the assumption is made that there is a weak Hg(2)–O(4) bond, based largely on the geometrical argument.

Relative to other Hg–φ (φ: unspecified anion) bond lengths in the deanesmithite structure, the Hg(1)–O(4) and Hg(2)–S(1) distances are very short. Together with the Hg(1)–Hg(2) dimer, they form an almost linear φ–Hg–Hg–φ group, similar to those reported from other Hg^{1+} compounds. The deviation from linearity is illustrated by O(4)–Hg(1)–Hg(2) and S(1)–Hg(2)–Hg(1) angles of 171.3 and 167.6°.

The rest of the Hg atoms in the structure are divalent. Two of these Hg atoms, Hg(3) and Hg(4), are at centers of symmetry; this accounts for the five Hg atoms in the formula unit. Hg(3), in the special position 1*a*, is bonded to two O(3) and two O(4) atoms in a planar rhombic coordination. The Hg(3)–O(3) and Hg(3)–O(4) distances are 2.84 and 2.01 Å, respectively, and the O–Hg–O angles are 87.2 and 92.8°. There are two S(1) atoms 3.464 Å away from Hg(3). Do these atoms form bonds with the Hg atom? The bond-valence contribution would be considerable (0.109 *vu*), but would contribute to overbonding at Hg(3) and at S(1). The assumption is that these atoms do not form bonds with Hg(3).

Hg in four-coordination is relatively common, although usually in a distorted tetrahedral arrangement, such as that seen in pinchite (Hawthorne *et al.* 1994). However, in hanawaltite (Roberts *et al.* 1996), one of the Hg atoms is bonded to two O (1.9 Å) and two Cl (2.994 Å) atoms in a similar planar rhombic configuration.

Hg(4), at the special position 1*e*, is coordinated by two S and four O atoms (in *trans* arrangement), forming a slightly distorted octahedron. The degrees of distortion (mean-square relative deviation from the average: Brown & Shannon 1973) for the bond lengths (Δ) and angles (σ^2) are 0.0063 and 39.2, respectively. The distances between Hg(4) and the S(2), O(1) and O(2) atoms are 2.352, 2.82 and 2.77 Å, respectively. The S–Hg–O angles range from 83.1 to 96.9°, and the O–Hg–O angles are 81.7 and 98.3°. The O atoms at the equatorial corners of the octahedron are shared with adjacent CrO_4 tetrahedra. Because of the short Hg–S distances, the Hg(4) octahedron is slightly compressed in the S–Hg–S direction.

Hg(5), at the general position 2*i*, is coordinated by two S and three O atoms at distances of 2.393 to 2.58 Å. There is a third S atom at a distance of 3.234 Å. If this atom is included in the Hg(5) coordination sphere, the resulting geometry is a distorted octahedron (with φ–Hg–φ angles ranging from 70.1 to 122.3°, and $\Delta = 0.0122$, $\sigma^2 = 166.4$). Note also that the closest non-bonded Hg atom is 3.4069 Å away from Hg(5). However, the bond-valence contribution of the S atom is 0.1535 valence units, which contributes to overbonding at both the Hg(5) and S(2) sites. Nevertheless, the assumption is

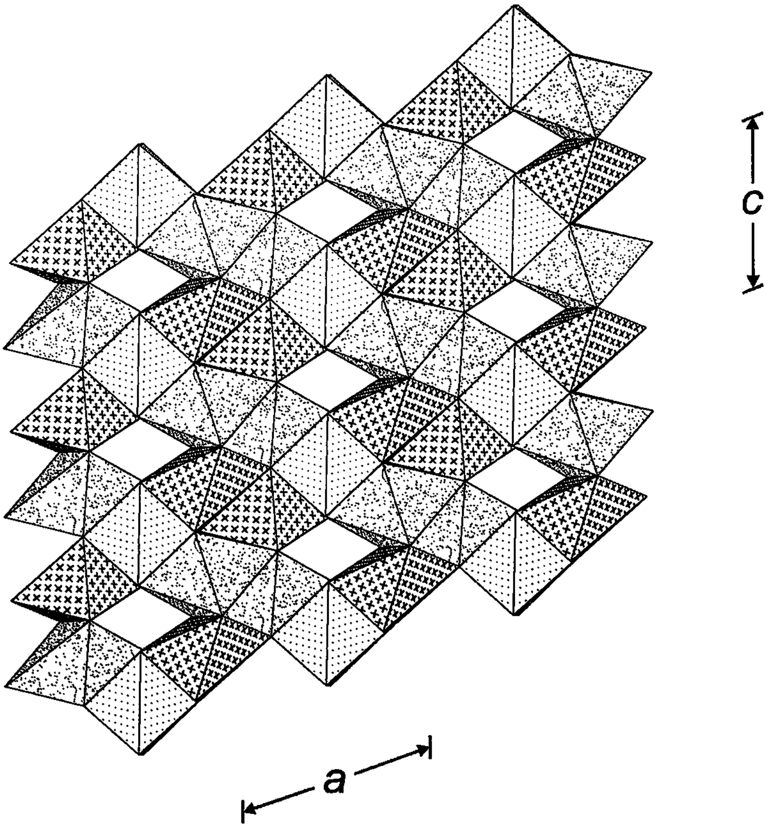

FIG. 2. The sheet of heteropolyhedra in deanesmithite, projected onto (010). Hg(4), Hg(5), and Hg(6) octahedra are denoted by regular dots, crosses, and random dots, respectively.

made that there is a weak bond between these two atoms, largely on the basis of the geometrical argument.

Hg(6), at the general position 2*i*, is coordinated by two S and four O atoms in a distorted octahedral coordination ($\Delta = 0.0120$, $\sigma^2 = 105.5$). The Hg(6)–S distances are 2.359 and 2.364 Å, and the Hg(6)–O distances range from 2.45 to 3.05 Å. The φ–Hg–φ angles vary from 73.0 to 106.4°. The closest non-bonded O and Hg atoms are at distances of 3.44 and 3.464 Å, respectively.

The Cr atom is tetrahedrally coordinated by four O atoms at distances of 1.64 to 1.69(1) Å, forming a typical tetrahedral $[CrO_4]^{2-}$ group. The <Cr–O> distance is 1.67 Å, and the O–Cr–O angles vary from 107.6 to 111.6°. The lengths of the tetrahedron edges range from 2.67 to 2.75 Å.

The Hg(4), Hg(5), and Hg(6) octahedra share edges to form corrugated sheets parallel to (010), with one vacancy for every five occupied octahedral sites (Fig. 2). This part of the structure may also be described as being composed of ribbons of edge-sharing Hg(4) and Hg(6) octahedra (parallel to [101]) linked by pairs of (edge-sharing) Hg(5) octahedra. The Hg(4) octahedra have four shared and eight unshared edges, with lengths of 3.66 to 3.88 Å and 3.45 to 4.23 Å, respectively. The Hg(5) and Hg(6) octahedra have five shared and seven unshared edges; the lengths are 3.38 to 3.93 Å (shared) and 3.33 to 3.81 Å (unshared) for Hg(5), and 3.36 to 4.51 Å (shared) and 3.47 to 4.38 Å (unshared) for Hg(6). The lengths of the edges of the vacant site are 3.45, 3.51 and 3.66 Å (each × 2).

The sheets of octahedra are decorated on each side by CrO_4 tetrahedra that share O(1), O(2), and O(5) atoms with the six octahedra surrounding each vacant octahedral site (Fig. 3). In effect, each vacant site shares two (opposite) faces with CrO_4 tetrahedra. The tetrahedra project from the sheets in approximately the [010] direction, and are offset because of the modulation of the sheet.

The sheets of heteropolyhedra are held together by the four-coordinated Hg(3) atoms and the Hg(1)–Hg(2) dimers. Each Hg(3) polyhedron shares O(3) atoms with CrO_4 tetrahedra, and O(4) atoms with Hg(5) and Hg(6) octahedra. The O(3) and O(4) atoms also form bonds with Hg(1)–Hg(2) dimers, as do the S(1), O(1), and O(2) atoms. Note that this part of the structure is very similar to that of hanawaltite (Roberts *et al.* 1996).

DISCUSSION

The results of the structural analysis confirm the formula of deanesmithite as $Hg^{1+}_2Hg^{2+}_3Cr^{6+}O_5S_2$. It is the second reported mercury chromate sulfide (after

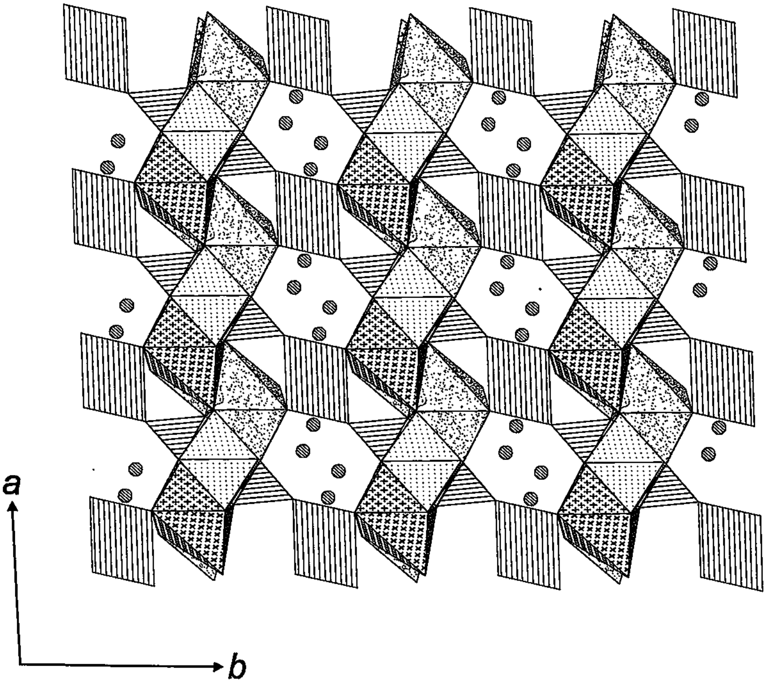

FIG. 3. The structure of deanesmithite viewed down [001], with shading as in Figure 2. Hg(3) and Cr polyhedra are denoted by parallel lines, and Hg(1) and Hg(2) atoms are shown as spheres.

edoylerite, $Hg^{2+}{}_3Cr^{6+}O_4S_2$: Erd *et al.* 1993) and the third reported mercury chromate (after edoylerite and wattersite, $Hg^{1+}{}_4Hg^{2+}Cr^{6+}O_6$: Roberts *et al.* 1991, Groat *et al.* 1995). The crystal structure of edoylerite has not been published. However, according to Erd *et al.* (1993), a preliminary structure refinement shows three Hg^{2+} atoms in octahedral coordination, two S^{2-} atoms in tetrahedral coordination, and one Cr^{6+} atom in tetrahedral coordination. This suggests that the structures of edoylerite and deanesmithite are similar, although there is no Hg^{1+}–Hg^{1+} dimer in the structure of edoylerite.

There are numerous similarities between the structures of deanesmithite and wattersite. In wattersite, there are three distinct Hg positions, one of which is divalent and in distorted octahedral coordination with O ($\langle Hg–O \rangle$ 2.50 Å, $\Delta = 0.0155$). Adjacent octahedra share edges and are linked to neighboring CrO_4 tetrahedra, forming chains (rather than sheets) that extend parallel to [001]. The units of heteropolyhedra are linked by O–Hg bonds to an Hg^{1+}–Hg^{1+} dimer. However, there is no equivalent to the deanesmithite $Hg^{2+}(3)$ position in wattersite.

According to Roberts *et al.* (1993), deanesmithite has been identified from the type specimen of edoylerite. Wattersite is most closely associated with cinnabar and native mercury at the Clear Creek deposit (Roberts *et al.* 1991). Although it is not generally found in close association with deanesmithite and edoylerite, the chemical and structural similarities are intriguing. Unlike deanesmithite and edoylerite, wattersite contains no S, but has a higher Hg^{1+}/Hg^{2+} ratio and a less polymerized structure than deanesmithite.

Deanesmithite is thought to have formed as a result of the reaction between a Cr-rich hydrothermal solution and pre-existing Hg-bearing minerals such as cinnabar (Roberts *et al.* 1993). Edoylerite is considered to be a primary alteration product of cinnabar (Erd *et al.* 1993). However, it is important to note that cinnabar is extremely insoluble. This raises the possibility that deanesmithite, edoylerite, and wattersite are primary phases. If so, the concentration of Hg in solution becomes an important factor (J.D. Grice, pers. comm.). An excess of Hg(liquid) readily reduces Hg^{2+} to $(Hg_2)^{2+}$ [and the addition of S^{2-} to $(Hg_2)^{2+}$ in solution gives Hg(l) + HgS]. If there is no excess Hg(l), oxidation proceeds entirely to Hg^{2+}. Excess Hg(l) would therefore result in Hg(l) + HgS + wattersite (mostly Hg^{2+}, no S); a deficiency in Hg(l) would produce HgS + deanesmithite + (with more oxidation) edoylerite (both with S, and Hg^{1+} in deanesmithite).

ACKNOWLEDGEMENTS

The authors thank T.S. Ercit and F.C. Hawthorne for helpful discussions concerning the deanesmithite structure, A.C. Roberts, D.K. Smith and J.-P. Charland for their comments on the original manuscript, and Gail Dunning, J.L. Jambor, and J.D. Grice for their thoughts on Hg-oxysalt paragenesis. Financial support was provided by the Natural Sciences and Engineering Research Council of Canada in the form of a Research Grant to LAG.

REFERENCES

ANGEL, R.J., CRESSEY, G. & CRIDDLE, A. (1990): Edgarbaileyite, $Hg_6Si_2O_7$: the crystal structure of the first mercury silicate. *Am. Mineral.* **75**, 1192-1196.

BRESE, N.E. & O'KEEFFE, M. (1991): Bond-valence parameters for solids. *Acta Crystallogr.* **B47**, 192-197.

BRODERSEN, K., GÖBEL, G. & LIEHR, G. (1989): Terlinguait $Hg_4O_2Cl_2$–ein Mineral mit ungewöhnlichen Hg_3–Baueinheiten. *Z. Anorg. Allg. Chem.* **575**, 145-153.

BROWN, I.D. (1981): The bond-valence method: An empirical approach to chemical structure and bonding. *In* Structure and Bonding in Crystals II (M. O'Keefe & A. Navrotsky, eds.). Academic Press, New York (1-30).

________ & SHANNON, R.D. (1973): Empirical bond-strength–bond-length curves for oxides. *Acta Crystallogr.* **A29**, 266-282.

CROMER, D.T. & LIBERMAN, D. (1970): Relativistic calculation of anomalous scattering factors for X rays. *J. Chem. Phys.* **53**, 1891-1898.

________ & MANN, B.J. (1968): X-ray scattering factors computed from numerical Hartree–Fock wave functions. *Acta Crystallogr.* **A24**, 321-324.

ERD, R.C., ROBERTS, A.C., BONARDI, M., CRIDDLE, A.J., LE PAGE, Y. & GABE, E.J. (1993) Edoylerite, $Hg^{2+}{}_3Cr^{6+}O_4S_2$, a new mineral from the Clear Creek claim, San Benito County, California. *Mineral. Rec.* **24**, 471-475.

GABE, E.J., LE PAGE, Y., CHARLAND, J.-P., LEE, F.L. & WHITE, P.S. (1989): NRCVAX – an interactive program system for structure analysis. *J. Appl. Crystallogr.* **A22**, 384-387.

GRICE, J.D. (1989): The crystal structure of magnolite, $Hg^{1+}{}_2Te^{4+}O_3$. *Can. Mineral.* **27**, 133-136.

GROAT, L.A., ROBERTS, A.C. & LE PAGE, Y. (1995): The crystal structure of wattersite, $Hg^{1+}{}_4Hg^{2+}Cr^{6+}O_6$. *Can. Mineral.* **33**, 41-46.

HAWTHORNE, F.C., COOPER, M. & SEN GUPTA, P.K. (1994): The crystal structure of pinchite, $Hg_5Cl_2O_4$. *Am. Mineral.* **79**, 1199-1203.

KAMENAR, B. & KAITNER, B. (1973): The crystal structure of mercury (I) orthoarsenate. *Acta Crystallogr.* **B29**, 1666-1669.

LIAO, M. & ZHANG, Q. (1995): Hg–Hg bonding in mercurous $Hg(I)_2L_2$ compounds: the influence of ligand electronegativity. *J. Molecular Structure* (*Theochem.*) **358**, 195-203.

Mereiter, K., Zemann, J. & Hewat, A.W. (1992): Eglestonite, $[Hg_2]_3Cl_3O_2H$: confirmation of the chemical formula by neutron powder diffraction. *Am. Mineral* **77**, 839-842.

North, A.C.T., Phillips, D.C. & Mathews, F.S. (1968): A semi-empirical method of absorption correction. *Acta Crystallogr.* **A24**, 351-359.

Roberts, A.C., Bonardi, M., Erd, R.C., Criddle, A.J. & Le Page, Y. (1991): Wattersite, $Hg^{1+}_4Hg^{2+}Cr^{6+}O_6$, a new mineral from the Clear Creek Claim, San Benito County, California. *Mineral. Rec.* **22**, 269-272.

________, ________, ________, ________, Stanley, C.J., Cressey, G., Angel, R.J. & Laflamme, J.H.G. (1990a): Edgarbaileyite – the first known silicate of mercury, from California and Texas. *Mineral. Rec.* **21**, 215-220.

________, Ercit, T.S., Erd, R.C. & Oscarson, R.L. (1990b): Szymańskiite, $Hg^{1+}_{16}(Ni,Mg)_6(CO_3)_{12}(OH)_{12}(H_3O)^{1+}_8\cdot 3H_2O$, 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, $Hg^{1+}_3(CO_3)(OH)\cdot 2H_2O$, a new mineral species from the Clear Creek claim, San Benito County, California. *Can. Mineral.* **33**, 47-53.

________, Grice, J.D., Gault, R.A., Criddle, A.J. & Erd, R.C. (1996): Hanawaltite, $Hg^{1+}_6Hg^{2+}[Cl,(OH)]_2O_3$–A new mineral from the Clear Creek claim, San Benito County, California: description and crystal structure. *Powder Diffraction* **11**, 45-50.

________, Szymański, J.T., Erd, R.C., Criddle, A.J. & Bonardi, M. (1993): Deanesmithite, $Hg^{1+}_2Hg^{2+}_3Cr^{6+}O_5S_2$, a new mineral species from the Clear Creek Claim, San Benito County, California. *Can. Mineral.* **31**, 787-793.

Solov'eva, L.P., Tsybulya, S.V., Zabolotnyl, V.A. & Pal'chik, N.A. (1991): Determination and refinement of the structure of the mineral kuznetsovite from X-ray diffraction powder data. *Sov. Phys. Crystallogr.* **36**, 731-732.

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.

Tillmans, E., Krupp, R. & Abraham, K. (1982): New data on the mercury antimony mineral shakovite: chemical composition, unit cell and crystal structure. *Tschermaks Mineral. Petrogr. Mitt.* **30**, 227-235.

Wyckoff, R.W.G. (1965): *Crystal Structures* **1, 3.** John Wiley & Sons, New York, N.Y.

Received November 25, 1996, revised manuscript accepted April 30, 1997.