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THE CRYSTAL STRUCTURE OF WATTERSITE, $Hg_4^{1+}Hg^{2+}Cr^{6+}O_6$*

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ABSTRACT

The crystal structure of wattersite, $Hg_4^{1+}Hg^{2+}Cr^{6+}O_6$, *a* 11.274(2), *b* 11.669(2), *c* 6.603(1) Å, β 98.19(2)°, *V* 859.8(3) Å^3, space group *C*2/*c*, *Z* = 4, has been solved by direct methods, and refined to an *R* index of 5.5% based on 1261 unique reflections measured with Mo*K*α radiation on an automated four-circle diffractometer. There are three distinct Hg positions in the wattersite structure. Hg(1) is divalent and is coordinated by six atoms of oxygen, forming a distorted octahedron. Hg(2) and Hg(3) form a diatomic Hg^+–Hg^+ bond and are coordinated by three and four oxygen atoms, respectively. Adjacent Hg(1) octahedra share edges and are linked to neighboring CrO_4 tetrahedra, forming chains of composition $[HgCrO_6]^{6-}$ that extend parallel to [001]. These heteropolyhedral chains are linked by O–Hg bonds to the Hg(2)–Hg(3) dimer.

Keywords: wattersite, crystal structure, mercury, chromate.

SOMMAIRE

La structure cristalline de la wattersite, $Hg_4^{1+}Hg^{2+}Cr^{6+}O_6$, *a* 11.274(2), *b* 11.669(2), *c* 6.603(1) Å, β 98.19(2)°, *V* 859.8(3) Å^3, groupe spatial *C*2/*c*, *Z* = 4, a été résolue par méthodes directes et affinée jusqu'à un résidu *R* de 5.5% sur 1261 réflexions uniques mesurées avec rayonnement Mo*K*α et un diffractomètre automatique à quatre cercles. Le mercure occupe trois positions distinctes. Hg(1) est bivalent, et lié à six atomes d'oxygène formant un octaèdre difforme. Hg(2) et Hg(3) forment une liaison Hg^+–Hg^+, et sont respectivement coordonnés par trois et quatre atomes d'oxygène. Les octaèdres Hg(1) adjacents partagent des arêtes, et sont liés aux tétraèdres CrO_4, formant des chaînes de composition $[HgCrO_6]^{6-}$ et parallèles à [001]. Ces chaînes hétéropolyédriques sont reliées au dimère Hg(2)–Hg(3) par des liaisons O–Hg.

Mots-clés: wattersite, structure cristalline, mercure, chromate.

INTRODUCTION

Wattersite was first described by Roberts *et al.* (1991) as a rare mineral collected from a prospect pit near the Clear Creek mercury mine, San Benito County, California. It is closely associated with cinnabar and native mercury in a host rock composed predominantly of quartz and chalcedony. Other mercury-bearing minerals present in the pit are calomel, deanesmithite, edgarbaileyite, edoylerite, eglestonite, gianellaite, metacinnabar, montroydite, mosesite, peterbaylissite, szymańskiite, terlinguaite, and four unidentified phases currently under investigation. Preliminary structural work by one of the authors (YL) showed that the space group is *C*2/*c* with one Hg^{2+} atom in octahedral coordination, four Hg^{1+} atoms with Hg–Hg bonds, and one Cr^{6+} atom in tetrahedral coordination. However, data collection was hampered by the extremely high absorption-coefficient (901.4 cm^{-1}), and details of the structure remained obscure. As part of a general study of the crystal chemistry of the mercury oxysalt minerals, the crystal structure of wattersite was re-examined.

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EXPERIMENTAL

The crystal studied was taken from the sample described by Roberts *et al.* (1991). Because of its small size, no attempt was made to grind a sphere, despite the high absorption-coefficient. The crystal was mounted on a Siemens *P*3 automated four-circle diffractometer equipped with a molybdenum-target X-ray tube (operating at 50 kV, 40 mA) and a highly oriented graphite-crystal monochromator mounted with equatorial geometry. Twenty-five reflections were centered using an automated search routine, and the correct unit-cell was selected from an array of real-space vectors corresponding to potential unit-cell axes. Least-squares refinement of these reflections produced the monoclinically constrained cell dimensions given in Table 1.

Intensity data were collected in the θ–2θ scan mode, using 96 steps with a scan range from $[2\theta(\mathrm{Mo}K\alpha_1 - 1.1]^\circ$ to $[2\theta(\mathrm{Mo}K\alpha_1 + 1.1]^\circ$ and a variable scan-rate between 0.5 and 29.3°/min depending on the intensity of an initial one-second count at the center of the scan range. Backgrounds were measured for half the scan time at the beginning and end of each scan. Two standard reflections were monitored every 23 measurements to check for stability and constancy of crystal alignment. Three sets of data were collected; the first two were rejected because of poor absorption corrections. Between collections, the crystal was remounted on the fiber at a new angle relative to the ϕ axis of rotation, in an attempt to improve the absorption correction. For the final collection, a total of 2635 reflections were measured over two asymmetric units from 3 to 60° 2θ. Eleven strong reflections uniformly distibuted with regard to 2θ were measured at 10° intervals of ψ (the azimuthal angle corresponding to rotation of the crystal about its diffraction vector) from 0 to 350°, after the method of North *et al.* (1968). These data were used to calculate an ellipsoid empirical absorption-correction, and the *R*(azimuthal) index was reduced from 37.7% to 6.0%. This correction was then applied to the entire data-set, and the merging *R*(symmetric) was 10.5%. The data were also corrected for Lorentz, polarization and background effects, averaged and reduced to structure factors. Of the 1261 unique reflections, 933 were classed as observed $[I \geq 3\sigma(I)]$.

TABLE 1. MISCELLANEOUS INFORMATION: WATTERSITE

a (Å)	11.274(2)	μ (cm^{-1})	901.4
b	11.669(2)	Rad/mono	Mo$K\alpha$/graphite
c	6.603(1)	Total I	2635
β (°)	98.19(2)	*R* (azimuthal) %	6.0
V (Å)	859.8(3)	Total $\lvert F_o\rvert$	1261
Space group	*C*2/*c*	$[I \geq 3\sigma(I)]$	933
Z	4	*R* (observed) %	5.5
Crystal size	0.02 × 0.05 × 0.07 mm	*wR* (observed) %	4.8

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

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

SOLUTION AND REFINEMENT OF THE STRUCTURE

The Siemens SHELXTL PC system of programs was used throughout this work. Scattering curves for neutral atoms together with anomalous dispersion coefficients were taken from Cromer & Mann (1968) and Cromer & Liberman (1970). *R* indices are of the form given in Table 1 and are expressed as percentages. The structure was solved by direct methods in the space group *C*2/*c*, as suggested by Roberts *et al.* (1991). The solution with the maximum figure of merit revealed most of the cation positions; positions of the remaining cations and of the anions were located on difference-Fourier maps, and the structure was refined to 9.9% for an isotropic displacement model. Conversion to anisotropic displacement factors

TABLE 2. ATOMIC PARAMETERS FOR WATTERSITE

Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	*Ueq**
Hg(1)	0	0	0	100(8)	149(5)	155(5)	25(5)	16(5)	-9(4)	135(4)
Hg(2)	0.2729(1)	0.07744(6)	0.2988(1)	308(8)	148(4)	286(5)	36(4)	10(5)	-70(4)	250(4)
Hg(3)	0.3363(1)	0.27667(6)	0.2099(1)	201(7)	134(4)	233(4)	14(4)	-7(4)	-50(3)	193(3)
Cr	1/2	0.8167(4)	1/4							133(9)
O(1)	0.3579(19)	0.4508(13)	0.1458(25)							264(37)
O(2)	0.5052(17)	0.7335(12)	0.0451(21)							192(34)
O(3)	0.3708(20)	0.8941(13)	0.2049(26)							268(37)

*The values given for all thermal parameters are × 10^4

for the Hg atoms resulted in convergence at an R index of 5.5%. Attempts to refine anisotropic displacement factors for the other atoms were unsuccessful, owing to problems associated with the very high absorption for this mineral, together with the poor quality of the crystal. Refinement in space group Cc did not significantly improve the final R index. Positional coordinates and anisotropic and equivalent 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, Ontario K1A 0S2.

TABLE 3. SELECTED INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN WATTERSITE

Hg(1)	-O(1)a	×2	2.06(2)	O(1)c-Hg(2)-O(3)h		78.1(7)
	-O(1)b	×2	2.70(2)	O(1)c-Hg(2)-O(3)g		96.1(6)
	-O(2)a	×2	2.74(1)	O(3)h-Hg(2)-O(3)g		102.2(6)
<Hg(1)	-O>		2.50	Hg(3)-Hg(2)-O(1)c		153.3(5)
				Hg(3)-Hg(2)-O(3)h		125.1(5)
Hg(2)	-Hg(3)		2.526(1)	Hg(3)-Hg(2)-O(3)g		91.6(3)
				<Hg, O-Hg(2)-O>		107.7
Hg(2)	-O(1)c		2.16(2)			
	-O(3)h		2.53(2)	O(1)-Hg(3)-O(2)e		78.8(6)
	-O(3)g		2.77(2)	O(1)-Hg(3)-O(2)g		96.8(6)
<Hg(2)	-O>		2.49	O(1)-Hg(3)-O(3)c		72.2(7)
				O(2)e-Hg(3)-O(2)g		93.4(4)
Hg(3)	-O(1)		2.10(2)	O(2)e-Hg(3)-O(3)c		143.6(5)
	-O(2)e		2.63(2)	O(2)g-Hg(3)-O(3)c		111.3(5)
	-O(2)g		2.71(2)	Hg(2)-Hg(3)-O(2)e		110.4(3)
	-O(3)c		2.83(2)	Hg(2)-Hg(3)-O(2)g		87.7(3)
<Hg(3)	-O>		2.57	Hg(2)-Hg(3)-O(3)c		97.5(3)
				<Hg, O-Hg(3)-O>		99.1
Cr	-O(2)	×2	1.67(2)			
	-O(3)	×2	1.70(2)	O(2)-Cr-O(2)f		109(1)
<Cr	-O>		1.69	O(2)-Cr-O(3)	×2	107.1(8)
				O(2)-Cr-O(3)f	×2	108.8(9)
O(1)a-Hg(1)-O(1)c		×2	86.6(7)	O(3)-Cr-O(3)f		116(1)
O(1)a-Hg(1)-O(1)d		×2	93.4(7)	<O-Cr-O>		109.5
O(2)a-Hg(1)-O(1)a		×2	103.4(6)			
O(2)a-Hg(1)-O(1)b		×2	76.6(6)			
O(2)a-Hg(1)-O(1)c		×2	96.7(4)			
O(2)a-Hg(1)-O(1)d		×2	83.3(4)			
<O-Hg(1)-O>			90.0			

Symmetry operations: a: $1/2+x-1, 1/2+y-1, z$; b: $1/2-x, 1/2-y, -z$; c: $1/2-x, 1/2+y-1, 1/2-z$; d: $1/2+x-1, 1/2-y, 1/2+z-1$; e: $1-x, 1-y, -z$; f: $1-x, y, 1/2-z$; g: $x, 1-y, 1/2+z$; h: $x, y-1, z$.

DESCRIPTION OF THE STRUCTURE

Coordination polyhedra of cations in the wattersite structure are shown in Figure 1. There are three distinct Hg positions in the structure. Hg(1) is divalent and occupies the special position 4*a* (at 0,0,0); it is coordinated by six oxygen atoms forming a distorted octahedron. Two short equatorial Hg(1)–O(1) bond lengths (2.06 Å) alternate with two longer Hg(1)–O(1) distances (2.70 Å); the apical O(2) atoms are 2.74 Å away from the Hg(1) position. Adjacent Hg(1) octahedra share O(1)*a*–O(1)*c* and O(1)*b*–O(1)*d* edges, forming chains parallel to [001]; the lengths of the shared and unshared edges are 3.30 and 3.50 Å, respectively. Because of the different lengths of the equatorial Hg(1)–O(1) bonds, the chains are slightly kinked, such that the apical O(2) atoms of adjacent octahedra form the O(2)–O(2) edges of neighboring CrO_4 tetrahedra (Figs. 2, 3).

Hg(2) and Hg(3), both in the general 8*f* position, form a diatomic Hg^{1+}–Hg^{1+} bond typical of mercurous compounds. The bond length (2.526 Å) is similar to those reported for deanesmithite (2.54 Å; Roberts *et al.* 1993), edgarbaileyite (2.522 and 2.524 Å; Angel *et al.* 1990), szymańskiite (2.494 and 2.513 Å; Szymański & Roberts 1990), magnolite (2.53 Å; Grice 1989), eglestonite (2.516 Å; Mereiter & Zemann 1976), $(Hg_2)_3(AsO_4)_2$ (2.535 Å, Kamenar & Kaitner 1973), Hg_2SO_4 (2.500 Å, Dorm 1969), Hg_2SeO_4 (2.51 Å, Dorm 1969), calomel (2.53 Å; Wyckoff 1965), synthetic mosesite (2.54 Å, Wyckoff 1965), and synthetic terlinguaite (2.66 Å, Šćavničar 1956).

Hg(2) also is coordinated by three oxygen atoms [O(1)*c*, O(3)*g*, O(3)*h*]; the Hg–O distances range from 2.16 to 2.77 Å. A second O(1) position is 3.11 Å away from Hg(2). Given the distance between O(1) and adjacent oxygen atoms [3.30 Å to O(1), 3.03 Å to O(2), 2.97 Å to O(3)], it is unlikely that this is a bond. Together with Hg(3), the three oxygen atoms form an extremely distorted tetrahedral coordination polyhedron around Hg(2).

The Hg(3) position is coordinated by Hg(2) and four atoms of oxygen. The coordination polyhedron of Hg(3) to the oxygen atoms is irregular, representing an approximately planar ring in which O(2)*e*, O(2)*g*, and O(3)*c* surround the Hg(3), with an apical O(1) atom opposite the apical Hg(2) atom at the other end. The Hg(3)–O distances range from 2.10 to 2.83 Å.

Relative to other Hg–O bond lengths, the Hg(2)–O(1)*c* and Hg(3)–O(1) distances are very short (2.16 and 2.10 Å). Together with the Hg(2)–Hg(3) dimer, they form an almost linear O–Hg–Hg–O group, similar to that seen in previously reported structures of Hg^{1+} compounds. The deviation from linearity is shown by the O(1)*c*–Hg(2)–Hg(3) and O(1)–Hg(3)–Hg(2) angles of 153.3° and 169.6°.

The Cr atom, at the general position 8*f*, is bonded to four atoms of oxygen in tetrahedral coordination. The

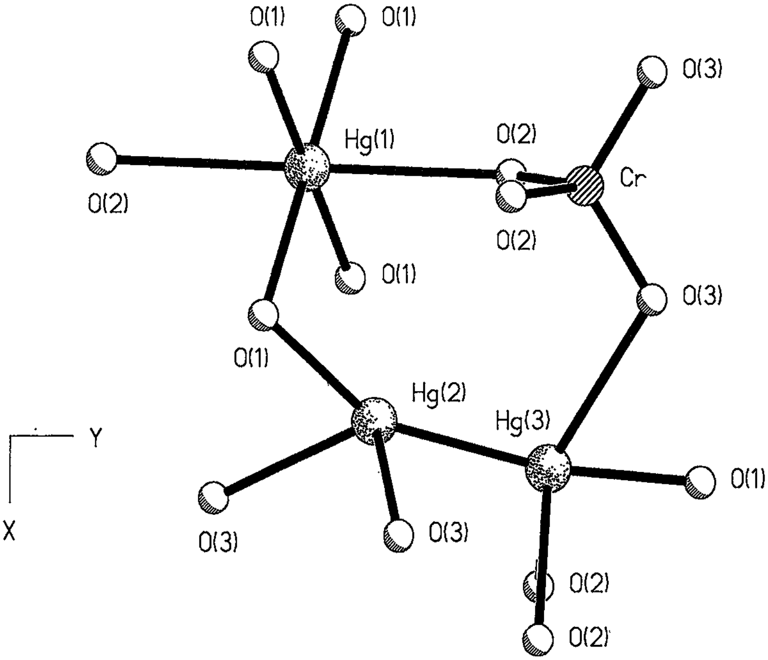

FIG. 1. Coordination polyhedra of cations in the wattersite structure, projected onto (001).

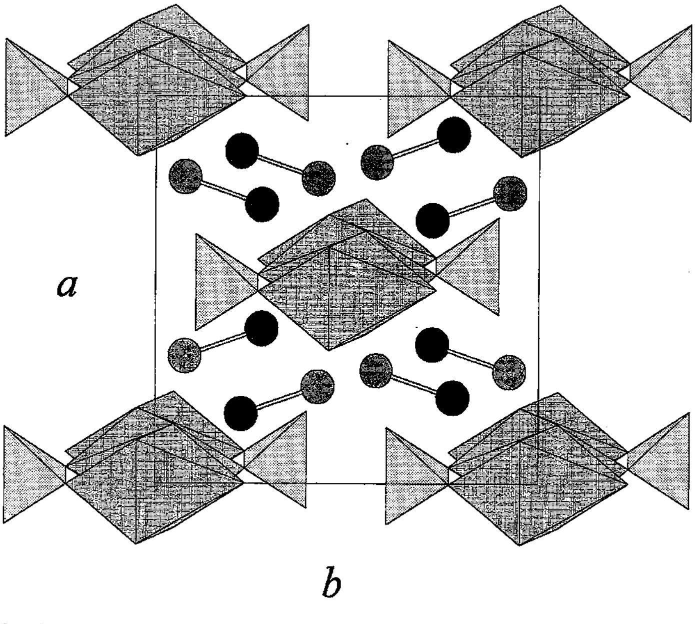

FIG. 2. The structure of wattersite projected onto (001), showing Hg(1) octahedra, Cr tetrahedra, and the Hg(2) (light shading) and Hg(3) (dark shading) pairs.

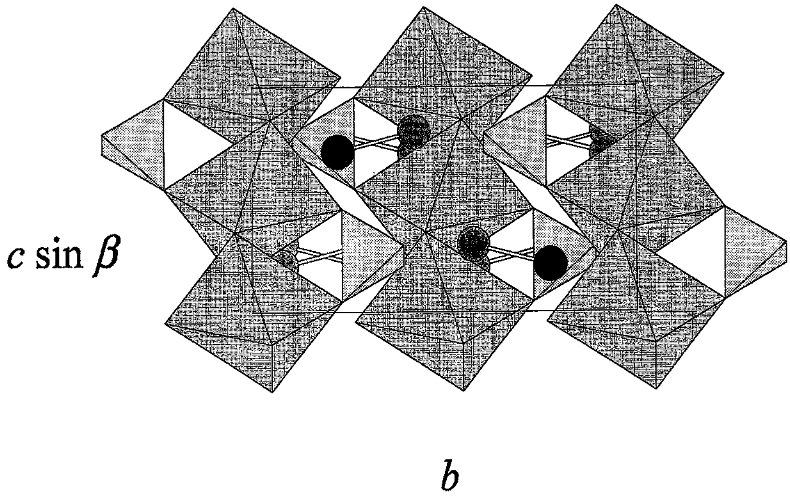

FIG. 3. The structure of wattersite viewed along [100]; shading as in Figure 2.

mean Cr–O distance is 1.69 Å; this is longer than most values in the literature, such as those reported for tarapacaite (1.643 Å; McGinnety 1972) and dietzeite (1.647 Å; Burns & Hawthorne 1993), but is closer to those published for the Pb chromate minerals hemihedrite (1.66 Å; McLean & Anthony 1970) and phoenicochroite (1.674 Å; Williams *et al.* 1970). Two of the anions are apical O(2) oxygen atoms from adjacent Hg(1) octahedra; the others are O(3) atoms that also form bonds to Hg(2) and Hg(3). The edges of the tetrahedra range from 2.72 to 2.74 Å, except for the O(3)–O(3) edge, which is somewhat longer (2.89 Å). The O–Cr–O angles vary from 107.1 to 109°, with the exception of the O(3)–Cr–O(3) angle (116°). Because the CrO_4 tetrahedra share apical O(2) oxygen atoms with adjacent Hg(1) octahedra, they form a staggered pattern of tetrahedra [related by the *c* glide parallel to (010)] projecting from the sides of the chain of octahedra in the [010] direction.

The entire structure may be thought of as consisting of edge-sharing Hg(1) octahedra with projecting CrO_4 tetrahedra forming zig-zag infinite chains of composition $[HgCrO_6]^{6-}$ that extend parallel to [001]. These units are similar to the $[M(T\phi_4)\phi_2]$ chains found in linarite $[PbCu(SO_4)(OH)_2]$ and schmiederite $[PbCu(SeO_4)(OH)_2$; Hawthorne 1990], which are linked by [9]-coordinated Pb atoms. In wattersite, the chains are linked by O–Hg bonds to the Hg(2)–Hg(3) dimers, which form gently modulated sheets parallel to (100).

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