

A redetermination of the crystal structure of livingstonite, $\text{HgSb}_4\text{S}_8^*$

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Auszug

Die Kristallstruktur von Livingstonit wurde neu bestimmt, um die neue chemische Formel HgSb_4S_8 (statt HgSb_4S_7) zu bestätigen und um die Koordination von Hg und die (S–S)-Bindung in der von NIIZEKI und BUERGER (1957) veröffentlichten Struktur zu studieren. Livingstonit kristallisiert monoklin mit den Gitterkonstanten $a = 30,567 \pm 0,006$, $b = 4,015 \pm 0,001$, $c = 21,465 \pm 0,003 \text{ \AA}$ und $\beta = 103,39 \pm 0,01^\circ$, in der Raumgruppe $C_{2h}^2 - A 2/a$ mit 8 Formeleinheiten pro Zelle. Die Struktur wurde mittels Block-Diagonal-Least-Squares-Methoden bis zu einem R -Wert von 7,3% für 596 beobachtete (10,2% für alle 1099) Reflexe verfeinert.

Die Strukturbestimmung bestätigt die neue chemische Formel. Es kommt eine S_2 -Gruppe mit $\text{S}-\text{S} = 2,06 \text{ \AA}$, die das zusätzliche achte S-Atom in der neuen Formel liefert, vor. In der Struktur sind zwei Schichtarten $\parallel c$ vorhanden. Die (S–S)-Bindung verknüpft zwei Sb_2S_4 -Doppelketten, wodurch zwischen ihnen eine S_2 -Gruppe entsteht. Die anderen Sb_2S_4 -Doppelketten werden durch Hg-Atome untereinander verbunden. Die Bindungen zwischen diesen Doppelketten sind eher schwach und erklären die perfekte Spaltbarkeit $\parallel (001)$.

Die Koordination der Hg-Atome ist oktaedrisch; zwei der S-Atome sind stark und linear gebunden, ähnlich wie in Zinnober. In der Struktur sind vier unabhängige Sb-Atome vorhanden. Zwei davon weisen eine Viererkoordination durch S-Atome auf, in Form einer deformierten trigonalen Pyramide plus ein zusätzliches S-Atom. Die beiden anderen Sb-Atome haben eine quadratisch-pyramidale bzw. die normale trigonal-pyramidale Koordination. Die Strukturformel von Livingstonit kann als $[(\text{Sb}_2\text{S}_4)_2 | \text{Hg}^{\text{II+IV}}]$ geschrieben werden [Typ IV.a₁ der Klassifikation von NOWACKI (1969)].

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Abstract

The crystal structure of livingstonite has been redetermined with a view to confirm the new chemical formula, HgSb_4S_8 (not HgSb_4S_7) as well as to study the coordination of mercury and the S—S bond in the structure, reported by NIIZEKI and BUERGER (1957). Crystals of livingstonite are monoclinic, having the cell dimensions $a = 30.567 \pm 0.006$, $b = 4.015 \pm 0.001$, $c = 21.465 \pm 0.003$ Å and $\beta = 103.39 \pm 0.01^\circ$. The space-group symmetry is $C_{2h}^6 - A 2/a$ and there are eight formula units in the unit cell. The structure was refined by block-diagonal least-squares method to a final R value of 7.3% for the 596 observed reflections (10.2% for all 1099 reflections).

The structure confirms the new chemical formula. There is an S_2 group with an S—S distance of 2.06 Å, which gives rise to the additional sulfur atom in the new chemical formula. There are two kinds of layers running parallel to the c axis in the structure. The S—S bond joins two Sb_2S_4 double chains. The other Sb_2S_4 double chains are joined together by the Hg atoms. The bonds between these two double chains are rather weak and hence explain the presence of a perfect cleavage $\parallel (001)$.

The coordination of the Hg atoms is octahedral; two of the S atoms are strongly and linearly bonded, as in cinnabar. There are four independent Sb atoms in the structure. Two of them have a coordination of four sulfur atoms which could be described as distorted trigonal pyramid plus one additional sulfur atom. The other two Sb atoms have a square pyramidal coordination and the familiar trigonal pyramidal coordination, respectively. The structural formula of livingstonite could be described as $[(\text{Sb}_2\text{S}_4)_2 | \text{Hg}^{\text{II+IV}}]$ [type IV.a₁ in the classification of the sulfosalts by NOWACKI (1969)].

Introduction

Livingstonite is a mercury antimony sulfide and derives its name after its discoverer, DAVID LIVINGSTONE. It is quite often found to occur along with cinnabar, which is regarded as its pseudomorph. It occurs in association with stibnite, sulfur, cinnabar and valentinite in a matrix of calcite and gypsum, at Huitzucó, Guerrero, Mexico and also at Guadalcazar, San Luis Potosi, with gypsum and sulfur (DANA, 1944). For a long time, its chemical composition was taken to be HgSb_4S_7 , until NIIZEKI and BUERGER (in 1957) gave the correct chemical composition as HgSb_4S_8 .

Livingstonite was first investigated by RICHMOND (1936), who described it as monoclinic, belonging to the space group $P2_1/c$. Later GORMAN (1954) reported it as triclinic. The cell dimensions reported by them are given in Table 1. NIIZEKI and BUERGER (1957) investigated its structure and found it to be monoclinic. They also found an anomaly in the chemical composition and concluded that the correct composition is HgSb_4S_8 instead of HgSb_4S_7 . Their analysis,

although based on three-dimensional diffractometer data, was not very accurate, probably due to the limitations of the quality of the data and to the limitations on computing and least-squares refinement techniques in 1957.

Quite recently, another mercury-containing sulfosalt, vrbaite, $\text{Hg}_3\text{Tl}_4\text{As}_8\text{Sb}_2\text{S}_{20}$ has been investigated in this laboratory (OHMASA and NOWACKI, 1971). We have undertaken the redetermination of livingstonite to resolve the anomaly in its chemical composition with more accurate data and also to study the coordination of mercury and compare it with that of vrbaite.

Experimental

The crystal used for the present study was prepared from a sample of livingstonite from the type locality in Mexico. It was a thin and fibrous needle, having the dimensions $0.152 \times 0.081 \times 0.046$ mm, with approximately cylindrical cross-section.

The lattice constants were determined with the help of back-reflection Weissenberg photographs, on which the diffraction pattern of standard silicon had been superimposed to calibrate the film shrinkage. The precise cell constants determined from a least-squares

Table 1. *Crystallographic data of livingstonite*

	RICHMOND (1936)	GORMAN (1954)	NIIZEKI and BUERGER (1957)	Present study
Space group	$P2_1/c$	$P1$ or $P\bar{1}$	$A2/a$	$A2/a$
a	15.14 Å	7.67 Å	30.25 Å	30.567 ± 0.006 Å
b	3.98	4.00	4.00	4.015 ± 0.001
c	21.60	10.84	21.49	21.465 ± 0.003
α	—	$99^\circ 12'$	—	—
β	$104^\circ 00'$	$102^\circ 1'$	$104^\circ 12'$	103.39 ± 0.02
γ	—	$73^\circ 48'$	—	—
V	—	—	—	2562 \AA^3
Cell content	4 HgSb_4S_7	HgSb_4S_7	8 HgSb_4S_8	8 HgSb_4S_8
Computed density	—	—	5.06	4.89 g cm^{-3}
Measured density	—	—	5.00	—
	—	—	(FRONDEL)	—
$F(000)$	—	—	—	3296 electrons
R for observed reflections	—	—	0.19	0.073

best fit of 20 ($h0l$) and 14 ($0kl$) reflections are given in Table 1, together with the values of NIIZEKI and BUERGER (1957), GORMAN (1945) and RICHMOND (1936). The calculations were made with the help of a program written by N. D. JONES (unpublished).

The crystal belongs to the monoclinic system. The systematic absences, as observed from Weissenberg photographs are

$$\begin{aligned}
 hkl: & \quad k + l = 2n + 1 \\
 h0l: & \quad l = 2n + 1 \quad (h \neq 4n) \\
 0k0: & \quad k = 2n + 1.
 \end{aligned}$$

The possible space groups are $A2/a$ or Aa . But the former space group has been assumed, because an analysis of the distribution of the normalized structure amplitudes suggested the centric rather than the acentric space group (see Table 2). The systematic absences in $h0l$ reflections are rather unusual. In addition to the space group extinctions of $h = 2n + 1$ and $l = 2n + 1$, there is an additional absence of $h \neq 4n$. This could be only interpreted as due to the structural arrangement. There are eight formula units in the unit cell and one in the asymmetric octant. In all this we follow and confirm the 1957 analysis by NIIZEKI and BUERGER.

Table 2. *Distribution of normalized structure factors*

	Experimental	Theoretical	
		centric	acentric
$\langle E \rangle$	0.657	0.798	0.886
$\langle E^2 \rangle$	1.029	1.000	1.000
$\langle E^2 - 1 \rangle$	1.312	0.968	0.736
$ E > 3.0$	2.3%	0.3%	0.01%
$ E > 2.0$	6.9%	5.0%	1.8%
$ E > 1.0$	24.4%	32.0%	36.8%

Three-dimensional intensity data were collected by a Supper-Pace automated diffractometer having Weissenberg geometry and using $\text{CuK}\alpha$ radiation. The intensities were corrected for Lorentz and polarization factors. Correction for absorption was made with the help of an ICR-10 program (JOHNSON, 1963), because of the high linear absorption coefficient of the material ($\mu = 1068 \text{ cm}^{-1}$ for $\text{CuK}\alpha$ radiation).

dimensional Patterson synthesis, corresponding to the Hg—Hg interactions. There are two kinds of Hg atoms in the structure. Hg(1) is located at the centre of symmetry and Hg(2) is placed on the twofold axis. A three-dimensional Fourier synthesis was computed with the Hg atoms and the antimony atoms could be located from this Fourier map. A structure-factor calculation with the mercury and antimony atomic coordinates and with the overall B of 4.6 \AA^2 , as indicated from the Wilson plot, yielded an R value of 45.6% for all 1099 reflections. A three-dimensional Fourier synthesis computed with these atoms, showed up all the sulfur atoms. The additional sulfur atom, found by the same procedure as by NIIZEKI and BUERGER, also showed up, with almost the same strength as the other sulfur atoms.

A structure-factor calculation with all these atoms, yielded an R value of 38.5% for all reflections (the final atomic coordinates, as reported by NIIZEKI and BUERGER, with an overall B of 4.6 \AA^2 gave an R value of 19% for observed reflections and 27.7% for all 1099 reflections). Three-dimensional block-diagonal least-squares refinements were started with the initial R value of 38.5%. After a series of isotropic block-diagonal least-squares refinements, the R value fell to 13.5% for all 1099 reflections. The refinements were continued with anisotropic thermal parameters for all the atoms and the final R value was 7.3% for the observed 596 reflections (10.2% for all 1099 reflections). The effect of anomalous dispersion was taken into account but no significant difference was found between the two enantiomorphs. Reflections with $I < 2.233 \sigma(I)$ were assigned as unobserved reflections. Neutral atom scattering factors as given by THOMAS, UMEDA were used for the Hg and Sb atoms and those given by DAWSON were used for the S atoms (*International tables*, 1962).

A block-diagonal least-squares refinement program written by ENGEL (1972) for IBM 370/155 was used in the structure refinement.

In the beginning stages of the refinement, unit weights were assigned to all the reflections, but in the final stages weights were calculated using the weighting function (ENGEL, 1972)

$$W = \frac{1}{(G_1 + F_{\text{obs}} + G_2 \cdot F_{\text{obs}}^2)},$$

where $G_1 = 8$ and $G_2 = 0$.

A list of the final observed and calculated structure amplitudes is given in Table 3.

Description of the structure

The final atomic coordinates are given in Table 4*a* and the anisotropic thermal parameters in Table 4*b*. The root-mean-squared displacements of the atoms along the principal axes of the vibration ellipsoid

Table 4*a*. *The final atomic coordinates of livingstonite, their standards deviations (in parentheses) and occupancy factors. In brackets: coordinates given by NIIZEKI and BUEGER (1957)*

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy factor
Hg(1)	0 [0]	0.5 [0.5]	0 [0]	0.5
Hg(2)	0.25 [0.25]	0.0089(11) [0.001]	0 [0]	0.5
Sb(1)	0.0395(2) [0.042]	0.0628(12) [0.095]	0.2115(2) [0.214]	1.0
Sb(2)	0.1244(1) [0.120]	0.0563(12) [0.063]	0.0779(2) [0.075]	
Sb(3)	0.1355(2) [0.131]	0.0586(12) [0.064]	0.4281(2) [0.425]	
Sb(4)	0.2057(2) [0.208]	0.1091(12) [0.078]	0.2847(2) [0.287]	
S(1)	0.0148(6) [0.022]	0.005(3) [0.021]	0.3169(7) [0.318]	
S(2)	0.0642(5) [0.062]	0.517(3) [0.493]	0.0979(5) [0.092]	
S(3)	0.0757(6) [0.078]	0.516(3) [0.507]	0.4625(6) [0.460]	
S(4)	0.1077(6) [0.102]	0.501(4) [0.483]	0.2881(6) [0.277]	
S(5)	0.1527(6) [0.149]	0.511(3) [0.521]	0.2300(5) [0.222]	
S(6)	0.1698(9) [0.172]	0.520(5) [0.506]	0.0352(13) [0.039]	
S(7)	0.2060(9) [0.189]	0.512(3) [0.494]	0.4216(9) [0.407]	
S(8)	0.2177(7) [0.229]	0.024(4) [0.028]	0.1795(9) [0.180]	

Table 4*b*. *The final anisotropic temperature factor coefficients*

The values are the coefficients in the expression
 $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg(1)	0.00188(11)	0.086(3)	0.00303(12)	0.0004(8)	0.0013(2)	-0.0015(9)
Hg(2)	177(10)	81(3)	266(10)	—	12(2)	—
Sb(1)	140(10)	86(4)	229(11)	-18(8)	14(2)	3(10)
Sb(2)	134(10)	83(4)	200(10)	-52(7)	11(2)	-41(8)
Sb(3)	125(9)	80(3)	217(11)	-41(7)	10(2)	-29(8)
Sb(4)	185(11)	78(3)	228(11)	56(8)	17(2)	26(10)
S(1)	0.0010(3)	0.039(7)	0.0023(4)	0.006(2)	0.0026(6)	0.007(3)
S(2)	3(2)	37(6)	10(2)	-3(2)	-3(3)	-2(2)
S(3)	15(3)	39(7)	11(3)	-7(2)	15(5)	-5(2)
S(4)	5(2)	70(10)	10(2)	-1(2)	2(4)	4(2)
S(5)	13(2)	26(6)	5(2)	2(2)	-13(3)	-2(2)
S(6)	15(5)	64(12)	49(8)	-10(3)	25(10)	-4(5)
S(7)	35(5)	2(6)	36(5)	-4(2)	52(9)	-3(3)
S(8)	4(2)	73(11)	24(4)	-1(2)	12(5)	-5(3)

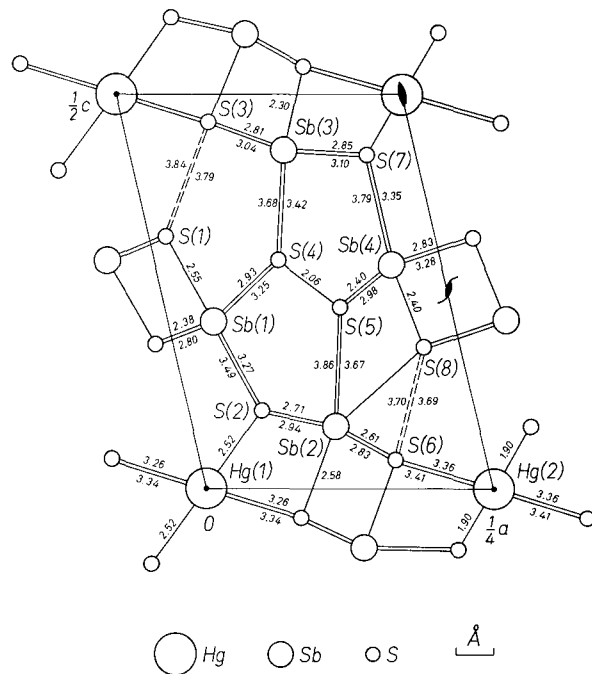


Fig. 1. The structure of livingstonite projected down [010]

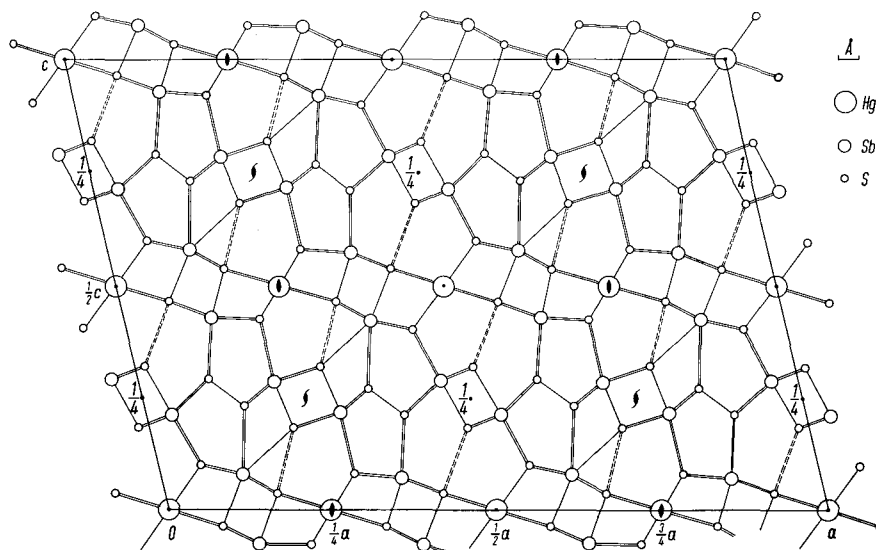


Fig. 2. A schematic representation of the structure of livingstonite, in the whole unit cell, projected down the *b* axis

are given in Table 5. The arrangement of atoms projected down the *b* axis is given in Fig. 1. In Fig. 2, the structural scheme is illustrated for the unit cell.

The structure proposed by NIIZEKI and BUERGER is essentially correct. For purposes of comparison, the final atomic coordinates of NIIZEKI and BUERGER are also given in Table 4*a*, in brackets, along with those of this investigation. The average shift in the coordinates of the Sb atoms from the model of NIIZEKI and BUERGER is 0.077 Å, while those in the S atoms is 0.128 Å. The largest shift in a Sb-atom coordinate is 0.086 Å and that in a sulfur atom is 0.302 Å.

The interatomic distances and angles are given in Tables 6*a* and 6*b* respectively. There are two kinds of Hg atoms in the structure. One of them is located at the centre of symmetry and the other on the twofold axis. Both these Hg atoms are included in the structure-factor calculation, with an occupancy factor of 0.5, so as to be consistent with the unit cell content of 8 Hg atoms. The coordination of the two Hg atoms by the S atoms are octahedral; two of the S atoms are nearer than the other four and linked to Hg in a diagonal linear bond. The octahedron around Hg(1) is formed by S(2), S(2)', S(3)', S(3)'', S(3)''' and S(3)'''. Out of these, S(2) and S(2)' are linearly bonded to Hg at a distance of 2.52 Å [S(2)—Hg(1)—S(2)' = 180.0°]. Such diagonal linear covalent linkage is characteristic of the structural chemistry of the Hg atom (GRDENIĆ, 1965) and is also found in the structure of cinnabar, HgS (Hg—S = 2.36 Å, S—Hg—S = 172°; AURIVILLIUS, 1950) and also in vrbaite (Hg—S = 2.38 Å, S—Hg—S = 166.0°; OHMASA and NOWACKI, 1971). The octahedral arrangement around Hg(1) is almost regular and runs almost parallel to the *c* axis. The average Hg—S distance is 3.04 Å and the average standard deviation in them is 0.013 Å. Hg(2) also has an octahedral arrangement with S(7)', S(7)'', S(6), S(6)', S(6)'' and S(6)'''. The atoms S(7)' and S(7)'' are almost linearly bonded to mercury. The angle S(7)'—Hg(2)—S(7)'' = 179.1°, but the covalent distance between the Hg and S atoms is 1.90 Å, shorter than the sum of the covalent radii of the atoms (2.36 Å). The standard deviation in these bonds is 0.02 Å and it is rather difficult to assert that this bond is really short. Similar short bonds, those less than, or equal to, the sum of the covalent radii, have been reported in some mercury-bearing compounds: in dimethyl thio-mercury (BRADLEY and KUNCHUR, 1964), the Hg—S distance is 2.36 Å; in KI · Hg(CN)₂, the Hg—C diagonal bond is 2.08 Å (KRUSE, 1963), which is less than the sum of the covalent radii 2.3 Å

Table 5. *The root-mean-squared displacements of the atoms along the principal axes of the vibration ellipsoids and direction cosines of these axes with respect to the crystallographic axes*

Atom	B_{isotr}	Axes	B	$\sqrt{u^2}$	$\cos \alpha_1$	$\cos \alpha_2$	$\cos \alpha_3$
Hg(1)	5.78	1	6.66	0.290	0.954	0.058	0.294
		2	5.69	0.268	0.092	0.877	-0.472
		3	5.00	0.252	-0.285	0.477	0.831
Hg(2)	5.35	1	6.27	0.282	0.977	0.000	0.215
		2	5.21	0.257	0.000	1.000	0.000
		3	4.56	0.240	-0.215	0.000	0.977
Sb(1)	4.72	1	4.96	0.251	0.664	0.490	0.565
		2	5.77	0.270	-0.477	0.859	-0.184
		3	3.43	0.209	-0.575	-0.147	0.805
Sb(2)	4.47	1	3.79	0.219	0.811	0.584	0.021
		2	6.39	0.284	-0.555	0.782	-0.284
		3	3.23	0.202	-0.182	0.218	0.959
Sb(3)	4.41	1	3.78	0.219	0.666	0.583	0.465
		2	5.90	0.273	-0.511	0.811	-0.285
		3	3.53	0.212	-0.543	-0.048	0.838
Sb(4)	5.03	1	7.42	0.307	0.801	0.487	0.348
		2	4.28	0.233	-0.386	0.865	-0.322
		3	3.40	0.207	-0.457	0.124	0.881
S(1)	2.92	1	0.56	0.084	0.832	-0.158	-0.531
		2	1.82	0.152	-0.098	0.901	-0.422
		3	6.38	0.284	0.545	0.404	0.735
S(2)	1.84	1	0.50	0.079	0.738	0.357	0.573
		2	2.64	0.183	-0.356	0.927	-0.119
		3	2.39	0.174	-0.573	-0.116	0.811
S(3)	3.03	1	6.14	0.279	0.831	-0.421	0.363
		2	1.79	0.151	0.506	0.843	-0.181
		3	1.16	0.121	-0.230	0.334	0.914
S(4)	2.71	1	1.88	0.154	0.989	0.145	0.019
		2	4.75	0.245	-0.145	0.963	0.228
		3	1.50	0.138	0.015	-0.228	0.973
S(5)	2.72	1	6.34	0.283	0.940	0.134	-0.315
		2	1.62	0.143	-0.162	0.985	-0.065
		3	0.19	0.049	0.301	0.112	0.947

Table 5. (Continued)

Atom	B_{isotr}	Axes	B	$\sqrt{u^2}$	$\cos \alpha_1$	$\cos \alpha_2$	$\cos \alpha_3$
S(6)	5.69	1	5.80	0.271	0.635	-0.648	-0.422
		2	2.13	0.164	0.696	0.716	-0.051
		3	9.12	0.340	0.335	-0.261	0.905
S(7)	5.51	1	13.74	0.417	0.817	-0.067	0.572
		2	0.07	0.031	0.051	0.998	0.044
		3	2.72	0.186	-0.574	-0.007	0.819
S(8)	3.35	1	1.01	0.113	0.985	0.000	-0.174
		2	5.43	0.262	-0.111	0.769	-0.630
		3	3.62	0.214	0.133	0.640	0.757

Table 6a. Interatomic distances in livingstonite

Hg(1)—S(2)	$2.52 \pm 0.01 \text{ \AA}$	[2 ×]	Sb(4)—S(8)	$2.40 \pm 0.02 \text{ \AA}$
S(3)'''	3.34 ± 0.01	[2 ×]	S(5)	2.40 ± 0.01
S(3)'	3.26 ± 0.01	[2 ×]	S(8)'	2.83 ± 0.02
Mean	3.04		S(5)'	2.98 ± 0.01
			Mean	2.65
Hg(2)—S(7)'	1.90 ± 0.02	[2 ×]	S(1)—S(1)'	3.42 ± 0.02
S(6)	3.41 ± 0.02	[2 ×]	S(1)''	3.47 ± 0.02
S(6)'	3.36 ± 0.02	[2 ×]	S(4)	3.64 ± 0.02
Mean	2.89		S(4)'	3.66 ± 0.02
Sb(1)—S(1)	2.55 ± 0.02		S(3)	3.84 ± 0.02
S(1)'	2.38 ± 0.01		S(3)'	3.79 ± 0.02
S(1)''	2.80 ± 0.01		S(4)''	3.90 ± 0.02
S(4)	2.93 ± 0.02		Sb(3)	3.91 ± 0.02
Mean	2.67			
Sb(2)—S(6)	2.61 ± 0.02		S(2)—Sb(1)	3.27 ± 0.01
S(6)'	2.83 ± 0.02		Sb(1)'	3.35 ± 0.02
S(2)	2.71 ± 0.01		S(5)	3.44 ± 0.02
S(2)'	2.94 ± 0.01		Sb(1)'	3.49 ± 0.01
S(3)'	2.58 ± 0.01		S(3)'	3.61 ± 0.02
Mean	2.73		S(3)''	3.62 ± 0.02
			S(6)	3.77 ± 0.03
Sb(3)—S(6)'	2.30 ± 0.03		S(4)	3.99 ± 0.02
S(3)	2.81 ± 0.01			
S(7)	2.85 ± 0.02		S(3)—S(6)'	3.55 ± 0.03
Mean	2.65		S(6)''	3.57 ± 0.03

