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Schuetteite, $Hg_3(SO_4)O_2$, a re-investigation

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Synthetic schuetteite [trimercury(II) dioxide sulfate(VI)], $Hg_3(SO_4)O_2$, has been prepared under hydrothermal conditions starting from $HgSO_4$ (520 K, 10 d) in demineralized water. The crystal structure comprises infinite two-dimensional cationic nets with an overall composition of $[Hg_3O_2]^{2+}$, and disordered SO_4^{2-} tetrahedra situated in the interstices of the nets.

Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Hg–O) = 0.008 Å
Disorder in main residue
R factor = 0.021
wR factor = 0.051
Data-to-parameter ratio = 18.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Schuetteite is a naturally occurring supergene mercury mineral found as a weathering product of cinnabar, HgS (Bailey *et al.*, 1959). In its synthetic form this basic mercury(II) sulfate has been described for the first time as 'Turbithum (Turbethum) Minerale' by Paracelsus (Theophrast von Hohenheim; 1493–1541) and was applied as a laxative.

The crystal structure of $Hg_3(SO_4)O_2$ was solved by Nagorsen *et al.* (1962). These authors reported the atomic coordinates to be provisional, because no absorption correction of the highly absorbing crystal (linear absorption coefficient μ *ca* 80 mm^{-1}) had been applied to the measured intensity data. For a more detailed knowledge of the crystal chemistry of mercury(II)–oxo compounds and an improvement of the structural data it seemed desirable to re-investi-

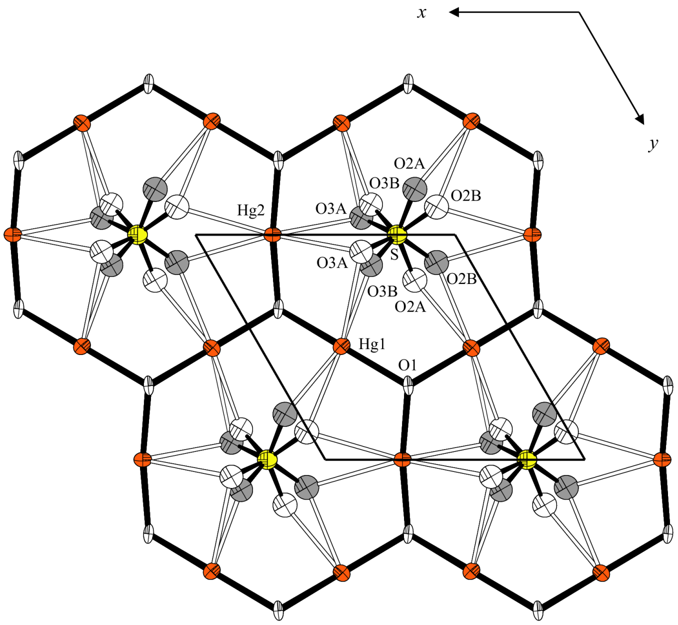

Figure 1
Part of an $[Hg_3O_2]^{2+}$ net with disordered SO_4^{2-} tetrahedra located inside the interstices in a projection along [001] and displacement ellipsoids drawn at the 74% probability level. One orientation of the disordered sulfate group is shown in white, the other in grey.

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gate the structure of schuetteite on the basis of modern intensity measurements and especially with application of an appropriate absorption correction. During this work the previously determined structure has, in principle, been confirmed. The most important result of the re-investigation is the information that the sulfate group is disordered; this was not elaborated in the original study.

The structure consists of layers perpendicular to [001] (Fig. 1). The layers are composed of slightly corrugated hexagonal $[Hg_3O_2]^{2+}$ nets with $\overline{d}$(Hg—O) = 2.092 Å and nearly linear (O—Hg—O) angles with a mean value of 170.5°. The Hg—O distances within the nets are considerably shorter than $\overline{d}$(Hg—O) = 2.712 Å to the O atoms of the disordered SO_4^{2-} tetrahedra located inside the interstices of the nets and to SO_4^{2-} groups of adjacent layers. The pronounced [2+ x] coordination with two short Hg—O bonds and an almost linear (O—Hg—O) angle is a frequently observed structural unit in the crystal chemistry of mercury(II)–oxo compounds (Aurivillius, 1965; Grdenić, 1965; Stålhandske, 1980; Müller-Buschbaum, 1995). The sulfate group is disordered around the twofold axis and is slightly distorted from the geometry of an ideal tetrahedron [$\overline{d}$(S—O) = 1.482 Å, mean angle of 109.5°].

Experimental

Single crystals of synthetic schuetteite were prepared by hydrothermal treatment of commercial $HgSO_4$ (Merck, p.A.) in demineralized water (steel autoclave with teflon-lined tubes, filling degree 70%, 520 K, 10 d). The crystals obtained were canary yellow in colour and had a hexagonal plate-like habit with [001] as the main crystal face.

Crystal data

$Hg_3SO_4O_2$
$M_r = 729.83$
Trigonal, $P3_121$
$a = 7.0429$ (5) Å
$c = 10.0166$ (7) Å
$V = 430.28$ (5) Å^3
$Z = 3$
$D_x = 8.450$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 2544 reflections
$\theta = 6.7–59.8°$
$\mu = 80.41$ mm^{-1}
$T = 293$ (2) K
Trigonal plate, yellow
0.10 × 0.06 × 0.01 mm

Data collection

Siemens SMART diffractometer
ω scans
Absorption correction: numerical
$T_{min} = 0.030$, $T_{max} = 0.458$
4712 measured reflections
845 independent reflections

801 reflections with $I > 2\sigma(I)$
$R_{int} = 0.059$
$\theta_{max} = 30.2°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -12 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.021$
$wR(F^2) = 0.051$
$S = 1.04$
849 reflections
45 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 0.0858P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.96$ e Å^{-3}
$\Delta\rho_{min} = -1.81$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00086 (11)
Absolute structure: Flack (1983)
Flack parameter = 0.16 (4)

Table 1
Selected geometric parameters (Å, °).

Hg1—O1^{i}	2.105 (6)	Hg2—O2A^{vi}	2.647 (15)
Hg1—O1^{ii}	2.123 (6)	Hg2—O3A^{vii}	2.657 (18)
Hg1—O2A	2.467 (16)	Hg2—O3A	2.657 (18)
Hg1—O3B^{iii}	2.473 (19)	Hg2—O2B^{viii}	2.775 (16)
Hg1—O2B	2.548 (15)	Hg2—O2B^{ix}	2.775 (16)
Hg1—O3A^{iv}	2.607 (19)	Hg2—O3B^{vii}	2.96 (2)
Hg1—O3B^{iv}	2.64 (2)	Hg2—O3B	2.96 (2)
Hg1—O1	2.674 (7)	Hg2—O2B^{v}	2.961 (17)
Hg1—O3A^{iii}	2.750 (18)	Hg2—O2B^{vi}	2.961 (17)
Hg1—O2A^{iii}	2.836 (17)	S—O2B	1.451 (15)
Hg2—O1^{v}	2.070 (7)	S—O3B	1.461 (19)
Hg2—O1^{vi}	2.070 (7)	S—O3A^{vii}	1.491 (19)
Hg2—O2A^{v}	2.647 (15)	S—O2A^{vii}	1.523 (16)
O1^{i}—Hg1—O1^{ii}	169.72 (6)	O3B—S—O3A^{vii}	108.6 (9)
O1^{v}—Hg2—O1^{vi}	171.3 (3)	O2B^{vii}—S—O2A	113.7 (11)
O2B^{vii}—S—O3B	111.1 (11)	O3B^{vii}—S—O2A	106.0 (9)
O2B—S—O3A^{vii}	110.0 (10)	O3A—S—O2A	107.4 (10)

Symmetry codes: (i) $1-y, 1+x-y, \frac{1}{3}+z$; (ii) $x-y, -y, \frac{2}{3}-z$; (iii) $-x, 1-x+y, \frac{1}{3}-z$; (iv) $y, x, 1-z$; (v) $1+x-y, -y, \frac{2}{3}-z$; (vi) $1-y, x-y, \frac{1}{3}+z$; (vii) $-x, -x+y, \frac{1}{3}-z$; (viii) $1+x, y, z$; (ix) $1-x, -x+y, \frac{1}{3}-z$.

All crystals examined were systematically twinned. In respect of racemic twinning a twin ratio of *ca* 5:1 was determined for the measured crystal. The crystal shape was optimized by minimizing the internal R-value of selected reflections [$I > 20\sigma(I)$] using the program *HABITUS* (Herrendorf, 1993–97). The habit so derived was used for the numerical absorption correction. In refinement with Hg and S atoms refined anisotropically and O atoms isotropically, large displacement parameters for the O atoms of the sulfate group were observed [fractional coordinates and isotropic displacement parameters for this model: (O2) $x = 0.178$ (3), $y = 0.155$ (3), $z = 0.2652$ (16), $U_{eq} = 0.074$ Å^2; (O3) $x = 0.3948$ (16), $y = 0.1067$ (19), $z = 0.4325$ (10), $U_{eq} = 0.037$ Å^2]. This could not be explained by crystal chemical arguments or a possibly inappropriate absorption correction, since the latter is expected to be essentially correct (R_{int} before absorption correction = 0.34, R_{int} after correction = 0.06; no significant remaining electron density after convergence). Therefore, a split atom model with disorder around the twofold axis was considered for the sulfate group, with occupation factors constrained to 0.5 for the O atoms (the 'free' occupation factors are close to this value) and the displacement parameters refined isotropically for O2A,B and O3A,B. The separation between the split O atoms is then 0.77 (2) (O2A—O2B) and 0.45 (2) Å (O3A—O3B). This model led to better R values and a better goodness-of-fit than the previous model without splitting of the sulfate O atoms.

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINT* (Siemens, 1996); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS for Windows* (Dowty, 1998); software used to prepare material for publication: *SHELXL*97.

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