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The Crystal Structure of Tin(II) Dithionite, $Sn_2(S_2O_4)_2$

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The title compound crystallizes in the monoclinic space group $P2_1/c$ with $a=7.015(1)$, $b=7.480(1)$, $c=12.652(1)$ Å, $\beta=133.59(1)$ Å, $Z=2$. $R=0.037$ for 1264 reflections. In the cage-like $Sn_2(S_2O_4)_2$ complex Sn^{2+} is coordinated to four oxygens from two $S_2O_4^{2-}$ ions in a slightly distorted square pyramidal configuration with Sn–O distances ranging from 2.237(2) to 2.323(3) Å. The dithionite ion has a slightly distorted C_{2v} configuration with an S–S distance of 2.350(1) Å and S–O distances from 1.503(3) to 1.517(3) Å. The smallest distance separating two $Sn_2(S_2O_4)_2$ complexes is 3.013(3) Å.

Due to the inherent instability of the dithionite ion only a few solid dithionites have been characterized so far. Among these, two of the more stable compounds, $Na_2S_2O_4$[1] and $ZnS_2O_4 \cdot$ pyridine,[2] have been investigated by X-ray single crystal methods. The present investigation was made in connection with studies on the reactions between metal surfaces and sulfur dioxide in the presence of water at ambient temperatures. It was found that when tin metal corroded in liquid sulfur dioxide containing some H_2O crystalline tin(II) dithionite was formed. Tin(II) dithionite was first prepared in an impure microcrystalline state by Brunck.[3] Later Cooke[4] reported a crystalline compound which had formed in tin piping used for liquid and gaseous sulfur dioxide. An elemental analysis for tin and sulfur indicated the empirical formula SnS_2O_4. He does not seem to have made any conclusive tests, however, as to whether dithionite was indeed present. Apparently the compound synthesized by us is identical with the one reported by Cooke.

EXPERIMENTAL

0.1 g of p.a. tin powder was placed in a sealed glass ampoule together with 3.0 g of liquid sulfur dioxide and 0.02 g water. No precautions were undertaken to exclude oxygen. The ampoule was then kept at *ca.* 278 K. After one week colourless, platelike crystals of sufficient size for single-crystal work had formed. In the absence of water no reaction takes place. If the synthesis is carried out at a temperature much higher than *ca.* 278 K the product decomposes. Decomposition also takes place if enough water is present to form two liquid phases. The tin powder must be oxide-free otherwise sulfate is produced rather than dithionite.

The IR spectrum was recorded on a Nicolet MX-1 spectrometer using the KBr-disc technique: 1045(s), 991(s), 878(s), 532(w), 460(w), 431(m), 412(vw) cm^{-1}. The spectrum showed no traces of sulfur–oxygen species other than dithionite.

Tin(II) dithionite is insoluble in water. It precipitates silver from an aqueous solution of silver nitrate, although only after heating. The compound is stable in dry air at room temperature but decomposes in presence of moisture. A thermal analysis made in air showed that $Sn_2(S_2O_4)_2$ decomposes exothermally between 398 and 438 K evolving SO_2, producing among other things elemental sulfur. 56 reflections were measured on a Guinier focussed powder photograph using Si as internal standard ($a_{Si}=5.43054$ Å at 298 K[5]). Determination of cell parameters was carried out with the program *TREOR*.[6] Powder data can be obtained from the authors on request.

CRYSTAL DATA

$Sn_2(S_2O_4)_2$, $M=493.62$, space group $P2_1/c$ (No. 14), $a=7.015(1)$ Å, $b=7.480(1)$ Å, $c=12.652(1)$ Å, $\beta=133.59(1)°$, $Z=2$, $D_c=3.41$ g cm^{-3}, $\mu(MoK\alpha)=6.06$ mm^{-1}.

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STRUCTURE DETERMINATION

Intensities from a crystal of size $0.10 \times 0.08 \times 0.05$ mm were measured on a Syntex $P2_1$ diffractometer by the $\omega - 2\theta$ scan technique with scan speeds of $2-14°$ min^{-1}. Graphite monochromated Mo$K\alpha$ radiation was used and data were collected with a maximum 2θ angle of 70°. 2223 reflections with $h \geq 0$ and $k \geq 0$ were measured. Of these 1264 had $I \geq 3\sigma(I)$ and were used in subsequent calculations. The crystal was stable during the data collection, as indicated by the measurement of a standard reflection ($\bar{1}\bar{2}2$; $I = 121\,000 \pm 4220$) at intervals of 50 reflections. The systematic absences $k = 2n+1$ for $0k0$ and $l = 2n+1$ for $h0l$ indicated space group $P2_1/c$. Intensities were calculated after the data collection from the 96 point intensity profile obtained for each reflection.[7,8] Correction was made for Lorentz and polarization effects but not for absorption or extinction. A ψ-scan of the $\bar{1}\bar{2}2$ reflection showed that the intensity decreased 20 % when the crystal was rotated from the least to the most absorbing position. The Sn atomic position was determined from a Patterson synthesis, and the S and O atoms were located from subsequent electron density summations.[9] The positional parameters, given in Table 1, and the anisotropic thermal parameters were refined to an R of 0.037, ($R = 0.077$ including unobserved reflections), using the program BLOCK.[10] Structure factors and anisotropic thermal parameters can be obtained from the authors on request. The structure factors were weighted according to $w = (\sigma^2(F_o) + 0.0006F_o^2)^{-1}$, $\sigma(F_o)$ being based on counting statistics. Scattering factors for Sn°, S° and O° were used.[12]

Table 1. Fractional coordinates and equivalent isotropic temperature factors (Å^2) with e.s.d.'s in parentheses. $B_{eq} = \frac{4}{3} \sum_{ij} b_{ij}(a_i a_j)$.[11]

	x	y	z	B_{eq}
Sn	0.22353(5)	0.74818(3)	0.91168(3)	2.20(1)
S(1)	0.7994(2)	0.8161(1)	0.9898(1)	1.86(3)
S(2)	0.4531(2)	0.9793(1)	0.7811(1)	1.96(3)
O(1)	0.6306(6)	0.7083(4)	1.0003(3)	2.5(1)
O(2)	0.2377(5)	0.8955(3)	0.7634(3)	2.4(1)
O(3)	0.9258(5)	0.9708(3)	1.0951(3)	2.6(1)
O(4)	0.5233(6)	1.1597(4)	0.8547(3)	2.6(1)

DISCUSSION

The structure of tin(II) dithionite is shown in Figs. 1 and 2. In Tables 2 and 3 some interatomic

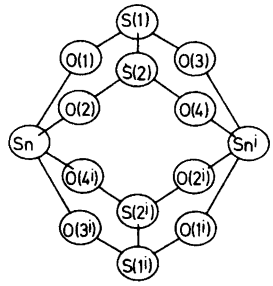

Fig. 1. The dimeric complex.

Table 2. Some distances (Å) and angles (°) with the e.s.d.'s in parentheses. Symmetry codes (i) $1-x$, $2-y$, $2-z$, (ii) $x-1$, $\frac{3}{2}-y$, $z-\frac{1}{2}$, (iii) $1-x$, $1-y$, $2-z$, (iv) $-x$, $y-\frac{1}{2}$, $\frac{3}{2}-z$, (v) $x-1$, y, z.

The Sn – O coordination			
Sn – O(1)	2.255(3)	Sn – O(3^i)	2.323(3)
Sn – O(2)	2.237(3)	Sn – O(4^i)	2.264(3)
O(1) – Sn – O(2)	73.1(3)	O(1) – Sn – O(3^i)	121.5(3)
O(3^i) – Sn – O(4^i)	72.6(3)	O(2) – Sn – O(4^i)	119.8(3)
O(1) – Sn – O(4^i)	78.9(1)		
O(2) – Sn – O(3^i)	78.6(1)		
Shortest intermolecular contacts			
Sn – O(3^{ii})	3.399(3)		
Sn – O(1^{iii})	3.518(3)		
Sn – O(2^{iv})	3.528(3)		
Sn – S(1^v)	3.761(1)		

Table 3. Bond lengths (Å), short non-bonded distances (Å) and angles (°) of the dithionite ion.

	$Sn_2(S_2O_4)_2$	$ZnS_2O_4 \cdot pyr^2$	$Na_2S_2O_4{}^1$
S(1)–S(2)	2.350(1)	2.386(2)	2.389
S(1)–O(1)	1.513(3)	1.517(3)	1.515
S(1)–O(3)	1.507(3)	1.511(3)	1.496
S(2)–O(2)	1.503(3)		
S(2)–O(4)	1.517(3)		
S(2)–S(1)–O(1)	96.3(3)	96.89(12)	99.4
S(2)–S(1)–O(3)	96.7(3)	96.61(12)	98.0
S(1)–S(2)–O(2)	96.0(3)		
S(1)–S(2)–O(4)	97.2(3)		
O(1)–S(1)–O(3)	110.5(3)	110.37(17)	108.3
O(2)–S(2)–O(4)	109.2(4)		
O(1)–S(1)–S(2)–O(4)	110.7(5)	111.5	110.0
O(2)–S(1)–S(2)–O(3)	111.2(5)		
S(1)–S(2)∠O(1)–S(1)–O(3)	101.2	101.8	105.3
S(1)–S(2)∠O(2)–S(2)–O(4)	101.8		

distances and angles are listed. The structure is seen to result from the stacking of a neutral cage-like dimer. The crystallographically equivalent tin atoms are at the apex of a slightly distorted square pyramid with oxygen atoms in the corners of the basal plane. The oxygen atoms belong to two dithionite ions which each contribute two to each tin atom, thus acting as four-dentate ligands. There are six lone pairs projecting from the dimer, one from each tin atom and one from every sulfur atom. The cage has C_i symmetry, but is quite close to D_{2h} symmetry.

The minimum distances separating two dimers are 3.013(3) and 3.044(3) Å. These, being S–O contacts, are shorter than would be expected from the sum of the van der Waals radii given by Pauling.[13] These are 1.40 and 1.85 Å for O and S, respectively.

As shown in Fig. 1 the eight oxygens form a distorted cube in the middle of the dimer. The edges of the oxygen polyhedron fall between 2.462(4) and 2.890(4) Å while the average value of the space-diagonals is 4.655(2) Å. With an ionic radius of oxygen of 1.40 Å[13] this would leave room in the centre of the complex for a particle with a radius somewhat less than 1 Å. Thus it hardly seems possible to trap an atom or a molecule inside the cage.

The dithionite ion has a slightly distorted C_{2v} structure. Bond distances and angles within the

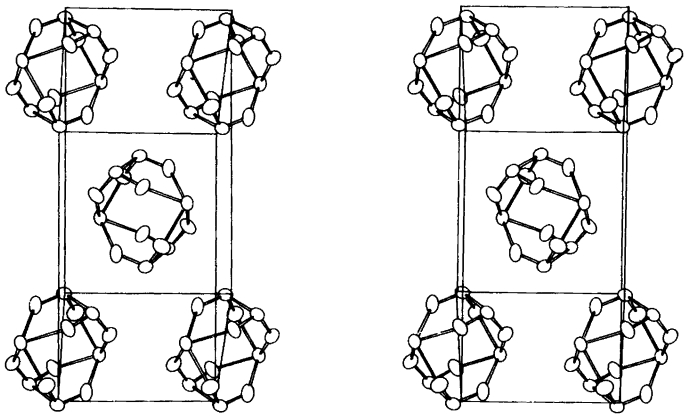

Fig. 2. A stereoscopic view of the unit cell. *b* and *c* are parallel to the picture plane.

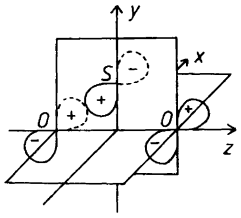

Fig. 3. A schematic view of the antibonding $3b_1$ orbital of SO_2^-.

dithionite group are similar to the values found for the two earlier reported structures. One exception is a small but significant shortening of the distance between the two "eclipsed" SO_2 units. This shortening is seen in the S–S bond. However, the S–S bond distance in tin(II) dithionite is much longer than is normally the case for disulfide links, indicating a weak S–S bond. As suggested by Dunitz[1] the dithionite ion may be regarded as two SO_2^--radicals weakly linked together. In solution the dithionite ion is known to be in equilibrium with the radical ion SO_2^-.[14] Thus a consideration of the electronic structure of the radical ion may be a starting point for a discussion of the structure of the dithionite ion.

According to Dacre and Elder[15] the least stable occupied orbital in the ground state of SO_2^- is the antibonding $3b_1$ orbital, *c.f.* Fig. 3. This orbital is built from *p* orbitals from all three atoms, overlapping out of phase. It may also have some sulfur 3*d* character. While it is S–O antibonding it is slightly O–O bonding. Being an antibonding orbital most of the electron density will be concentrated around the sulfur atom. If two such radical ions, each having one electron in a $3b_1$ orbital, approach each other in such a way that the $3b_1$ orbitals give an in-phase overlap, dimerization will occur. Most of the overlap will occur between the sulfur atoms. It is however probable, as put forward by Kiers and Vos,[2] that some bonding exists between the oxygens in the two SO_2 groups, thus explaining the eclipsed configuration of the ion.

The coordination of divalent tin in most compounds may be described as either a trigonal pyramidal configuration, *i.e.* $Sr[Sn(CH_2ClCO_2)_3]_2$[16] or as a square pyramidal configuration, *i.e.* $Na_2Sn(C_2O_4)_2$.[17] In both cases the tin atom occupies the apex of the pyramid. These coordination figures are thought to result from the stereochemical activity of the lone pair on tin, the lone pair being pictured as projecting from the apex of the pyramid, away from the ligands. The only tin(II) compound with a completely regular square pyramidal coordination is SnO,[18] in all other cases the ideally square pyramid is more or less distorted. The nature of this distortion is normally such that two of the four ligands are considerably closer to the tin than the other two[17] (*c.f.* Table 4). As seen in Table 4 this type of distortion is not present in $Sn_2(S_2O_4)_2$. This probably results from the constraints forced upon the tin environment by the configuration of the dimeric complex with the dithionite ion acting as a four-dentate ligand. The average Sn–O distance in tin(II) dithionite of 2.270(2) Å is typical for compounds belonging to this class, *c.f.* Table 4.

The somewhat simplified picture of the coordination of divalent tin given above disregards the existence of weak tin–ligand interactions in the directions not occupied by the three or four closest neighbours. Such interactions, increasing the coordination of tin to six or more, are a conspicious

Table 4. Sn–O distances (Å) in some compounds containing four-coordinated divalent tin.

Compound	Ref.	Four closest Sn–O contacts	Average	Fifth closest Sn–O contact
$Sn_2(S_2O_4)_2$	This work	2.237(2), 2.255(3), 2.264(3), 2.323(3)	2.270(2)	3.399(3)
SnO	18	2.21(1) × 4	2.21	4.15(1)
$SnC_4H_2O_4 \cdot H_2O$	19	2.176(7), 2.196(3), 2.312(9), 2.440(6)	2.281	2.817(5)
$Sn(H_2PO_4)_2$	20	2.209(2) × 2, 2.466(2) × 2	2.338	2.913(3)
SnC_2O_4	21	2.23 × 2, 2.39 × 2	2.31	2.88
$K_2Sn(C_2O_4)_2 \cdot H_2O$	21	2.13, 2.14, 2.31, 2.36	2.24	3.00
$Na_2Sn(C_2O_4)_2$	17	2.25(1) × 2, 2.36(2) × 2	2.30	2.91(2)
$Sn_3O(OH)_2 \cdot SO_4$	22	2.094(8), 2.144(9), 2.394(8), 2.467(7)	2.275	3.331(9)
		2.062(7), 2.161(8), 2.384(8), 2.485(11)	2.273	3.225(9)

feature of the crystal chemistry of divalent tin.[23] However, in $Sn_2(S_2O_4)_2$ the closest Sn contacts outside the complex, *i.e.* one oxygen belonging to another dimer at 3.399(3) Å which is too far for the oxygen to be bonded to tin.

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