

## The Crystal Structure of Disodium Bisoxalatostannate(II), $\text{Na}_2\text{Sn}(\text{C}_2\text{O}_4)_2$

BY J. D. DONALDSON AND M. T. DONOGHUE

*Department of Chemistry, Chelsea College, Manresa Road, London SW3 6LX, England*

AND C. H. SMITH

*Department of Physics, Chelsea College, Manresa Road, London SW3 6LX, England*

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The crystal structure of the title compound has been determined from single-crystal X-ray diffraction data by Patterson and Fourier methods. Crystals are monoclinic, space group  $C2/c$  with  $Z=4$  in a unit cell of dimensions  $a=10.422$  (8),  $b=5.676$  (4),  $c=13.618$  (7) Å,  $\beta=108.50$  (5)°. The structure was refined by least-squares methods to  $R=0.071$  for 1193 reflexions. The oxalates are equivalent and are chelated to Sn through one oxygen on each carbon atom to give one Sn–O bond of 2.25 and one of 2.36 Å. The tin atoms are in distorted pyramidal sites surrounded by two oxygen atoms at 2.25 and two at 2.36 Å.

### Introduction

The crystal structures of a few tin(II) complexes are known. Two different types of distorted coordination have been found for the tin atoms in these materials: (1) trigonal-pyramidal environments in which the tin forms three short bonds to the ligands, and in which a distorted octahedron around the tin is completed by three much longer tin–ligand distances, and (2) distorted square-pyramidal environments in which the tin usually forms two short bonds and two somewhat longer bonds with the ligands. The first type of environment is found in  $\text{CsSnCl}_3$  (Poulsen & Rasmussen, 1970),  $\text{NaSn}_2\text{F}_5$  (McDonald, Larson & Cromer, 1964),  $\text{KSn}(\text{HCO}_2)_3$  (Jelen & Linquist, 1969),  $\text{KCl} \cdot \text{KSnCl}_3 \cdot \text{H}_2\text{O}$  (Kamenar & Grdenić, 1962),  $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$  (Kiryama, Nakamura, Kitahama & Kiriyama, 1972),  $\text{Sn}_3\text{F}_5\text{Br}$  (Donaldson & Puxley, 1972a) and in one Sn site in  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  (Davies, Donaldson, Laughlin, Howie & Beddoes, 1975). The second type of environment is found in  $2\text{KSnF}_3 \cdot \text{H}_2\text{O}$  (Bergerhoff, Goost & Schultze-Rhnhof, 1968),  $\text{SnSO}_4 \cdot 2\text{SC}(\text{NH}_2)_2$  (Donaldson, Nicholson, Puxley & Howie, 1973) and in two Sn sites in  $\text{Sn}_3\text{O}(\text{OH})_2\text{SO}_4$  (Davies *et al.*, 1975).

There has been no crystal structure determination of a tin(II) complex with a simple potentially chelating ligand, such as oxalate, which could lead to either of the environments described above or to a regular square-pyramidal tin(II) site as found in tetragonal  $\text{SnO}$  (Moore & Pauling, 1941). We now report the crystal structure of disodium bisoxalatostannate(II),  $\text{Na}_2\text{Sn}(\text{C}_2\text{O}_4)_2$ , and show that the oxalate groups are chelated to Sn and that the tin atom has distorted square-pyramidal coordination.

### Experimental

Tin(II) oxalate (0.05 mol), prepared by the method of Hausmann & Löwenthal (1854) was dissolved in a hot solution of sodium oxalate (0.05 mol in 25 ml

water). The volume of the colourless solution was reduced to about 10 ml and allowed to cool to room temperature, when white crystals of the required product were deposited.

Single-crystal rotation and Weissenberg photographs were taken of a crystal mounted along the  $b$  axis, and cell dimensions were deduced from them. These values were then used as the basis for a least-squares refinement of measurements from a Debye-Scherrer powder photograph.

### Crystal data

Disodium bisoxalatostannate(II),  $\text{Na}_2\text{Sn}(\text{C}_2\text{O}_4)_2$ , M.W. 341.0; monoclinic,  $a=10.422 \pm 0.008$ ,  $b=5.676 \pm 0.004$ ,  $c=13.618 \pm 0.007$  Å,  $\beta=108.50 \pm 0.05^\circ$ ,  $V=764.0$  Å<sup>3</sup>;  $D_c=2.96$  for  $Z=4$ ,  $D_m=2.91$  g cm<sup>-3</sup> (displacement of propylene glycol). Total number of electrons per unit cell,  $F(000)=640$ . Systematic absences:  $hkl$  for  $h+k=2n+1$ ,  $h0l$  for  $l=2n+1$ . Possible space groups:  $Cc$  or  $C2/c$ . The lower symmetry space group ( $Cc$ ) was at first assumed but least-squares refinement of the atomic positions showed convergence towards the centrosymmetric space-group positions which were used in the final refinement.

### Structure determination

Diffraction intensity data were collected from a small crystal (mean diameter 0.20 mm), mounted along the  $b$  axis on a Nonius equi-inclination integrating Weissenberg camera, using Zr-filtered  $\text{Mo K}\alpha$  radiation ( $\lambda=0.7107$  Å). The 1197 reflexions which were collected from layers 0 to 6 were measured on a Nonius Microdensitometer Mk II. The measurements were processed and  $L_p$  corrections were applied by computer, to give a set of relative intensities. The crystal was sufficiently small for no absorption correction to be necessary ( $\mu R=0.351$ ).

The positions of the Sn atoms were determined from a three-dimensional Patterson synthesis and refined by full-matrix least squares before obtaining the po-

sitions of the Na atoms from a three-dimensional Fourier synthesis. The positions of the O atoms and finally the C atoms were obtained from Fourier and difference Fourier syntheses phased on the Sn and Na positions.

Full-matrix least-squares refinement of layer scale factors, atomic positions and isotropic temperature factors indicated convergence towards the positions corresponding to the centrosymmetric space group, which was then used for the final refinement. Four reflexions for which  $|F_o| > 2|F_c|$  or  $|F_c| > 2|F_o|$  were removed at this stage. Refinement of layer scales, atomic positions and anisotropic temperature factors for Sn converged with  $R = \sum ||F_o| - |F_c|| / (\sum |F_o|)$  as 0.071 using unit weights throughout. Atomic scattering factors for neutral Sn, Na, C and O atoms were taken from *International Tables for X-ray Crystallography* (1962). A final difference Fourier map showed a highest peak of +10, corresponding to about half an electron.

The final atomic coordinates, temperature factors and their standard deviations are given in Table 1. The significant bond distances and angles based on the coordinates of Table 1 are listed in Table 2 along with their standard deviations.\*

The computer programs used were (i) *NUCLS4*, a version of the Ibers & Doedens least-squares program,

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31680 (12 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

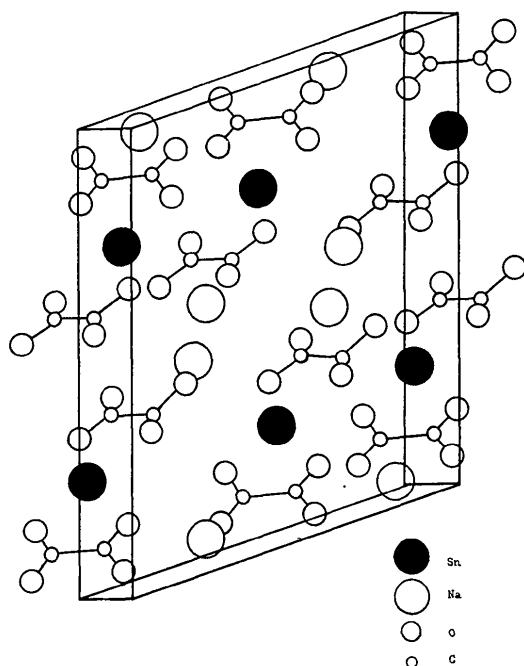


Fig. 1. (130) projection of the unit cell of  $\text{Na}_2\text{Sn}(\text{C}_2\text{O}_4)_2$ .

Table 1. *Positional and thermal atom parameters* ( $\times 10^4$ )

The figures given in parentheses are the standard deviations in the parameters.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
Sn	0	1725 (2)	2500	*
Na	3103 (4)	4898 (8)	4478 (3)	1.4 (1)
O(1)	2636 (7)	843 (14)	4016 (5)	1.6 (1)
O(2)	1762 (7)	2958 (14)	1881 (5)	1.7 (1)
O(3)	4869 (7)	2770 (14)	585 (5)	1.7 (1)
O(4)	734 (7)	4787 (3)	3576 (5)	1.5 (1)
C(1)	1542 (9)	4869 (18)	1341 (6)	1.2 (1)
C(2)	4896 (8)	888 (18)	3899 (6)	1.2 (1)

\* Anisotropic temperature factors, of the form

$$\exp [-(b_{11}h^2 + b_{22}k^2 + b_{33}l^2 + 2b_{12}hk + 2b_{13}hl + 2b_{23}kl)]:$$

$b_{11}$	$b_{22}$	$b_{33}$	$b_{12}$	$b_{13}$	$b_{23}$
41 (1)	120 (10)	16 (1)	0	12 (1)	0

Table 2. *Interatomic distances* (Å) *and angles* (°) *with errors*

(a) Tin coordination

Sn-O(2), two bonds to different oxalates at	2.357 (15)
Sn-O(4), two bonds to different oxalates at	2.246 (14)
O(2)-Sn-O(4) (same oxalate)	71.5 (5)
O(2)-Sn-O(4) (different oxalates)	81.9 (5)
O(2)-Sn-O(2)	145.5 (5)
O(4)-Sn-O(4)	78.7 (5)

(b) Oxalate groups

C(1)-O(1)	1.241 (25)	C(2)-O(3)	1.259 (22)
C(1)-O(2)	1.289 (23)	C(2)-O(4)	1.261 (26)
C(1)-C(2)	1.543 (25)		
O(1)-C(1)-O(2)	125.5 (16)	O(3)-C(2)-O(4)	125.2 (17)
O(1)-C(1)-C(2)	119.5 (16)	O(3)-C(2)-C(1)	116.4 (17)
O(2)-C(1)-C(2)	115.0 (16)	O(4)-C(2)-C(1)	118.5 (15)

The dihedral angle between planes [O(1), C(1), O(2)] and [O(3), C(2), O(4)] is 176.1 (16).

(c) Sodium coordination

Na-O(1)	2.395 (17)	Na-O(3)	2.464 (18)
Na-O(1)	2.443 (18)	Na-O(3)	2.377 (15)
Na-O(2)	2.575 (18)	Na-O(4)	2.385 (14)

The O-Na-O bond angles  $\pm 0.5^\circ$  are given in Fig. 3.

(ii) *FORDAP*, the Zalkin Fourier program, (iii) *ORFFE*, Busing & Levy's function and error program and (iv) *CELLPLOT*, an Algol program written for the Elliott 503 computer and graph plotter. The last draws ordinary or stereoscopic views of a unit cell from any angle. Unlike previous plotting programs (Johnson, 1965; Cole & Adamson, 1969) it draws clinographic projections on crystallographic planes of space-filling or 'ball and stick' models. Details of this program are available from the authors.

## Discussion

The structure contains discrete dioxalato-stannate(II) anions,  $\text{Sn}(\text{C}_2\text{O}_4)_2^{2-}$ , in which the oxalate groups are chelated to the tin atoms, although the Sn-O bond

distances to the two oxygen atoms in an oxalate ion are not the same. Fig. 1 shows a (130) projection of the structure.

#### The tin environment

The tin atoms are surrounded by four oxygen atoms from the two chelating oxalate groups, as illustrated in Fig. 2. There are two short bonds (2.246 Å) and two slightly longer distances (2.357 Å), giving the tin atoms a distorted square-pyramidal environment. The apex of the pyramid must be occupied by a stereochemically active lone-pair orbital, and the next-nearest, non-bonding, Sn–O distance is 2.910 Å. The pyramidal bond angles are less than 90°. The two to oxygen atoms in the same oxalate group are 71.5°, while the two to oxygen atoms in different oxalate groups are 81.9°.

Tin in most of its tin(II) compounds is in a distorted environment because of the presence of a stereochemically active lone-pair of non-bonding electrons. The most common tin(II) environment consists of a trigonal-pyramidal arrangement of three nearest-neighbour tin–ligand bonds with three longer, non-bonding contacts completing a distorted octahedral coordination. These longer contacts arise because close approach to the tin in their approach directions is prevented by the lone-pair orbitals. Tin(II) compounds in which this type of environment is found for oxygen-containing materials include SnSO<sub>4</sub> (Donaldson & Puxley, 1972*b*), SnHPO<sub>4</sub> (Berndt & Lamberg, 1971), KSn(HCO<sub>2</sub>)<sub>3</sub> (Jelen & Linquist, 1969), SnCl<sub>2</sub>·2H<sub>2</sub>O (Kiriyaama, Nakamura, Kitahama & Kiriyaama, 1972) and one site in Sn<sub>3</sub>O(OH)<sub>2</sub>SO<sub>4</sub> (Davies *et al.*, 1975). This type of environment is found in many other tin(II) compounds including SnS (Hofmann, 1935), SnCl<sub>2</sub> (van den Berg, 1961, 1962), NaSn<sub>2</sub>F<sub>5</sub> (McDonald, Larson & Cromer, 1964) and Sn<sub>3</sub>F<sub>5</sub>Br (Donaldson & Puxley, 1972*a*). Because of the presence of the chelating oxalate groups, the present compound does not have this typical trigonal-pyramidal environment for tin atoms nor does it have the regular square-pyramidal environment of the tin(II) oxide structure (Moore & Pauling, 1941). The structure of SnO is unique in tin(II) chemistry and its regular square-pyramidal coordination probably results from solid-state effects rather than from any other factors (Donaldson & Silver, 1974). The present compound instead has a distorted square-pyramidal coordination which is found in a few other tin(II) derivatives including 2KSnF<sub>3</sub>·H<sub>2</sub>O (Bergerhoff, Goost & Schultze-Rhnhof, 1968), SnSO<sub>4</sub>·2SC(NH<sub>2</sub>)<sub>2</sub> (Donaldson, Nicholson, Puxley & Howie, 1973) and two Sn sites in Sn<sub>3</sub>O(OH)<sub>2</sub>SO<sub>4</sub> (Davies *et al.*, 1975).

The main structural feature found in all four-coordinated tin environments, including Na<sub>2</sub>Sn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>, is the existence of two bonds of considerably greater length than those normally found in tin(II) compounds. It therefore appears probable that, if there are no specific solid-state effects such as the tin–tin interac-

tions in blue-black tin(II) oxide, the coordination about the tin atoms in stannous compounds can only be increased from the trigonal-pyramidal environment if one of the three bond lengths is increased.

#### The sodium environment

The sodium ions in the structure are in distorted octahedral sites with the bond distances and angles shown in Fig. 3.

#### The oxalate group

In many oxalate-containing crystals the C<sub>2</sub>O<sub>4</sub><sup>2-</sup> ions are planar and centrosymmetric, *e.g.* in K<sub>2</sub>C<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O (Pedersen, 1964) and Sc<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>·6H<sub>2</sub>O (Hansson, 1972). In other materials, such as KHC<sub>2</sub>O<sub>4</sub> (Einspahr, Marsh & Donohue, 1972) and 2NH<sub>4</sub>HC<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O

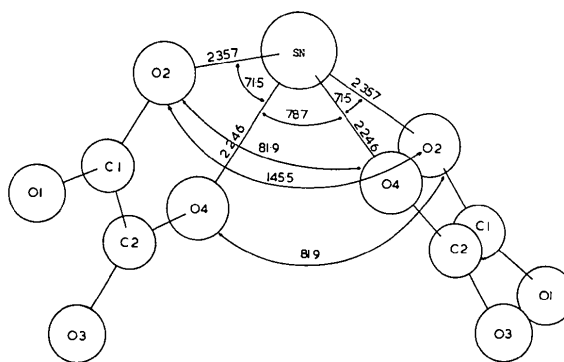


Fig. 2. The environment of the tin atoms in Na<sub>2</sub>Sn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>.

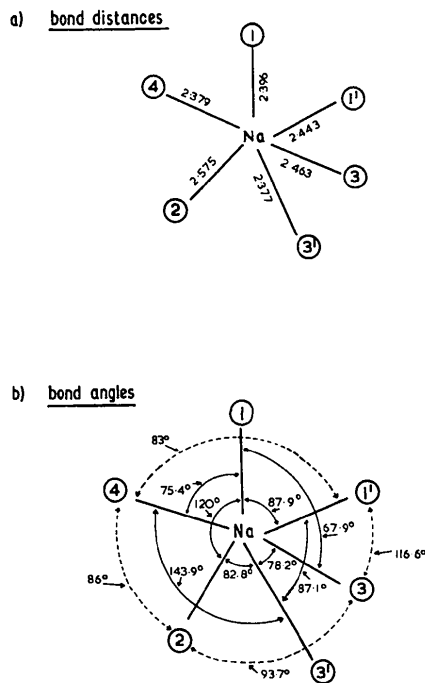


Fig. 3. The environment of the sodium atoms in Na<sub>2</sub>Sn(C<sub>2</sub>O<sub>4</sub>)<sub>2</sub>.

(Küppers, 1973) the group is non-centrosymmetric while in  $(\text{NH}_4)_4\text{UO}_2(\text{C}_2\text{O}_4)_3$  (Alcock, 1973) the ends of the oxalate groups are twisted relative to each other by  $37^\circ$ . The oxalate groups in the present compound are almost planar [the sums of the angles at C(1) and C(2) are  $360^\circ$  within experimental error and the dihedral angle between the plane containing O(1), C(1), and O(2) and the plane containing O(3), C(2) and O(4) is  $176.1^\circ$ ] but non-centrosymmetric. The bond distances and angles for the oxalate groups in  $\text{Na}_2\text{Sn}(\text{C}_2\text{O}_4)_2$  are very similar to those found in other crystal structures. It is, however, interesting that the longest C–O bonds are to the oxygen atoms forming the longer of the two Sn–O bonds.

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## The Crystal and Molecular Structure of Trihydrazinotriazine

BY D. S. BROWN, J. D. LEE AND P. R. RUSSELL

*Department of Chemistry, Loughborough University of Technology, Loughborough LE11 3TU, England*

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The crystal structure of trihydrazinotriazine,  $\text{C}_3\text{N}_3(\text{NHNH}_2)_3$ , has been determined by Patterson and trial-and-error methods and refined to a conventional  $R$  of 0.087 for 632 observed reflexions. Crystals are monoclinic,  $Cc$ , with  $a = 3.625$  (1),  $b = 17.603$  (4),  $c = 11.026$  (2) Å and  $\beta = 101.93$  (2)°;  $Z = 4$ . Individual molecules are hydrogen-bonded to neighbouring molecules to form a planar ribbon-like structure with the ribbons connected to one another by normal van der Waals contacts. One particularly close N–H...N hydrogen bond of 2.83 (2) Å is reported.

### Introduction

Trihydrazinotriazine (THT) is used commercially as a blowing agent for producing plastic foams since its thermal decomposition yields gaseous products. As part of a kinetic study of the decomposition of a number of blowing agents, the crystal structure of

THT has been determined in order to provide structural evidence for the mechanism of decomposition.

### Experimental

Commercial THT (Fisons) was recrystallized from aqueous solution to give colourless crystals in the