# Tin-119 Mössbauer and *X*-Ray Crystallographic Evidence for Differences in the Co-ordination of Tin in Oxalatostannates(II) and Malonatostannates(II) †

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The Mössbauer parameters for the series of oxalatostannates(II) $M_2Sn(C_2O_4)_2\cdot xH_2O$ are rationalised in terms of distorted square-pyramidal tin environments. The crystal structure of the malonato-complex $K_2Sn_2[CH_2(CO_2)_2]_3\cdot H_2O$ is reported: monoclinic, space group $P2_1/n$, with $a$ = 11.233(2), $b$ = 18.776(2), $c$ = 8.171(1) Å, β = 90.15(1)°, and $Z$ = 4; $R$ = 0.0277 for 5 805 reflections. Unlike the oxalate groups in the oxalato-complexes, the malonate moieties are bridging rather than chelating and the tin atoms are in trigonal rather than distorted four-pyramidal environments. Mössbauer data are reported for the malonate series of compounds $M_2Sn_2[CH_2(CO_2)_2]_3\cdot xH_2O$ (M = $NH_4$, K, Na, Rb, or Cs; $x$ = 0, 1, or 3) and the data for the potassium salt are shown to be consistent with the crystal structure.

The crystal structures of only five carboxylatostannate(II) complexes are known. The structures determined to date can be described as one of two types *viz.* (*i*) monocarboxylato-complexes with unidentate ligands and (*ii*) dicarboxylato-complexes with bidentate ligands. The monocarboxylato-complexes $KSn(O_2CH)_3$,[1] $KSn(O_2CCH_2Cl)_3$,[2] $Ca[Sn(O_2CMe)_3]_2$,[3] and $Sr[Sn(O_2CCH_2Cl)_3]_2$[4] have tin atoms surrounded by trigonal-pyramidal arrangements of nearest-neighbour oxygen atoms with short Sn–O bonds to three unidentate ligands. Distorted octahedral environments for the tin atoms are completed by three long tin-to-oxygen distances. This is the most common environment found for tin in tin(II) compounds and the longer Sn ⋯ O contacts arise because close approach of oxygen atoms to the tin in these directions is prevented by the presence of sterically active non-bonding electron pairs.[5] The complexes $Na_2Sn(C_2O_4)_2$[6] and $K_2Sn(C_2O_4)_2\cdot H_2O$[7] contain bidentate oxalato-groups and have tin atoms in distorted four-pyramidal sites with two shorter and two longer Sn–O bonds. The series of complexes formed between tin(II) and the potentially bidentate malonate groups, however, cannot belong to either of the two known types because the complexes have the compositions $M_2Sn_2[CH_2(CO_2)_2]_3\cdot xH_2O$ (M = $NH_4$, K, Na, Rb, or Cs).

We now report the crystal structure determination of dipotassium trimalonatodistannate(II) monohydrate and discuss the thermal analytical data and $^{119}Sn$ Mössbauer parameters of the complex tin(II) malonates and oxalates in the light of the structural information available on them.

## Experimental

*Preparations—Tin*(II) *malonate.* Blue-black tin(II) oxide (13.4 g, 0.1 mol) was added to an aqueous solution of malonic acid (40% w/v; 50 cm³, 0.2 mol) and the mixture heated under reflux, in an oxygen-free atmosphere, until the oxide had completely dissolved. The cloudy solution was filtered hot and the clear filtrate allowed to cool slowly to room temperature. The white crystalline product was filtered off, washed with acetone and diethyl ether, and dried *in vacuo* over KOH pellets.

*Malonato-complexes* $M_2Sn_2[CH_2(CO_2)_2]_3\cdot xH_2O$. Tin(II) malonate (2.2 g, 10 mmol) was added to a solution of malonic acid (3.1 g, 30 mmol) in distilled water (25 cm³) and the mixture heated under reflux until all the tin(II) malonate had dissolved. To this solution was added the appropriate alkali-metal or ammonium carbonate (10 mmol). The resulting mixture was filtered and colourless crystals were obtained when the solution was kept for several days. The crystals were filtered off, washed with acetone and diethyl ether, and dried *in vacuo* over KOH pellets. Analytical data are in Table 1.

*Oxalato-complexes* $M_2Sn(C_2O_4)_2\cdot H_2O$. The ammonium, sodium, and potassium derivatives of tin(II) oxalate were prepared by the literature method.[8] The crystalline products analysed as $M_2Sn(C_2O_4)_2\cdot H_2O$ (M = $NH_4$ or K) and $M_2Sn(C_2O_4)_2$ (M = Na). To prepare the rubidium and caesium derivatives, the metal carbonate (40 mmol) was dissolved in a solution of oxalic acid (5.4 g, 60 mmol) in water (25 cm³). Tin(II) oxalate (4.1 g, 20 mmol) was then added and the mixture heated until the oxalate had dissolved completely. The volume of the solution was then reduced and the products crystallised out on cooling the solution. These products also analysed as $M_2Sn(C_2O_4)_2\cdot H_2O$ (M = Rb or Cs).

*Thermal Analysis.*—The thermal analyses of the complex tin(II) malonates and oxalates from ambient temperatures to 400 °C were obtained using a Stanton Redcroft ST760 analyser with a heating rate of 3 °C min⁻¹. The tin(II) derivatives of the dicarboxylic acids were also decomposed *in vacuo* and the gaseous and solid products collected for identification by i.r. spectroscopy and *X*-ray powder diffraction respectively. The presence of carbon in the residue was shown by heating it in a stream of oxygen and analysing the outflowing stream by i.r. spectroscopy for $CO_2$. The only identifiable condensate in the cold-trap was water.

*Tin*-119 *Mössbauer Spectra.*—The spectra of all materials were recorded at liquid-nitrogen temperature using a barium stannate source. The Mössbauer equipment has been described previously.[9]

*Crystal Data.*—$C_9H_6K_2O_{12}Sn_2\cdot H_2O$, $M$ = 639.7, monoclinic, $a$ = 11.233(2), $b$ = 18.776(2), $c$ = 8.171(1) Å, β = 90.15(1)°, $U$ = 1 723.4 Å³, $D_m$ = 2.38 g cm⁻³, $Z$ = 4, $D_c$ = 2.46 g cm⁻³, $F(000)$ = 1 216, space group $P2_1/n$ ($P2_1/c$, no. 14), from systematic absences $0k0$ for $k = 2n + 1$, $h0l$ for $h + l = 2n + 1$ (Mo-$K_\alpha$ radiation: $\lambda$ = 0.710 7 Å, $\mu$ = 31.92 cm⁻¹).

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† *Supplementary data available* (No. SUP 23957, 36 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

**Table 1.** Analytical data (calculated values in parentheses) for the malonato-complexes $M_2Sn_2[CH_2(CO_2)_2]_3{\cdot}xH_2O$

| M | $x$ | Formula | Analyses (%) | | | |
|---|---|---|---|---|---|---|
| | | | C | H | M | Sn |
| $NH_4$ | 0 | $C_9H_{14}N_2O_{12}Sn_2$ | 18.6 (18.6) | 2.5 (2.4) | 5.0 (4.8) * | 40.9 (41.0) |
| Na | 3 | $C_9H_{12}Na_2O_{15}Sn_2$ | 17.0 (16.8) | 1.7 (1.9) | 7.0 (7.1) | 36.8 (36.9) |
| K | 1 | $C_9H_8K_2O_{13}Sn_2$ | 17.1 (16.9) | 1.2 (1.3) | 12.1 (12.2) | 37.1 (37.1) |
| Rb | 3 | $C_9H_{12}O_{15}Rb_2Sn_2$ | 14.1 (14.1) | 1.4 (1.6) | 22.0 (22.2) | 30.7 (30.9) |
| Cs | 3 | $C_9H_{12}Cs_2O_{15}Sn_2$ | 12.5 (12.5) | 1.4 (1.4) | 30.7 (30.8) | 27.6 (27.5) |

* Values for N.

**Table 2.** Fractional atomic co-ordinates for $K_2Sn_2[CH_2(CO_2)_2]_3{\cdot}H_2O$

| Atom | *X/a* | *Y/b* | *Z/c* | Atom | *X/a* | *Y/b* | *Z/c* |
|---|---|---|---|---|---|---|---|
| Sn(1) | −0.041 3(1) | 0.397 4(1) | −0.613 5(1) | O(10) | −0.166 1(2) | 0.326 9(1) | −0.341 5(3) |
| Sn(2) | 0.570 3(1) | 0.366 4(1) | −0.619 0(1) | O(11) | −0.982(2) | 0.246 9(1) | −0.669 6(3) |
| K(1) | 0.244 2(1) | 0.339 2(1) | −0.367 1(1) | O(12) | 0.165 9(4) | 0.102 4(2) | −0.434 7(11) |
| K(2) | 0.286 9(1) | 0.312 4(1) | 0.120 1(1) | O(13) | 0.192 9(3) | 0.069 3(2) | −0.380 4(4) |
| O(1) | 0.073 6(2) | 0.303 0(1) | −0.629 0(3) | C(1) | −0.080 2(2) | 0.355 4(1) | −0.275 1(4) |
| O(2) | −0.507 6(2) | 0.507 3(2) | −0.704 4(5) | C(2) | 0.078 2(3) | 0.176 3(2) | −0.640 0(3) |
| O(3) | 0.035 2(3) | 0.179 8(2) | −0.356 4(3) | C(3) | 0.005 2(3) | 0.277 5(2) | −0.073 5(3) |
| O(4) | −0.000 8(2) | 0.390 6(2) | 0.352 8(3) | C(4) | −0.058 9(3) | 0.347 6(2) | −0.091 7(3) |
| O(5) | −0.110 7(2) | 0.089 6(1) | −0.150 0(4) | C(5) | 0.281 8(3) | 0.514 7(1) | −0.718 9(5) |
| O(6) | 0.557 4(2) | 0.721 0(1) | −0.443 8(3) | C(6) | 0.175 1(2) | 0.466 0(1) | −0.719 7(4) |
| O(7) | 0.126 0(2) | 0.454 2(1) | −0.581 8(3) | C(7) | 0.399 1(3) | 0.476 5(2) | −0.691 6(4) |
| O(8) | 0.141 4(2) | 0.438 8(1) | −0.848 0(2) | C(8) | 0.009 9(3) | 0.246 1(1) | −0.648 4(3) |
| O(9) | 0.384 7(2) | 0.775 5(1) | −0.413 1(4) | C(9) | 0.096 9(3) | 0.151 0(2) | −0.465 0(4) |

**Table 3.** Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses, for $K_2Sn_2[CH_2(CO_2)_2]_3{\cdot}H_2O$

(*a*) Tin co-ordination

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sn(1)–O(1) | 2.199(8) | Sn(1)–O(8A) | 2.916(9) | Sn(2)–O(3) | 2.161(2) | Sn(2)–O(2A) | 2.872(0) |
| Sn(1)–O(4) | 2.177(2) | Sn(1)–O(10A) | 2.945(1) | Sn(2)–O(5) | 2.206(3) | Sn(2)–O(9A) | 2.724(4) |
| Sn(1)–O(7) | 2.177(6) | Sn(1)–O(11A) | 2.933(0) | Sn(2)–O(6) | 2.240(8) | Sn(2)–O(1A) | 2.857(5) |

| | | | | | |
|---|---|---|---|---|---|
| O(1)–Sn(1)–O(4) | 83.69 | O(4)–Sn(1)–O(7) | 74.65 | O(3)–Sn(2)–O(6) | 78.22 |
| O(1)–Sn(1)–O(7) | 84.07 | O(3)–Sn(2)–O(5) | 83.32 | O(5)–Sn(2)–O(6) | 73.23 |

(*b*) Malonate group co-ordination

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| O(1)–C(8) | 1.362(3) | C(3)–O(6) | 1.282(9) | C(6)–C(5) | 1.504(4) | C(8)–O(11) | 1.226(5) |
| O(4)–C(1) | 1.281(2) | C(3)–O(9) | 1.238(1) | O(8)–C(6) | 1.231(3) | C(8)–C(2) | 1.449(5) |
| O(7)–C(6) | 1.273(8) | O(3)–C(9) | 1.248(7) | C(5)–C(7) | 1.514(5) | C(2)–C(9) | 1.520(6) |
| C(1)–O(10) | 1.228(6) | O(5)–C(7) | 1.290(6) | C(7)–O(2) | 1.201(6) | C(9)–O(12) | 1.220(7) |
| C(1)–C(4) | 1.524(8) | C(6)–O(8) | 1.231(3) | C(4)–C(3) | 1.504(9) | C(9)–C(12) | 1.520(6) |

| | | | | | |
|---|---|---|---|---|---|
| Sn(1)–O(1)–C(8) | 110.32 | O(6)–C(3)–C(4) | 117.88 | O(5)–C(7)–C(5) | 114.83 |
| Sn(1)–O(4)–C(1) | 111.98 | O(9)–C(3)–C(4) | 119.60 | O(1)–C(8)–O(11) | 117.83 |
| Sn(1)–O(7)–C(6) | 110.86 | O(7)–C(6)–O(8) | 123.34 | O(1)–C(8)–C(2) | 115.56 |
| O(4)–C(1)–O(10) | 123.41 | O(7)–C(6)–C(5) | 116.64 | O(11)–C(8)–C(2) | 112.29 |
| O(4)–C(1)–C(4) | 115.62 | O(8)–C(6)–C(5) | 119.99 | O(3)–C(9)–O(12) | 112.18 |
| O(10)–C(1)–C(4) | 120.93 | C(6)–C(5)–C(7) | 114.05 | O(3)–C(9)–C(2) | 117.24 |
| C(1)–C(4)–C(3) | 104.65 | O(2)–C(7)–O(5) | 123.85 | O(12)–C(9)–C(2) | 120.51 |
| O(6)–C(3)–O(9) | 122.32 | O(2)–C(7)–C(5) | 121.29 | | |

*Structure Determination.*—Preliminary unit-cell data were obtained from oscillation and Weissenberg photographs, whilst the intensity data were collected at Queen Mary College, London, on an Enraf–Nonius CAD4 diffractometer for θ up to a maximum value of 35°. Graphite-monochromatised Mo-$K_\alpha$ radiation was used with an ω—2θ scan technique. Two standard reflections were measured every hour as a check on the crystal and instrument stability. Each scan consisted of 96 steps with the first and last 16 forming the background counts; the final structure factors were computed taking account of variable measuring times, Lorentz–polarisation factors, and appropriate crystal-decay factors and absorption. A total of 5 805 unique reflections with $I \geqslant 2.0\sigma(I)$ were measured and used in the calculations, which were carried out on a CDC 7 600 computer at the University of London Computer Centre, using SHELX 76.[10] Stereographic projections of the unit cell were obtained using PLUTO.[11]

The co-ordinates of the tin atoms were determined from a Patterson vector map. Fourier syntheses phased on the refined tin positions located the K, O, and C atoms. Least-squares refinement of the atom positions gave an $R$ value of 0.098 8. On the Fourier map a peak corresponding to approximately ten electrons and due to an atom, bonded neither to tin nor to part of the carboxylate group, was assigned to a molecule of water of crystallisation at *ca.* $x = 0.31, y = 0.04, z = 0.88$. Full-matrix least-squares refinement of all the

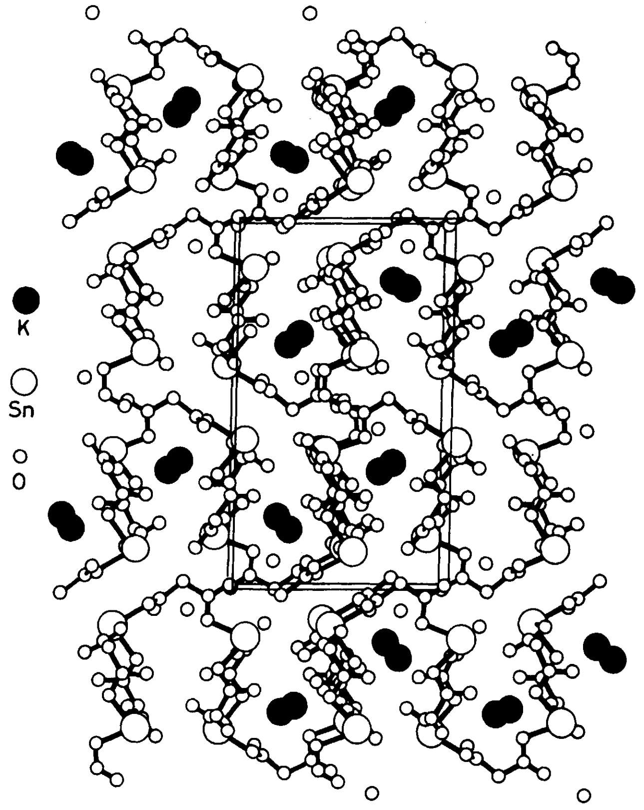

**Figure 1.** Projection of the unit cell of $K_2Sn_2[CH_2(CO_2)_2]_3 \cdot H_2O$; viewed down *z*

atoms including the oxygen of the water molecule resulted in an *R* value of 0.081 6. At this stage 85 weak reflections, for which $|F_o| \leqslant 2|F_c|$ or $|F_c| \leqslant 2|F_o|$, were removed and a final refinement was made with anisotropic thermal parameters for all non-hydrogen atoms. The hydrogen atoms were located in a Fourier map but not refined and all the remaining peaks on a final Fourier difference map corresponded to less than one electron. Refinement converged at $R = 0.0277$. Atomic co-ordinates are in Table 2 and bond distances and angles in Table 3.

## Results and Discussion

The thermal analyses of the oxalatostannates(II) confirm that the ammonium, potassium, rubidium, and caesium derivatives are monohydrates and that the sodium complex is anhydrous. The only gaseous product of the thermal decompositions of the complex oxalates at higher temperatures is $CO_2$ except in the case of the ammonium derivative where ammonia is also liberated. The solid residues contain tin(II) oxide, carbon, and metal oxalates (metal = Na, K, Rb, or Cs).

The thermal analyses of the malonatostannates(II) confirm that the ammonium derivative is anhydrous, that the potassium derivative is a monohydrate, and that the sodium, rubidium, and caesium derivatives are trihydrates. The complexes all decompose *in vacuo* with the loss of water, CO, $CO_2$, and acetone (plus $NH_3$ for the $NH_4$ derivative) to give a final residue containing tin(II) oxide.

The fact that tin(II) oxide is the final tin-containing product of the decompositions of the alkali-metal tin(II) oxalates and malonates is consistent with strong complex formation between tin(II) and the dicarboxylate oxygen atoms.[12]

The structure of dipotassium trimalonatodistannate(II) monohydrate consists of polymeric anionic layers of $\{Sn_2[CH_2(CO_2)_2]_3\}_n^{2n-}$ moieties with discrete potassium ions and water molecules located between the layers (Figure 1). Both tin atoms in the asymmetric unit are co-ordinated through single oxygen atoms of two of the three malonate groups forming a twelve-membered ring. The third malonate group is bonded to two tin atoms of neighbouring twelve-membered rings; *e.g.* Sn(2) of one ring is linked to Sn(1) of a neighbouring ring (Figure 2). The overall structure is that of extended polymeric layers composed of twelve-membered ring systems bridged by malonate groups to neighbouring ring systems through Sn–O bonds.

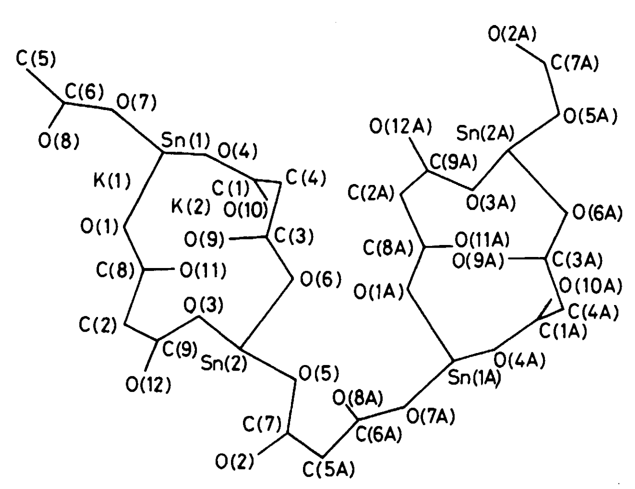

**Figure 2.** Schematic diagram of the asymmetric unit of $K_2Sn_2[CH_2(CO_2)_2]_3 \cdot H_2O$

The bond distances and angles in the malonate groups are typical of those found in many malonates.[13] The length of the C–O bond varies according to whether or not the oxygen atom is co-ordinated. Not surprisingly the C–O bond of a co-ordinated oxygen atom is longer than that of an unco-ordinated oxygen atom; C–O bonds of both types are found in other tin(II) carboxylates and their complex derivatives. The environments of the two potassium atoms are different. One is surrounded by seven nearest-neighbour malonate oxygen atoms at distances of 2.948, 2.887, 3.081, 2.964, 3.132, 2.941, and 2.929 Å, and an oxygen atom of the water molecule at 2.745 Å, and the other is co-ordinated to eight malonate oxygen nearest-neighbour atoms at 2.920, 2.688, 2.894, 3.229, 2.868, 3.162, 2.653, and 2.799 Å and an oxygen atom of the water molecule at 2.971 Å. The water molecule itself participates in hydrogen bonding to the malonate moiety with the hydrogen atom, H(8), of the water molecule bonding to the oxygen atom, O(9), of the malonate group (2.99 Å).

The co-ordination about each tin(II) atom is that of a trigonal pyramid, in which each tin atom is co-ordinated by three oxygen atoms from bridging malonate groups, and three longer contacts to malonate oxygen atoms complete a distorted octahedral environment about the tin. Although each tin(II) atom lies in a trigonal pyramidal environment, Sn(1) has two short (2.177 and 2.177 Å) and one long bond (2.199 Å) to oxygen, whilst Sn(2) has one short (2.161 Å) and two long bonds (2.206 and 2.240 Å) to oxygen. Unlike oxalate ions which chelate tin(II) to give the metal distorted four-pyramidal environments, the malonate groups, although bidentate, form bridges between different tin atoms; interestingly, each anisobidentate malonate group forms one short (*ca.* 2.17 Å) and one long (*ca.* 2.20 Å) Sn–O bond. This gives rise to an extended polymeric anionic system of $\{Sn_2[CH_2(CO_2)_2]_3\}_n^{2n-}$ and not to discrete $[SnL_2]^{2-}$ ions as found in $Na_2Sn(C_2O_4)_2$.[6] A consequence of the trigonal pyramidal co-ordination is that

**Table 4.** Mössbauer parameters of complex tin(II) dicarboxylates *

| Compound | $\delta$/mm s$^{-1}$ | $\Delta$/mm s$^{-1}$ |
|---|---|---|
| $Sn(C_2O_4)$ | 3.70 | 1.54 |
| $(NH_4)_2Sn(C_2O_4)_2 \cdot H_2O$ | 3.42 | 1.88 |
| $Na_2Sn(C_2O_4)_2$ | 3.67 | 1.47 |
| $K_2Sn(C_2O_4)_2 \cdot H_2O$ | 3.38 | 1.97 |
| $Rb_2Sn(C_2O_4)_2 \cdot H_2O$ | 3.19 | 2.06 |
| $Cs_2Sn(C_2O_4)_2 \cdot H_2O$ | 3.17 | 2.06 |
| $Sn[CH_2(CO_2)_2]$ | 3.51 | 1.74 |
| $(NH_4)_2Sn_2[CH_2(CO_2)_2]_3$ | 3.25 | 1.70 |
| $Na_2Sn_2[CH_2(CO_2)_2]_3 \cdot 3H_2O$ | 3.04 | 1.81 |
| $K_2Sn_2[CH_2(CO_2)_2]_3 \cdot H_2O$ | 3.15 | 1.74 |
| $Rb_2Sn_2[CH_2(CO_2)_2]_3 \cdot 3H_2O$ | 3.23 | 1.79 |
| $Cs_2Sn_2[CH_2(CO_2)_2]_3 \cdot 3H_2O$ | 3.09 | 1.99 |

* Chemical shifts relative to $BaSnO_3$.

$K_2Sn_2[CH_2(CO_2)_2]_3 \cdot H_2O$ has a shorter average tin-to-nearest-oxygen bond length than the compounds with distorted four-co-ordination such as $Sn(C_2O_4)$,[14] $Na_2Sn(C_2O_4)_2$,[6] $K_2Sn(C_2O_4)_2 \cdot H_2O$,[7] and $Sn(O_2CCH{=}CHCO_2) \cdot H_2O$.[15] This arises because the co-ordination about tin can only be increased from three to four if one of the bonds is lengthened. The short Sn–O bonds are consistent with the thermal analytical data in that they confirm that strong complexes are formed.

The tin-119 Mössbauer parameters for the complex tin(II) malonates and oxalates are in Table 4 together with the data for the parent tin(II) carboxylates. The decrease in chemical isomer shift in going from a tin(II) dicarboxylate to a complex is the expected result for the formation of complex tin(II) ligand anions.[5] The Mössbauer shift parameters for tin(II) oxalate and its alkali-metal derivatives can be rationalised in terms of known crystal structures. We have previously[5] pointed out that there is a relationship between chemical shift and tin-to-ligand bond lengths. In $Sn(C_2O_4)$, $K_2Sn(C_2O_4)_2 \cdot H_2O$, and $Na_2Sn(C_2O_4)_2$ the tin atoms are in four-co-ordinate environments with the oxalate anions acting as bidentate ligands with two short and two somewhat longer Sn–O bond distances. The structure of $Sn(C_2O_4)$ consists of infinite chains of alternating tin atoms and oxalate groups in which the shorter and longer Sn–O bond distances are 2.23 and 2.39 Å respectively; $Na_2Sn(C_2O_4)_2$ contains $Sn(C_2O_4)_2^{2-}$ moieties in which the corresponding shorter and longer Sn–O bonds are 2.25 and 2.36 Å. The environments in tin(II) oxalate and the sodium complex are very similar; the average Sn–O bond length in the complex is shorter than in the parent compound although the shortest Sn–O bonds are slightly longer than in $Sn(C_2O_4)$. The similarity in these environments is reflected in the similarity of the Mössbauer parameters for $Sn(C_2O_4)$ and $Na_2Sn(C_2O_4)_2$. In contrast the potassium complex has both a smaller average Sn–O bond length and a shorter minimum Sn–O distance. The lower chemical shift for the potassium complex is consistent with the increased use of tin *s*-electron density in forming shorter Sn–O bonds. The quadrupole splitting reflects the imbalance in the *p*-electron density at the tin atom. The increase in asymmetry in the potassium salt compared with the tin(II) oxalate and the sodium salt could arise from greater asymmetry of the environment and/or the increased *p*-electron density in the lone pair that must result from the formation of shorter Sn–O bonds. The values of the shift and splitting parameters for tin(II) malonate suggest that it involves stronger Sn–O interactions and that the overall electronic environment of the tin atom is more asymmetric than in tin(II) oxalate. The lower shifts for the $M_2Sn_2[CH_2(CO_2)_2]_3 \cdot xH_2O$ complexes are consistent with complex formation. The average Sn–O bond length in $K_2Sn_2[CH_2(CO_2)_2]_3 \cdot H_2O$ and its shift value are consistent with the trend found in shift and bond-length data for compounds containing trigonal pyramidal Sn–O co-ordination (Table 5).

**Table 5.** Relationship between Mössbauer chemical shift data and average tin-to-ligand bond length

| Compound | Average Sn–L bond length/Å | $\delta$/mm s$^{-1}$ * |
|---|---|---|
| $Ca[Sn(O_2CMe)_3]_2$ | 2.14 | 2.90 |
| $KSn(O_2CCH_2Cl)_3$ | 2.16 | 2.96 |
| $KSn(O_2CH)_3$ | 2.16 | 3.08 |
| $K_2Sn_2[CH_2(CO_2)_2]_3 \cdot H_2O$ | 2.19 | 3.15 |
| $SnSO_4$ | 2.26 | 3.95 |

* Chemical shift relative to $BaSnO_3$.

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## References

1 A. Jelen and O. Linquist, *Acta Crystallogr., Sect. B*, 1971, **27**, 1092.

2 S. J. Clark, J. D. Donaldson, J. C. Dewan, and J. Silver, *Acta Crystallogr., Sect. B*, 1979, **35**, 2550.

3 J. C. Dewan, J. Silver, J. D. Donaldson, and M. J. K. Thomas, *J. Chem. Soc., Dalton Trans.*, 1977, 2319.

4 J. D. Donaldson and J. C. Dewan, personal communication.

5 J. D. Donaldson and S. M. Grimes, *Rev. Silicon, Germanium, Tin, Lead, Compd.*, in the press.

6 J. D. Donaldson, M. T. Donoghue, and C. H. Smith, *Acta Crystallogr., Sect. B*, 1976, **32**, 2098.

7 R. M. A. Grimsey, Ph.D. Thesis, London, 1980; A. D. Christie, R. A. Howie, and W. Moser, *Inorg. Chim. Acta*, 1979, **36**, L447.

8 S. Hausmann and J. Lowenthal, *Liebigs Ann. Chem.*, 1954, **89**, 104.

9 J. D. Donaldson and B. J. Senior, *J. Chem. Soc. A*, 1966, 1769.

10 G. M. Sheldrick, SHELX Program for Crystal Structure Determination, University of Cambridge, 1976.

11 W. D. S. Motherwell, PLUTO, Plotting Molecular and Crystal Structures, University of Cambridge, 1979.

12 J. D. Donaldson, *Prog. Inorg. Chem.*, 1967, **8**, 287.

13 A. Pajunen and S. Pajunen, *Acta Crystallogr., Sect. B*, 1980, **36**, 2425.

14 A. D. Christie, R. A. Howie, and W. Moser, *Inorg. Chim. Acta*, 1979, **36**, L447; A. Gleiges and J. Galy, *J. Solid State Chem.*, 1979, **30**, 23.

15 J. C. Dewan, J. Silver, R. H. Andrews, J. D. Donaldson, and D. R. Laughlin, *J. Chem. Soc., Dalton Trans.*, 1977, 368.

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