

Fig. 3. *trans*-Co(mesityl)<sub>2</sub>(PPhEt)<sub>2</sub>: coordination of mesityl ligands showing slight 'misdirected valency' of donor C atom and asymmetry of Co...H contacts.

Owston & Rowe (1963). The ethyl and phenyl substituents of the phosphines are swept back from the Co atom in that all C—P—C bond angles are less than the idealized tetrahedral value. A rationale of this form of phosphine stereochemistry has been given by Mason & Meek (1977) in terms of an increased *s* character of the P atom orbital directed towards the central metal.

The planar mesityl groups lie almost exactly perpendicular to the coordination plane: the angle is 90.6 (9)°. As required by the inversion centre, the two mesityl groups are coparallel; they are not, however, coplanar (Fig. 3*a*). Their planes lie 0.324 (10) Å apart with the Co atom mid-way between. As reported earlier, the orientation of the mesityl groups is such that the fifth and sixth octahedral coordination sites are blocked by the  $\alpha$ -methyl groups. There is no evidence for facile rotation of these methyl groups and there are two close Co...H contacts of 2.56 [Co...H(3)] and 2.79 Å [Co...H(9)]. The asymmetry of these close contacts (Fig. 3*b*) is consistent with a further small coordination distortion in which the Co atom lies 0.188 (10) Å from the local mesityl diads.

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## The Structure of Potassium Tris(monochloroacetato)stannate(II)

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#### Abstract

$K[\text{Sn}(\text{C}_2\text{H}_2\text{ClO}_2)_3]$ ,  $\text{K}^+$ ,  $\text{C}_6\text{H}_6\text{Cl}_3\text{O}_6\text{Sn}^-$ , is monoclinic, space group  $B2_1/c$  (non-standard form of  $P2_1/c$ ) with  $a = 15.96$  (2),  $b = 11.80$  (2),  $c = 14.19$  (2) Å,  $\beta =$

99.40 (10)°,  $Z = 8$ . Final  $R = 0.049$  for 2433 reflexions. The structure consists of discrete  $[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]^-$  ions and independent cations. The Sn atoms are in distorted trigonal pyramidal sites with Sn—O 2.14, 2.18 and 2.18 Å. A distorted octahedral

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coordination is completed by three further O atoms at 2.92, 2.97 and 3.05 Å. The O—Sn—O angles in the  $[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]^-$  ion are all  $< 90^\circ$ .

### Introduction

The crystal structures of only four  $\text{Sn}^{\text{II}}$  carboxylate compounds are known,  $\text{K}[\text{Sn}(\text{HCO}_2)_3]$  (Jelen & Lindqvist, 1969),  $\text{Na}_2[\text{Sn}(\text{C}_2\text{O}_4)_2]$  (Donaldson, Donoghue & Smith, 1976),  $\text{Sn}(\text{C}_4\text{H}_2\text{O}_4) \cdot \text{H}_2\text{O}$  (Dewan, Silver, Andrews, Donaldson & Laughlin, 1977) and  $\text{Ca}[\text{Sn}(\text{CH}_3\text{CO}_2)_3]_2$  (Dewan, Silver, Donaldson & Thomas, 1977). We now describe the structure of  $\text{K}[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]$ . This is the first report of a structure determination of a  $\text{Sn}^{\text{II}}$  derivative of a halogen-substituted carboxylic acid.

Crystals were prepared by the method of Donaldson & Jelen (1968a).  $\text{Sn}^{\text{II}}$  oxide (0.075 mol) was dissolved in monochloroacetic acid (0.5 mol in 100 ml water) by heating with reflux under  $\text{N}_2$ . Potassium carbonate (0.075 mol in 25 ml of water) was added dropwise to the  $\text{Sn}^{\text{II}}$  solution. After effervescence had ceased, the hot solution was filtered and allowed to cool, when the product crystallized out. The crystals were washed with petroleum ether (b.p. 313–333 K) and dried *in vacuo* over KOH.

Precession and Weissenberg photographs were taken of a crystal mounted along the needle axis *b*. The cell dimensions deduced from these data were refined with powder diffraction data.

### Crystal data

$\text{K}[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]$  forms colourless acicular crystals which show no birefringence in polarized light.  $M_r = 438.59$ ; monoclinic,  $a = 15.96$  (2),  $b = 11.80$  (2),  $c = 14.19$  (2) Å,  $\beta = 99.40$  (10) $^\circ$ ,  $V = 2634.8$  Å<sup>3</sup>,  $D_c = 2.21$  for  $Z = 8$ ,  $D_m = 2.45$  Mg m<sup>-3</sup> (displacement of chlorobenzene),  $F(000) = 1680$ . Systematic absences:  $hkl$  for  $h + l$  odd;  $h0l$  for  $l$  odd;  $0k0$  for  $k$  odd.  $B2_1/c$  is the only possible space group and is a non-standard form of  $P2_1/c$ . Mo  $K\alpha$  radiation ( $\lambda = 0.7107$  Å,  $\mu = 2.67$  mm<sup>-1</sup>).

### Structure determination

Intensities were collected about **b** [layers ( $h0-11l$ )] on a Stoe two-circle computer-controlled diffractometer with graphite-monochromated Mo  $K\alpha$  radiation and a scintillation counter. The non-standard setting of the space group was chosen because of the requirement of the diffractometer that, to obtain the best possible results from refinement of axial lengths, as many reflexions as possible be present at both low and high

$2\theta$ . The stationary-counter moving-crystal method was used with an  $\omega$ -scan range of  $2.0^\circ$  on the lower levels, counting for 1.5 s at  $0.1^\circ$  intervals. This corresponds to a scan rate of  $4^\circ$  min<sup>-1</sup>. For reflexions on the fifth and higher layers ( $\mu > 7^\circ$ ) a variable range was scanned with  $\Delta\omega$  defined by  $(A + B \sin \mu/\tan \theta')$ , where  $2\theta'$  is the azimuth angle (Buerger, 1942),  $A = 1.0$  and  $B = 0.5$ . Stationary background counts were measured at the extremities of each scan for 10 s. Within the range  $0.1 < \sin \theta/\lambda \leq 0.65$  Å<sup>-1</sup>, 2908 independent reflexions were measured, 2533 of which had  $I > 3\sigma(I)$  and were considered observed. Data were corrected for Lorentz and polarization factors but not for absorption.

The position of the Sn atom was determined from a Patterson synthesis and refined by full-matrix least squares before the positions of the Cl, O, C and finally K atoms were obtained from Fourier syntheses phased on the Sn position. 100 reflexions for which  $|F_o| > 2|F_c|$  or  $|F_c| > 2|F_o|$  were removed and the interlayer scale factors and atomic positions were refined and then held constant while the refinement of anisotropic temperature factors was carried out for all atoms. The H atoms were located but their positions not refined.

In the final stages the weighting scheme  $w = [\sigma^2(F_o) + 0.01|F_o|^2]^{-1}$  was used.  $R = \sum (|F_o| - |F_c|) / (\sum |F_o|)$  converged to 0.0493 and a final difference map showed no significant features.\* The calculations were carried out on the CDC 7600 at the University

\* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34672 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic positions with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Sn	0.0075 (1)	0.7723 (1)	0.6619 (1)
Cl(1)	0.1733 (1)	0.1170 (2)	0.1621 (2)
Cl(2)	0.3669 (1)	0.5185 (2)	0.3127 (1)
Cl(3)	0.7056 (1)	-0.0941 (2)	0.4559 (2)
O(11)	0.3598 (3)	0.2390 (4)	0.3470 (4)
O(12)	0.4891 (3)	0.3116 (4)	0.4877 (3)
O(13)	0.5083 (3)	0.0976 (4)	0.3784 (4)
O(21)	0.3578 (4)	0.1697 (5)	0.2000 (4)
O(22)	0.5921 (3)	0.4367 (4)	0.4798 (3)
O(23)	0.6460 (3)	0.1400 (4)	0.4173 (4)
C(11)	0.3209 (4)	0.1915 (6)	0.2683 (5)
C(12)	0.5483 (4)	0.3810 (5)	0.5243 (4)
C(13)	0.5864 (4)	0.0719 (6)	0.4090 (4)
C(21)	0.2293 (4)	0.1707 (6)	0.2735 (6)
C(22)	0.4468 (4)	0.6139 (6)	0.3677 (4)
C(23)	0.5959 (4)	-0.0526 (6)	0.4321 (5)
K	0.8150 (1)	0.1364 (1)	0.5040 (1)
H(11)	0.198 (5)	0.245 (5)	0.285 (5)
H(12)	0.497 (5)	0.409 (5)	0.642 (5)
H(13)	0.574 (5)	0.933 (5)	0.504 (5)
H(21)	0.223 (5)	0.121 (5)	0.339 (5)
H(22)	0.565 (5)	0.307 (5)	0.657 (5)
H(23)	0.572 (5)	0.891 (5)	0.372 (5)

of London Computer Centre with *SHELX-76* (Sheldrick, 1976), *BONDLA* from *XRAY 72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) and the diagrams were drawn by *CELLPLOT* (Donaldson & Puxley, 1972) with the ICL 4130 computer and graph plotter at Chelsea College Computer Centre.

The atomic coordinates are given in Table 1, significant bond distances and angles in Table 2.

Table 2. Bond lengths (Å) and angles (°), *e.s.d.'s* in parentheses

(a) Tin coordination

Sn—O(11)	2.177 (10)	O(11)—Sn—O(12)	78.6 (4)
Sn—O(12)	2.182 (9)	O(11)—Sn—O(13)	83.3 (4)
Sn—O(13)	2.143 (11)	O(12)—Sn—O(13)	88.0 (4)
Sn—O(21)	2.923 (10)	O(21)—Sn—O(22)	162.3 (3)
Sn—O(22)	3.047 (10)	O(21)—Sn—O(23)	120.5 (4)
Sn—O(23)	2.966 (10)	O(22)—Sn—O(23)	77.1 (3)
O(11)—Sn—O(21)	49.4 (4)	O(12)—Sn—O(23)	83.9 (4)
O(11)—Sn—O(22)	118.9 (4)	O(13)—Sn—O(21)	79.8 (4)
O(11)—Sn—O(23)	129.3 (4)	O(13)—Sn—O(22)	114.2 (4)
O(12)—Sn—O(21)	227.4 (4)	O(13)—Sn—O(23)	48.6 (4)
O(12)—Sn—O(22)	46.8 (4)		

(b) Chloroacetate groups (mean bond lengths and angles)

C(2)—Cl	1.792 (14)	O(1)—C(1)	1.297 (15)
C(2)—H(1)	1.048 (80)	C(1)—O(2)	1.229 (17)
C(2)—H(2)	1.073 (80)	C(1)—C(2)	1.509 (19)
O(1)—C(1)—O(2)	124.1 (1.2)	C(1)—C(2)—H(1)	108 (3)
O(1)—C(1)—C(2)	110.7 (1.2)	C(1)—C(2)—H(2)	111 (4)
O(2)—C(1)—C(2)	125.1 (1.2)	Cl—C(2)—H(1)	107 (4)
C(1)—C(2)—Cl	111.7 (1.0)	Cl—C(2)—H(2)	109 (8)
		H(1)—C(2)—H(2)	110 (8)

(c) Potassium coordination

K—O(11)	2.856 (10)	K—Cl'(1)	3.442 (6)
K—O(12)	2.890 (10)	K—Cl''(2)	3.483 (6)
K—O'(21)	2.781 (11)	K—Cl'''(3)	3.243 (6)
K—O''(22)	2.773 (11)	K—Cl''''(3)	3.257 (6)
K—O'''(23)	2.775 (11)		

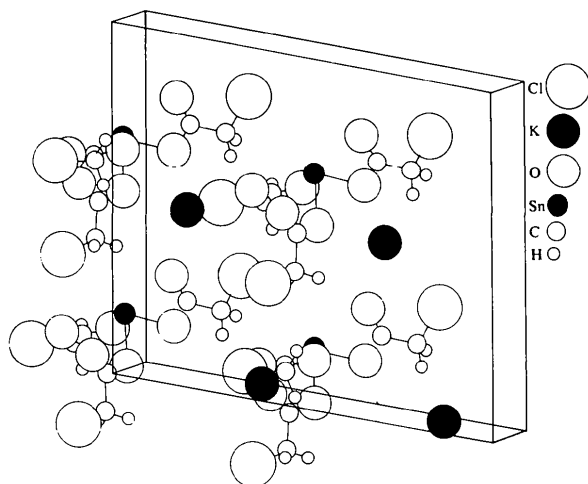


Fig. 1.  $(3\bar{5}1)$  projection of half the unit cell of  $\text{K}[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]$ .

## Discussion

The structure (Fig. 1) consists of discrete  $[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]^-$  anions and  $\text{K}^+$  cations in a three-dimensional network, and confirms the suggestions from Mössbauer evidence (Donaldson & Jelen, 1968*b*) that the substituted tricarbonylato-stannates(II) have Sn in trigonal pyramidal coordination. Each Sn atom (Fig. 2) is bonded to two O atoms at 2.18 and a third at 2.14 Å in an irregular trigonal pyramidal configuration with O—Sn—O angles of 78.6, 83.3 and 88.0° with three more O atoms at 2.92, 3.05 and 2.97 Å which complete a very distorted octahedral arrangement. The Sn environment in this complex is similar to those found in the two acetate complexes  $\text{K}[\text{Sn}(\text{HCO}_2)_3]$  (Jelen & Lindqvist, 1969), in which Sn has three nearest neighbours at 2.17, 2.18 and 2.14 Å and next-nearest-neighbour O atoms at 2.89 Å, and  $\text{Ca}[\text{Sn}(\text{CH}_3\text{CO}_2)_3]_2$  (Dewan, Silver, Donaldson, & Thomas, 1977), which has a regular trigonal pyramidal Sn coordination due to crystal packing effects, with three Sn—O bonds at 2.14 and next-nearest-neighbour distances of 2.93 Å. The O—Sn—O bond angle in the regular coordination of  $\text{Ca}[\text{Sn}(\text{CH}_3\text{CO}_2)_3]_2$  is 83.5°. Unidentate O atom ligands such as acetate and monochloroacetate appear to favour the formation of three-coordinated triligand stannate(II) species in contrast to chelating ligands which give rise to distorted square-pyramidal  $\text{Sn}^{\text{II}}$  sites with two long and two short Sn—O distances such as those in  $\text{Na}_2[\text{Sn}(\text{C}_2\text{O}_4)_2]$  (Donaldson, Donoghue & Smith, 1976) and  $\text{Sn}(\text{C}_4\text{H}_2\text{O}_4) \cdot \text{H}_2\text{O}$  (Dewan, Silver, Andrews, Donaldson & Laughlin, 1977).

$^{119}\text{Sn}$  Mössbauer data for  $\text{K}[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]$  were measured with a  $\text{BaSnO}_3$  source and absorber at 80 K and methods previously described (Donaldson, Silver, Thomas & Tricker, 1976).  $\text{K}[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]$  has a chemical isomer shift ( $\delta$ ) of 2.96 (2)  $\text{mm s}^{-1}$  (relative to  $\text{BaSnO}_3$ ) and a quadrupole splitting ( $\Delta$ ) of 1.77 (2)  $\text{mm s}^{-1}$ . These values compare with  $\delta = 3.15 \text{ mm s}^{-1}$  and

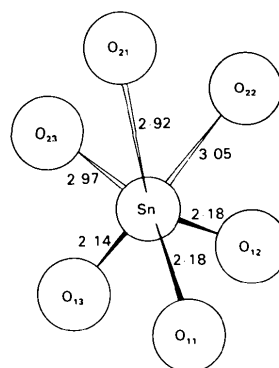


Fig. 2. Environment of Sn atoms in  $\text{K}[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]$  showing the distorted octahedral coordination including longer Sn—O bond distances.

$\Delta = 1.66 \text{ mm s}^{-1}$  for  $\text{Sn}(\text{ClCH}_2\text{CO}_2)_2$  (Donaldson & Jelen, 1968*b*). The smaller chemical shift of the  $[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]^-$  ion indicates a reduction in the 5s electron density around the Sn nucleus corresponding to a shift away from the carboxylated-bridged  $\text{Sn}^{\text{II}}$  carboxylate (Fig. 3) to the full  $sp^3$ -hybridized covalent bonding of the  $[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]^-$  ion in which all three nearest-neighbour O atoms are directly bonded to Sn. Fig. 2 shows that there is no close approach of O atoms to the Sn on the side opposite the short Sn—O bonds. This must be due to the presence of the stereochemically active lone pair on the Sn which would prevent the close approach of O atoms along the direction in which it points. The presence of the non-bonding electron pair also gives rise to an asymmetry in the distribution of  $p$ -electron density in the Sn environment and to quadrupole splitting of the Mössbauer resonance line.

All three chloroacetate groups are identical within the quoted e.s.d.'s. The configuration of the chloroacetate groups is very similar to other related ligands of known structure: chloroacetamide,  $\text{ClCH}_2\text{CONH}_2$  (Dejace, 1957), and the acetate group in  $\text{Ca}[\text{Sn}(\text{CH}_3\text{CO}_2)_3]_2$ . The bond lengths and angles show the absence of any intramolecular hydrogen bonding and that the C—Cl distance of 1.79 Å is unusually long; this increased bond length can be attributed to the presence of some interaction with the  $\text{K}^+$  cation.

The  $\text{K}^+$  cation (Fig. 4) is surrounded by five O atoms with  $\text{K—O} = 2.77, 2.78, 2.78, 2.86$  and  $2.89 \text{ \AA}$  and by four Cl atoms at 3.24, 3.26, 3.44 and 3.48 Å. These distances compared with the  $\text{K—O}$  lengths 2.6–2.74 Å in  $\text{K}_2\text{O}_2$  (Föppl, 1957) and with the  $\text{K—Cl}$  distance of 3.15 Å in  $\text{KCl}$  indicate some interaction between the  $\text{K}^+$  ion and both its nearest-neighbour O and Cl atoms.

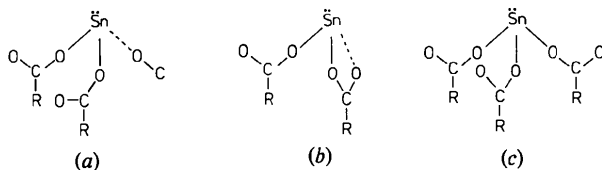


Fig. 3. Carboxylate bridging in  $\text{Sn}(\text{ClCH}_2\text{CO}_2)_2$  (a) and (b) compared with (c) the full  $sp^3$ -hybridized bonding in  $[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]^-$ .

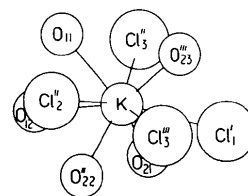


Fig. 4.  $\text{K}^+$  environment in  $\text{K}[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]$ .

After the submission of this paper for publication our attention was drawn to concurrent work by Lindgren & Jelen (1978) on the crystal structure of  $\text{K}[\text{Sn}(\text{ClCH}_2\text{CO}_2)_3]$ . The results obtained and their final residual (0.051) are similar to those reported in the present work.

We thank the SRC for a studentship to SJC.

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