^{119m}Sn Mössbauer Parameters and Crystal Structure of the $SnCl_3^-$ Ion in Two Forms of Chlorobis[bis-(1,2-diphenylphosphino)ethane]cobalt(II) Trichlorostannate(II)

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Summary [Co(dpe)$_2$Cl]SnCl$_3$ crystallizes in two forms, each containing an isolated trichlorotin(II) group, the first such arrangement found in transition metal compounds containing SnX_3^- groups.

COMPOUNDS of empirical composition Co(dpe)$_2$SnX$_4$ [dpe = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ and X = Cl, Br, I] have been isolated from non-aqueous solutions containing a cobalt(II) halide, the corresponding tin(II) halide, and the diphosphine ligand.[1] From the bromide and chloride systems, either a deep red or a deep green crystalline material can be isolated, depending on the solvent, temperature, and isolation procedures.

To ascertain the difference between the red and green forms, the ^{119m}Sn Mössbauer spectra have been obtained, (see Table 1), and the structures of red-[Co(dpe)$_2$Cl]SnCl$_3$

(**1**) and green-[Co(dpe)$_2$Cl]SnCl$_3$·C$_6$H$_5$Cl (**2**) have been determined by *X*-ray crystallography.

The red complex (**1**) crystallized from boiling butan-1-ol in space group C_{2h}^5-$P2_1/c$ of the monoclinic system, with four molecules in a unit cell of dimensions $a = 17{\cdot}727(7)$, $b = 16{\cdot}431(6)$, $c = 19{\cdot}741(8)$ Å; $\beta = 122{\cdot}128(11)°$ ($t = 23°$). The green compound (**2**) was crystallized with some difficulty from an ethanol–chlorobenzene mixture. Elemental analyses indicated the presence of one mol of chlorobenzene per mol of complex. The material crystallizes in space group C_i^1-$P\bar{1}$ of the triclinic system, with two molecules of complex and two molecules of chlorobenzene in a unit cell of dimensions $a = 11{\cdot}781(11)$, $b = 12{\cdot}846(12)$, $c = 19{\cdot}893(19)$ Å; $\alpha = 106{\cdot}38(1)$, $\beta = 93{\cdot}76(2)$, $\gamma = 101{\cdot}81(2)°$ ($t = 24°$). Both structures have been solved by the heavy atom method from three-dimensional *X*-ray data collected by counter methods.

Table 1

^{119m}Sn *Mössbauer parameters*[a]

	IS (mm s^{-1})	QS (mm s^{-1})	Γ_1	Γ_2
[Co(dpe)$_2$Cl]SnCl$_3$(**1**)	3·10 ± 0·06	1·36 ± 0·12	0·90	0·82
[Co(dpe)$_2$Cl]SnCl$_3$·C$_6$H$_5$Cl(**2**)	3·08 ± 0·06	1·25 ± 0·12	0·96	0·84
[Co(dpe)$_2$Br]SnBr$_3$	3·22 ± 0·12[b]	1·03 ± 0·12[b]	1·02	1·20

[a] Recorded at 77 K *vs.* a Ba^{119}mSnO$_3$ source (New England Nuclear Corp.) held at ambient temperature by methods previously described.[3] [b] The spectra of the bromo- and iodo-analogues were very feeble due to gamma-ray scattering. The data were fitted by double-averaging adjacent counts, but only the spectrum of the bromide is considered reliable.

The structure of (**1**) has been refined to a conventional *R* factor of 0·065 based on the 5706 reflections for which $F_o^2 > 3\sigma(F_o^2)$, while the structure of (**2**) has been refined to a conventional *R* factor of 0·100 using 3484 reflections.

Table 2

Bond lengths and angles for SnCl$_3^-$ *in* [Co(dpe)$_2$Cl]SnCl$_3$ (**1**) *and* [Co(dpe)$_2$Cl]SnCl$_3$·C$_6$H$_5$Cl (**2**)

	Bond length (Å)	
Atoms	(1)	(2)
Sn–Cl$_2$	2·440(4)	2·425(8)
Sn–Cl$_3$	2·445(3)	2·429(8)
Sn–Cl$_4$	2·447(2)	2·438(11)
	Angle (°)	
Atoms	(1)	(2)
Cl$_2$–Sn–Cl$_3$	94·8(1)	93·6(3)
Cl$_2$–Sn–Cl$_4$	94·1(1)	96·2(3)
Cl$_3$–Sn–Cl$_4$	94·6(1)	91·3(4)

Both (**1**) and (**2**) have discrete, well-separated [Co(dpe)$_2$Cl]$^+$ cations and SnCl$_3^-$ anions in the unit cell; (**2**) also has a molecule of chlorobenzene not associated with either cation or anion, but located in a large 'hole' in the packing structure. The difference in colour between (**1**) (red) and (**2**) (green) can be ascribed to a difference in cation configuration: (**1**) is square pyramidal with an apical Cl atom, whereas (**2**) is based on the trigonal bipyramidal geometry with two P atoms at the apices and two P atoms and one Cl atom in the equatorial plane.

The geometry of the SnCl$_3^-$ anion is pyramidal in both complexes (see Table 2). The average Sn–Cl bond distances in (**1**) (2·44 Å) and (**2**) (2·43 Å) are equivalent within the standard deviations given. These results are in disagreement with an earlier less accurate structure determination of the SnCl$_3^-$ ion in KCl·KSnCl$_3$·H$_2$O,[2] in which the Sn–Cl distances were reported as 2·63 and 2·54 Å, and the Cl–Sn–Cl bond angles as 87·7 and 90·8°. The Cl–Sn–Cl angles are similar for (**1**) and (**2**), with an average Cl–Sn–Cl angle of 93·7° for (**1**) and 94·5° for (**2**). Individual variations could be due to intermolecular, non-bonded interactions.

The SnCl$_3^-$ group in (**2**) is near a centre of symmetry in the unit cell, resulting in a relatively short Sn–Sn distance of 3·60 Å (the three Cl atoms bonded to each Sn are all away from the Sn–Sn vector). However, this distance is somewhat larger than the sum of the covalent radii; furthermore, the Sn atom is clearly pyramidal rather than tetrahedral so that the lone pair of electrons can be assumed to occupy an orbital of predominantly *s*-character. The Mössbauer results indicating the similarity of the Sn atoms in (**1**) and (**2**) lend additional support to the hypothesis that there is no chemical interaction between adjacent SnCl$_3^-$ groups in (**2**).

The isomer shifts (IS) listed in Table 1 specify the tin as Sn$^{\text{II}}$ in both structures; the cations are low-spin complexes of Co$^{\text{II}}$, which exhibit magnetic moments of *ca.* 2·0 B.M. per cobalt. All other compounds studied, in which *X*-ray results[4–6] have confirmed direct tin–cobalt bonding rather than the isolated anionic Sn$^{\text{II}}$ groups reported here, are diamagnetic and can be characterized from Mössbauer data as derivatives of Sn$^{\text{IV}}$.[7] The latter type of trichlorotin transition metal complexes exhibit IS values in the range 1·78 to 1·90 mm s^{-1}, which are typical of tetravalent tin in covalent compounds such as SnCl$_4$.[8]

The IS values of 3·08 to 3·22 mm s^{-1} given in Table 1 represent the first Mössbauer determination of tin as Sn$^{\text{II}}$ in a transition metal compound; they are similar to those found for Sn$^{\text{II}}$ in KSnCl$_3$·H$_2$O and SnCl$_2$·2H$_2$O.[7] These results lend further support to the idea that transition metal complexes containing bonded trichlorotin groups can best be described as derivatives of Sn$^{\text{IV}}$,[7,8] as the IS values are much smaller than those found in these Sn^{II} compounds containing discrete, anionic, $SnCl_3^-$ groups.

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