# Tin-119 Mössbauer Spectra of Trichlorotin Complexes

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The range of available $^{119}$Sn Mössbauer data for the trichlorotin system has been extended. Variations of the Mössbauer parameters are rationalised by considering the effect of the donor ability of the ligand L in the complex $LSnCl_3$. This approach is shown to be consistent with available i.r. and crystallographic data. The data strongly suggest that the Mössbauer centre shift does not provide a good distinction between formal $Sn^{II}$ and $Sn^{IV}$ species in many cases and that a valence-bond (hybridisation) approach is more meaningful.

MOST organometallic trichlorotin complexes studied to date show $^{119}$Sn Mössbauer centre shifts characteristic of tin(IV) compounds.[1-4] Their centre shifts are, in the main, less than 2·0 mm s$^{-1}$ and their quadrupole splittings

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[1] D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, 1969, **8**, 1771.

[2] W. R. Cullen, J. R. Sams, and J. A. J. Thompson, *Inorg. Chem.*, 1971, **10**, 843.

[3] A. N. Karasev, N. E. Kolobova, L. S. Polak, V. S. Shpinel, and K. N. Anisimov, *Teor. i. eksp. Khim. Akad. Nauk. Ukr. S.S.R.*, 1966, **2**, 126.

[4] N. Dominelli, E. Wood, P. Vasudev, and C. H. W. Jones, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 1077.

are in the range 1·5—2 mm s$^{-1}$. Complexes are also known for which the tin nucleus in an $SnCl_3$ moiety has Mössbauer parameters more characteristic of tin(II) species, *e.g.* $[Et_4N][SnCl_3]$ [5] and $[CoCl(dppe)_2][SnCl_3]$ [dppe = 1,2-bis(diphenylphosphino)ethane].[6] However, Fenton and Zuckerman's assignment of such oxidation states merely on the ground of centre-shift values has been questioned in more recent papers.[7,8]

In this work, we have extended the range of available $^{119}Sn$ Mössbauer data for the trichlorotin system, paying particular attention to organometallic complexes which show large $^{119}Sn$ centre shifts. The variations of the Mössbauer parameters throughout the available range of data may be rationalised by considering the effect of the donor ability of the ligand L in the complex $LSnCl_3$. This approach, which removes the formal distinction between tin(II) and tin(IV) in this system, is also consistent with available i.r. and crystallographic data.

## EXPERIMENTAL

Mössbauer spectra were run on a spectrometer described elsewhere,[9] and fitted to lines of Lorentzian shape as described in an appendix to ref. 9. Data from spectra of $^{57}Fe$-enriched iron foil run immediately before and after each sample were used to calibrate the spectrum of the sample.

## RESULTS AND DISCUSSION

$^{119}Sn$ Mössbauer parameters of a number of trichlorotin compounds are given in Table 1. Twenty two of these had not been subjected to earlier Mössbauer investigation, though Mössbauer parameters for five have subsequently been published elsewhere.[10] The Figure demonstrates that the tin centre shift ($\delta$) of each compound and its quadrupole splitting ($\Delta$) are interrelated.* This suggests that $\delta$ and $\Delta$ may both be expressed as function of one variable. The likely physical manifestation of such a variable is the $\sigma$-donor ability of the group L in $LSnCl_3$. Parameters of the series of complexes from $ClSnCl_3$ up to $[Et_4N][SnCl_3]$ may thus be seen as depicting gradual transfer of negative charge from the L–Sn bond in $LSnCl_3$ to the $SnCl_3$ moiety. This transfer has a number of consequences.

Considering first tetrahedral $SnCl_4$, the symmetry of the molecule requires $sp^3$ hybridisation of the tin bonding orbitals. If one chlorine atom is now denoted L, and this ligand then undergoes a steady change in its nature becoming a better $\sigma$-donor, then the L–Sn bond will become more polar in the $L^{\delta+}$–$Sn^{\delta-}$ sense. Alternatively, we may view this as a change in hybridisation of the tin bonding orbitals. An increase in the electron-donating ability of L requires greater tin 5*s* orbital character in the hybrid

TABLE 1

$^{119}Sn$ Mössbauer data (mm s$^{-1}$) [a]

| Compound | $\delta$ | $\Delta$ | Ref. |
|---|---|---|---|
| $[Et_4N][SnCl_3]$ | 3·6 | | 5 |
| $Cs[SnCl_3]$ | 3·40 | 1·22 | 10 |
| $[(cp)Ni(PPh_3)_2][SnCl_3]$ | 3·18 | 1·20 | *b* |
| *trans*-$[Co(en)_2(NO_2)_2][SnCl_3]$ | 3·16 | 1·26 | |
| $[Co(dppe)_2Cl][SnCl_3]$ | 3·10 | 1·36 | 6 |
| $[(\textit{p}\text{-}MeOC_6H_4NC)_2Au(SnCl_3)]$ [c] | 3·06 | 1·24 | |
| $[(PhMe_2P)_2Au(SnCl_3)]$ [c] | 2·92 | 1·35 | |
| $[(Ph_3P)_3Ag(SnCl_3)]$ [c] | 2·54 | 1·70 | |
| | 2·54 | 1·69 | 10 |
| $[(Ph_3P)_2Rh(cod)SnCl_3]$ | 2·41 | 1·83 | 10 |
| $[(Ph_3P)_2Rh(nbd)SnCl_3]$ [d] | 2·38 | 1·70 | |
| $[(Ph_3P)_3Cu(SnCl_3)]$ [c] | 2·29 | 1·80 | |
| | 2·46 | 1·88 | 10 |
| $[(Ph_3As)_2Rh(cod)SnCl_3]$ | 2·28 | 1·89 | 10 |
| $[(Ph_3As)_3Au(SnCl_3)]$ [c] | 2·26 | 1·67 | |
| $[(Ph_3P)_3Au(SnCl_3)]$ [c] | 2·25 | 1·66 | |
| | 2·44 | 1·58 | 10 |
| $[(nbd)_2Rh(SnCl_3)]$ [d] | 2·23 | 1·72 | |
| $[(Me_2AsPh)_2Ir(cod)SnCl_3]$ [d] | 2·17 | 1·83 | |
| $[(Ph_3P)_2Ir(nbd)SnCl_3]$ [d] | 2·16 | 1·82 | |
| $[(cod)_2Rh(SnCl_3)]$ | 2·16 | 1·72 | 10 |
| $[Me_4N]_2[PtCl_2(SnCl_3)_2]$ | 1·80 | 1·61 | 1 |
| $[(dpae)Ir(cod)SnCl_3]$ [d] | 2·15 | 1·79 | |
| $[(Ph_3Sb)_2Rh(cod)SnCl_3]$ | 2·15 | 2·04 | 10 |
| $[(dpdae)Ir(nbd)SnCl_3]$ [d] | 2·12 | 1·88 | |
| $[\{(MeO)_2PhP\}_2Ir(nbd)SnCl_3]$ [d] | 2·08 | 1·89 | |
| $[(cod)_2Ir(SnCl_3)]$ [d] | 2·06 | 1·77 | |
| $[\{(MeO)_2PhP\}_2Ir(cod)SnCl_3]$ [d] | 2·04 | 1·87 | |
| $[(diars)_2Fe(Cl)SnCl_3]$ | 1·98 | 1·81 | 10 |
| $[(nbd)_2Ir(SnCl_3)]$ [d] | 1·98 | 1·86 | |
| $[(tfbb)_2Ir(SnCl_3)]$ [d] | 1·98 | 1·92 | |
| $[Me_4N]_2[RuCl_2(SnCl_3)_2]$ | 1·93 | 1·64 | 1 |
| | 1·84 | 1·93 | 10 |
| $[(cp)Fe(dppe)SnCl_3]$ [f] | 1·92 | 1·76 | *e* |
| $[Me_4N]_2[Rh_2Cl_2(SnCl_3)_4]$ | 1·90 | 1·62 | 1 |
| | 1·70 | 1·85 | 10 |
| $[(cp)Fe(PPh_3)(CO)SnCl_3]$ | 1·88 | 1·88 | 2 |
| $[(cp)Ni(PPh_3)SnCl_3]$ | 1·85 | 1·90 | *b* |
| $[(Ph_3P)_3Rh(SnCl_3)]$ | 1·78 | 1·73 | 1 |
| | 2·10 | 1·91 | 10 |
| $[(cp)Fe(CO)_2SnCl_3]$ | 1·77 | 1·80 | 2 |
| $[Et_4N]_2[Rh(CO)(Cl)_2SnCl_3]$ | 1·77 | 1·93 | 10 |
| $[Et_4N]_2[Rh(CO)Cl(SnCl_3)_2]$ | 1·74 | 2·15 | 10 |
| $[Mn(CO)_5SnCl_3]$ | 1·73 | 1·56 | 3 |
| $[Ph_3HP]_4[Ir_2Cl_6(SnCl_3)_4]$ | 1·72 | 2·01 | 10 |
| $[Et_4N]_2[Rh(CO)(SnCl_3)_3]$ | 1·68 | 2·25 | 10 |
| $[Ph_3PhCH_2P]_4[Rh_2Cl_2(SnCl_3)_4]$ | 1·67 | 1·90 | 10 |
| $[Me_4N]_4[Ir_2Cl_6(SnCl_3)_4]$ | 1·67 | 1·94 | 10 |
| $[Et_4N]_3[Pt(SnCl_3)_5]$ | 1·64 | 1·53 | 1 |
| $[(Bu^n{}_3P)Co(CO)_3SnCl_3]$ | 1·59 | 1·68 | *f* |
| $[Et_4N]_2[PtCl_2(SnCl_3)_2]$ | 1·56 | 1·61 | 1 |
| *cis*-$[Fe(CO)_4Cl(SnCl_3)]$ | 1·55 | 1·40 | 4 |
| *cis*-$[Fe(CO)_4(SnCl_3)_2]$ | 1·53 | 1·25 | 4 |
| *trans*-$[Fe(CO)_4(SnCl_3)_2]$ | 1·53 | 1·26 | 4 |
| $[(MeNO_2)Pt_3(cod)(SnCl_3)_2]$ | 1·50 | 1·20 | 1 |
| $PhSnCl_3$ | 1·27 | 1·80 | *g* |
| $SnCl_4$ | 0·85 | 0 | *h* |

cp = $\eta$-Cyclopentadienyl, en = ethylenediamine, dppe = 1,2-bis(diphenylphosphino)ethane, dpae = 1,2-bis(diphenylarsino)ethane, dpdae = 1-diphenylarsino-2-diphenylphosphinoethane, nbd = norbornadiene, cod = cyclo-octa-1,5-diene, tfbb = tetrafluorobenzylbarrelene, and diars = *o*-phenylenebis(dimethylarsine).

[a] All centre-shift values are quoted relative to a $BaSnO_3$ source at *ca.* 295 K with the sample at *ca.* 80 K. Linewidths at half height were *ca.* 0·8 mm s$^{-1}$. [b] P. A. McArdle and A. R. Manning, *Chem. Comm.*, 1967, 417. [c] Prepared by J. Bailey. [d] Prepared by R. Schrock and J. A. Osborn, University of Harvard. [e] M. J. Mays and P. L. Sears, *J.C.S. Dalton*, 1973, 1873. [f] K. Ogino and T. L. Brown, *Inorg. Chem.*, 1973, **10**, 517. [g] H. A. Stockler and H. Sano, *Trans. Faraday Soc.*, 1968, **64**, 577. [h] V. A. Bukarev, *Zhur. eksp. teor. Fiz.*, 1963, **44**, 249.

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* Where two differing sets of data are reported for a given compound (Table 1) both sets have been plotted.

[5] R. J. H. Clark, L. Maresca, and P. J. Smith, *J. Chem. Soc.* (*A*), 1970, 2687.

[6] J. K. Stalik, D. W. Meek, B. Y. K. Ho, and J. J. Zuckerman, *J.C.S. Chem. Comm.*, 1972, 630.

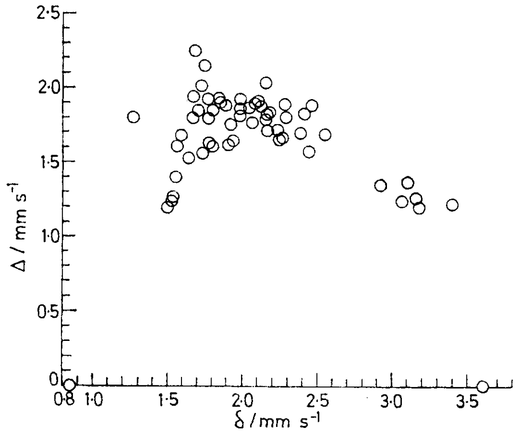
[7] S. R. A. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 1311.

[8] G. M. Bancroft and K. D. Butler, *J.C.S. Dalton*, 1972, 1209.

[9] G. M. Bancroft, W. K. Ong, A. G. Maddock, R. M. Prince, and A. J. Stone, *J. Chem. Soc.* (*A*), 1967, 1966.

[10] R. V. Parish and P. J. Rowbotham, *J.C.S. Dalton*, 1973, 37.

directed towards L, in order to maximise orbital overlap for bonding. This also has consequences for the other Sn–Cl bonds, which must now undergo reduction in their tin 5*s*, and an increase in their tin 5*p*, orbital content, resulting in a decrease in the Cl–Sn–Cl bond angles from the tetrahedral 109° 28′. The significance of the change in the Sn–Cl bond lies more in its geometrical implications than in the increased $Sn^{\delta+}$–$Cl^{\delta-}$ polarity of these bonds. The transition from $SnCl_4$ to $[SnCl_3]^-$ is thus accompanied by a steady increase in *s* electron density at the tin nucleus, and hence a steady increase in $\delta$.



Correlation of $^{119}$Sn centre shift with quadrupole splitting for compounds in Table 1

However, the electric-field gradient (e.f.g.) at the nucleus shows more complex behaviour. In the two limiting cases of $sp^3$-hybridised tin in $SnCl_4$ and $p^3$-bonded tin in 'ideal' $[SnCl_3]^-$ the e.f.g. is zero. The e.f.g. becomes negative as Cl is replaced by a better $\sigma$-donor L in $LSnCl_3$, but when the *s* character of the L–Sn bond reaches a certain point the e.f.g. begins to drop in magnitude, until it becomes zero once again when the L–Sn 'bond' is 100% *s* in character, *i.e.* the ideal $[SnCl_3]^-$ ion. The Figure is consistent with this view. Tin tetrachloride is four-co-ordinate in the solid state,[11] and the absence of a resolved quadrupole splitting in its Mössbauer spectrum shows that any distortion from regular tetrahedral geometry must be small. Initial departure from this tetrahedral state gives rise to increasing $\delta$, while $\Delta$ rises rapidly to a maximum of *ca.* 1·9 mm s$^{-1}$ at $\delta$ 2 mm s$^{-1}$ and subsequently declines as $\delta$ increases further. The only serious deviation from this general pattern is for $PhSnCl_3$, for which $\Delta$ is much larger than would be expected for a $\delta$ value of 1·27 mm s$^{-1}$. It is, however, quite probable that solid $PhSnCl_3$ is polymeric, and does not contain four-co-ordinate tin. Those complexes with very large $\Delta$ values also lie away from the main group of data points in the Figure. It will be noted, though, that these are sterically crowded species such as $[Rh(CO)(SnCl_3)_3]^{2-}$. Distortions of the $SnCl_3$ ligands resulting from such crowding complicate the discussion of bonding in these species.

A rather disturbing feature of published $^{119}$Sn Mössbauer data on the trichlorotin system is the discrepancies between results recorded by different authors. While most results, including those in this study, have claimed an accuracy of *ca.* ±0·03 mm s$^{-1}$, discrepancies of up to 0·2 mm s$^{-1}$ in both $\delta$ and $\Delta$ values exist in the literature (ref. 10 and Table 1). This does not invalidate a general study of the data, but it appears that some of the data for individual compounds should be treated with some caution.

Parish and Rowbotham[10] demonstrated a correlation of Mössbauer $\delta$ values with an average i.r. Sn–Cl stretching frequency. In their study, the lowest $\delta$ values were shown to be associated with the highest i.r. frequency, $\nu$. This is consistent with the view of the bonding described above, where lowest $\delta$ values are associated with the greatest tin 5*s* character in the Sn–Cl bonds.

Crystallographic data for this system are very limited, but those which are available show that the mean Cl–Sn–Cl angle $\theta$, which is 109° 28′ in tetrahedral $SnCl_4$, decreases with increasing $\delta$ (Table 2), approaching 90° for the 'ionic' salts $[Co(dppe)_2Cl][SnCl_3]$ and $Cs[SnCl_3]$. This observation also supports the model of the bonding described above.

TABLE 2

Correlation of Mössbauer and crystallographic data

| Compound | $\delta$/mm s$^{-1}$ | $\theta$/° | Ref. (for $\theta$) |
|---|---|---|---|
| $SnCl_4$ | 0·85 | 109·5 | |
| $[(cp)Fe(CO)_2SnCl_3]$ | 1·77 | 98·3 | *a* |
| $[(cod)_2Ir(SnCl_3)]$ | 2·06 | 96·0 | *b* |
| $[Co(dppe)_2Cl][SnCl_3]$ | 3·10 | 94·5 | 6 |
| $Cs[SnCl_3]$ | 3·40 | 89·8 | *c* |
| $[Et_4N][SnCl_3]$ | 3·60 | | |

[a] P. J. Greene and R. F. Bryan, *J. Chem. Soc.* (*A*), 1970, 1696. [b] H. Porta, H. M. Powell, R. J. Mawby, and L. M. Veranzi, *J. Chem. Soc.* (*A*), 1967, 455. [c] F. R. Paulsen and S. E. Rosmussen, *Acta Chem. Scand.*, 1970, **24**, 150.

These data then strongly suggest that the Mössbauer centre shift does not provide a good distinction between formal $Sn^{II}$ and $Sn^{IV}$ species in many cases, and a valence-bond (hybridisation) approach is more meaningful.

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[11] N. N. Greenwood and T. C. Gibb, 'Mössbauer Spectroscopy,' p. 390.