Inorganica Chimica Acta, 15 (1975) 201–204

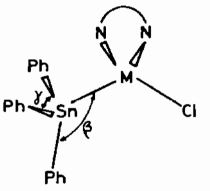
Mössbauer Spectroscopic Studies on Compounds Containing Tin–Cadmium and Tin–Zinc Bonds

R. BARBIERI, L. PELLERITO, N. BERTAZZI and G. ALONZO
Istituto di Chimica Generale, Università di Palermo, 90123 Palermo, Italy
J. G. NOLTES
Organisch Chemisch Instituut TNO, Utrecht, Nederland
Received February 21, 1975

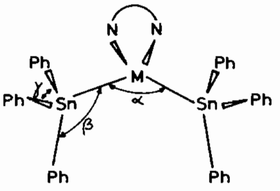
The Mössbauer parameters of compounds Ph_3Sn $MCl \cdot TMED$ (M = Cd, Zn; TMED = N,N,N′,N′-tetramethylethylenediamine), $(Ph_3Sn)_2CdL_2$ (L_2 = TMED, 2,2′-bipyridine and o-phenanthroline) and $(Ph_3Sn)_2Zn \cdot TMED$ have been determined and are discussed in connection with Mössbauer data concerning Ph_3Sn^{IV} derivatives with other Sn–metal bonds. The isomer shift values suggest a high s character in Sn–Cd and Sn–Zn bonds resulting in deviations from regular tetrahedral environments around tin. Experimental quadrupole splittings and calculated partial quadrupole splitting values indicate reduced donor abilities towards the tin atom of an individual Ph_3Sn^{IV} moiety by Cd-and $Zn(Ph_3Sn)_{1-n}Cl_nL_2$ (i.e., the remaining part of the molecule, n = 0,1) compared to other metal bearing groups, and a limited p character in Sn–Cd and Sn–Zn bonds.

Introduction

The synthesis, reactivity, as well as the electronic and vibrational spectral characteristics of a number of triphenyltinzinc and triphenyltincadmium compounds have been previously reported[1–3]. The compounds "$Ph_3SnZnCl$" and $Ph_3SnZnCl \cdot TMED$ (I; N,N,N′,N′-tetramethylethylenediamine = TMED) have also been investigated by Mössbauer spectroscopy, and shown to give a single peak (δ = 1.56 mm s^{-1}) and two peak (δ = 1.56 mm s^{-1}; ΔE = 1.31 mm s^{-1}) spectra, respectively[4].



(I)



(II)

M = Cd, Zn

It seemed worthwhile to extend the Mössbauer study to other members of this series of compounds in order to get further information on their solid state configuration. The parameters of $Ph_3SnCdCl \cdot TMED$ (I), $(Ph_3Sn)_2CdL_2$ (L_2 = TMED; 2,2′-bipyridine, Bipy; *o*-phenanthroline, *o*-Phen) (II) and $(Ph_3Sn)_2Zn \cdot TMED$ (II) have therefore been determined and are discussed in this paper in the light of existing Mössbauer data on compounds of the type Ph_3SnM.

Experimental

The compounds studied here have been previously reported[1,2]. The preparation of the discs (in a copper holder, pressed between aluminium foil) of powdered samples was carried out in a glove bag under N_2 atmosphere, and discs were wrapped in small sealed polyethylene bags, in order to prevent decomposition of the compounds.

The Mössbauer spectra were determined at 80° K by using the Elscint–Laben spectrometer described earlier[5]. The source ($Ca^{119m}SnO_3$, 5 mC, from R.C., Amersham) was at room temperature, and its motion was determined by a sawtooth waveform, at constant

TABLE I. Mössbauer Parameters of $(Ph_3Sn)_{2-n}MCl_nL_2$ (M = Cd, Zn) at Liquid N_2 Temperature.

Compound[a]	δ[b]	ΔE[c]	Γ_+[d]	Γ_-[d]
$Ph_3SnCdCl \cdot TMED$	1.51	1.03	0.91	1.01
$(Ph_3Sn)_2Cd \cdot TMED$	1.54	1.05	0.82	1.00
$(Ph_3Sn)_2Cd \cdot Bipy$	1.54	1.01	0.83	1.10
$(Ph_3Sn)_2Cd \cdot$*o*-Phen	1.55	1.00	0.95	0.97
$Ph_3SnZnCl \cdot TMED$[e]	1.57	1.20	0.87	1.35[f]
$(Ph_3Sn)_2Zn \cdot TMED$	1.60	1.25	0.96	1.15

[a] Symbols: see Introduction, this paper. [b] Isomer shift, mm s^{-1}, ± 0.03, with respect to $CaSnO_3$ R.T. spectra. [c] Quadrupole splitting, mm s^{-1}, ± 0.03. [d] Full width at half maximum of the resonant peak; + and – refer to the doublet components at greater and lesser velocity than the spectrum centroid, respectively. [e] Lit.[4]: δ = 1.56, ΔE = 1.31. [f] Due to a Sn^{IV} impurity which appears as a weak shoulder around 0 Doppler velocity.

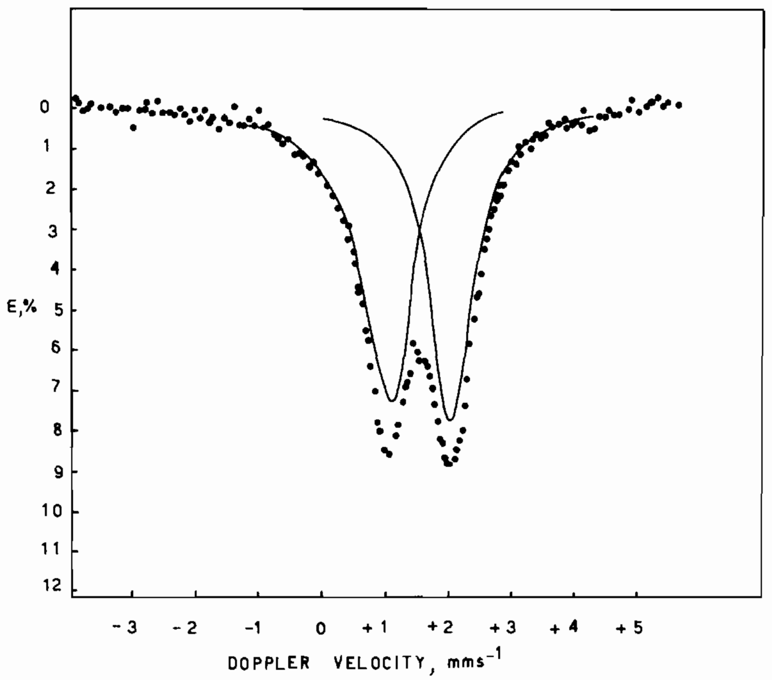


Figure 1. Mössbauer spectrum of $(Ph_3Sn)_2Cd \cdot TMED$ at 80° K. Resonance effect magnitude, ε % (= 100 $(I_\infty - I)/I_\infty$) *vs.* Doppler velocity (with respect to R.T. $CaSnO_3$–$CaSnO_3$ spectra). Solid lines are computed Lorentzians.

acceleration between the velocity limits 0 to 8 mm s^{-1}; the spectrum was spanned over the 400 channels of the analyzer. The velocity calibration of the spectrometer (using a 5 mC ^{57}Co source from R.C.), the determination of the zero velocity point, the computer reduction of experimental spectra, as well as other experimental details and apparatus, were described elsewhere[5]. The quality of the spectra is shown in Figure 1, while Table I reports the determined parameters.

Discussion

The isomer shifts, δ[6], of compounds $(Ph_3Sn)_{2-n}MCl_nL_2$ (n = 0,1; M = Cd, Zn; L_2 = N,N bidentate ligand) listed in Table I fall to the high end of the Ph_3SnM (and in general of R_3SnM) δ range, M being a metal atom, as can be observed by comparison with the data in Table II. Besides, δ of Ph_3Sn^{IV} derivatives of Cd and Zn, in the context of compounds examined here, are practically insensitive to the nature of the ligands bound to Cd and Zn (Table I).

In order to rationalize these peculiarities of our compounds, the existing views on Sn-to-metal bonds must be taken into account, as extracted from Mössbauer and other spectroscopic and structural investigations. The model employed in discussing electronic properties and configurations of $R_nhal_{3-n}SnM$ and X_nSnM_{4-n} (X = halide, organic radical) compounds, where the environment of Sn is a more or less distorted tetrahedron, is based on Bent's second order hybridization concept[18], according to which, *inter alia, s* character is concentrated in orbitals used by an atom to form bonds with more electropositive substituents. In our case these would be groups containing the metal atom M bound to Sn, so that 5*s* Sn electrons would be concentrated in Sn–M σ bonds. Upon increase of the *s* character of the latter bonds, the angles $M\widehat{Sn}M$ and $M\widehat{Sn}L$ (L = carbon or hal) would increase over the ideal tetrahedral value, while decreasing $L\widehat{Sn}L$, and concurrently the Sn–M distances would diminish (and Sn–L augment); these effects would be paralleled by increments of δ_{Sn}, whose magnitude reflects the order of *s* character of Sn–M (and Sn–L) bonds, Cl< C_6F_5<Ph<Me<$Co(CO)_4$<$Mn(CO)_5$<$Fe(CO)_2$ (π-C_5H_5)[7,12–14,16,19,20].

In consonance with this model, from the δ values of Tables I and II it is deduced that the *s* character of Sn–Cd and Sn–Zn bonds in our compounds is generally larger than that involved in Sn–Fe, –Mn, –Re, –Co and –Ir bonds, being comparable to Sn–Mg and lesser than Sn–Fe in $Ph_3SnFe(PMe_2Ph)_2(\pi\text{-}C_5H_5)$ only. The series of "ligands" $Cd(Ph_3Sn)_{1-n}Cl_nL_2$~$Zn(Ph_3Sn)_{1-n}Cl_nL_2$ (n = 0,1) [~MgBr~$Fe(PPh_2Mc)_2(\pi\text{-}C_5H_5)$<$Fe(PMe_2Ph)_2(\pi\text{-}C_5H_5)$] will be thus the continuation of Bancroft's above reported order of character[12]. In addition, we would accordingly predict distortions of tetrahedra shown in structures (I) and (II) (angles α and β being presumably larger, and γ

TABLE II. Mössbauer Parameters of Ph_3SnM Derivatives.

Compound	δ[a]	ΔE[b]	References
$Ph_3SnFe(PR_2R')_2(\pi\text{-}C_5H_5)$	1.58[c]; 1.71[d]	1.14[c]; 1.25[d]	7
$(Ph_3SnMgBr)_2$	1.52	0.00	4
$Ph_3SnFe(CO)(\pi\text{-}C_5H_5)L$[e]	1.36–1.50	0.00–0.78	7–9
$Ph_3SnMn(CO)_4L$[f]	1.35–1.51	0.00–0.41	8, 10–15
$Ph_3SnRe(CO)_4L$	1.45[g]; 1.50[h]	0.00	15
$Ph_3SnCo(CO)_3L$[i]	1.41–1.50	not resolved –1.20[l]	14–16
$Ph_3SnIr(HX)(CO)L_2$[m]	1.42–1.46	>0	17

[a] Isomer shift, mm s^{-1}. [b] Quadrupole splitting, mm s^{-1}. [c] R = Ph, R′ = Me. [d] R = Me, R′ = Ph. [e] L = CO, PPh_3, $AsPh_3$, $SbPh_3$, PPh_2CF_3, PPh_2Me, PMe_2Ph, $Ph_2P\overline{C{=}CP(Ph_2)(CF_2)_2C}F_2$. [f] L = CO, PPh_3. [g] L = CO. [h] L = PPh_3. [i] L = CO, PPh_3, PBu^n_3. [l] 1.00–1.20 for L = CO. [m] X = Cl, I; L = PPh_3, PPh_2Me.

lesser, than 109.47°) as well as particularly short Sn–Cd and –Zn bonds.

The invariance of δ of (I) and (II) with changes of the environments of Cd and Zn (Table I) finds analogies in a $R_3SnFe(CO)(\pi\text{-}C_5H_5)L$[7] series, where this effect was interpreted in terms of absence of d_π–d_π Sn–Fe interactions. A similar situation could then be assumed to hold also for our Sn–Cd and Sn–Zn compounds, where the occurrence of extensive d_π–d_π Cd–Sn and Zn–Sn bonding would imply a decrease of δ on substitution of a Ph_3Sn group with Cl, owing to the increase of d_π charge donation from Cd or Zn to the Sn atom and consequent increased shielding of Sn 5*s* electrons. The observed constancy of δ_{Sn} may then be attributed to charge equalization effects in Cd– and Zn–N,N moieties, which would assure constant 5*s*, 4*s* Cd and Zn character in their σ bonds with Sn. On the other hand, variations of δ_{Sn} were observed in $R_3SnFe(CO)(\pi\text{-}C_5H_5)L$[7], $Ph_3SnMn(CO)_4L$[13] (see Table II for the nature of L) and $X_{4-n}Sn[Co(CO)_3L]_n$[16] (X = hal, R; L = CO, PR_3; n = 1,2) on substitution of L = CO with a different ligand, which is consistent with transfer of electron charges across Sn–M bonds. However, Sn–M π bonding was again considered irrelevant or absent also in these systems.

In the context of π bonding Greenwood and his coworkers[19] state that "Mössbauer spectroscopy is rather insensitive to the participation of tin 5*d* electrons in the bonds because of their greater radial extension", and a note of care should be injected in the assumed absence of Sn–Cd and Sn–Zn π-bonding. It must be remembered also that, unlike the $(Ph_3Sn)_2M\cdot$TMED complexes, the $(Ph_3Sn)_2M\cdot$Bipy complexes (M = Zn, Cd) display a pronounced charge-transfer absorption in the visible spectrum[1]. This band has been proposed to arise from a π-type interaction between the $(Ph_3Sn)_2M$ moiety and the Bipy ligand[1]. It would be reasonable to assume that any transfer of electron density involved in this type of π interaction would affect the Sn–M bond. However, the Mössbauer parameters of $(Ph_3Sn)_2Cd\cdot$Bipy (Table I) fail to reflect the occurrence of this interaction.

The quadrupole splittings, ΔE[6], of our compounds (Table I) also fall to the high end of the quadrupole splitting range for compounds of the type Ph_3SnM. This parameter varies between zero and 1.25 mm s^{-1} for compounds with Sn–Fe, –Mn, –Re, –Co and –Ir bonds, being larger than ~0.5 mm s^{-1} only for terms of the series $Ph_3SnFe(CO)(\pi\text{-}C_5H_5)L$, for $Ph_3SnFe(PR_2R')_2(\pi\text{-}C_5H_5)$ and for $Ph_3SnCo(CO)_4$ (Table II). According to the model discussed above, ΔE would originate mainly from unbalance of *p* electron density in the four hybrid orbitals centered at Sn and by the consequent distortions from the ideal tetrahedral structure. Taking the direction of the Sn–M bond as z axis, M→Sn charge donation would occur towards the hybrid made up mainly of 5*s* and $5p_z$ Sn orbitals, while p_x and p_y would be essentially employed in Sn–C bonds, and ΔE would arise from differences between donor strengths of M and Ph as well as from the respective *p* characters of Sn–M and Sn–C(Ph) bonds[7, 10–13, 20]. Thus, taking into account that ΔE_{Sn} of $n\text{-}Bu_3SnFe(CO)_2$ $(\pi\text{-}C_5H_5)$ is negative[19] and assuming that the same ΔE sign holds also for our derivatives (which is supported by the limited distortions from tetrahedral symmetry generally exhibited by Ph_3SnM compounds[12, 19]), the relatively high ΔE of Table I may be interpreted in terms of a poor donor ability of $M(Ph_3Sn)_{1-n}Cl_nL_2$ to those hybrid orbitals which have a reduced *p* character[12] (*i.e.*, those involved in Sn–M bonds). In other words, the partial quadrupole splitting[21] (p.q.s.) due to these groups would fall to the less negative end of the p.q.s. range of groups bearing metal atoms linked to Sn[12, 14].

In order to test this statement, p.q.s. values $1/2\ e^2|Q|([M]\text{–}[hal])$[21] were calculated for Cd– and Zn $(Ph_3Sn)_{1-n}Cl_nL_2$ (= M) as well as for other ligand groups (estimators being Ph_3Sn^{IV} derivatives of known ΔE) by employing the point-charge[22, 23] equation for $MSnPh_3$ in an ideal tetrahedral configuration[9]:

$$(-)\Delta E = 1/2\ eQV_{zz}(1 + \eta^2/3)^{1/2} = 1/2\ e^2Q\{2([M]-[Ph])\} \quad (1)$$

TABLE III. Partial Quadrupole Splittings[a] $1/2e^2|Q|([M]\text{–}[hal])$, mm s^{-1}, for Ligands M Coordinated to Sn^{IV} in Compounds with Sn–M Bonds, Estimated from ΔE of Ph_3SnM Derivatives.

M	p.q.s.	Ref.[b]
$Zn(Ph_3Sn)\cdot TMED$	–0.63	c
$Fe(PMe_2Ph)_2(\pi\text{-}C_5H_5)$	–0.63	7
$ZnCl\cdot TMED$	–0.66[d]	c
$Fe(PPh_2Me)_2(\pi\text{-}C_5H_5)$	–0.69	7
$Cd(Ph_3Sn)\cdot TMED$	–0.73	c
$CdCl\cdot TMED$	–0.74	c
$Cd(Ph_3Sn)\cdot Bipy$	–0.75	c
$Cd(Ph_3Sn)\cdot o\text{-}Phen$	–0.76	c
$Fe(CO)(\pi\text{-}C_5H_5)(PMe_2Ph)$	–0.87	7
$Fe(CO)(\pi\text{-}C_5H_5)(PPh_3)$	–0.91	7
$Fe(CO)(\pi\text{-}C_5H_5)(AsPh_3)$	–0.92	7
$Fe(CO)(\pi\text{-}C_5H_5)(SbPh_3)$	–0.98	7
$Fe(CO)(\pi\text{-}C_5H_5)(PPh_2Me)$	–0.98	7
$Fe(CO)(\pi C_5H_5)(PPh_2CF_3)$	–1.04	7

[a] Calculated from equation (1), using the p.q.s. $1/2e^2Q([Ph]\text{–}[hal]) = +1.26^{21}$ mm s^{-1}. [b] For $|\Delta E|$ of estimator compounds. [c] This work. [d] –0.60 by ΔE of Ref. 4.

where symbols have the usual meaning[6,21–23], the asymmetry parameter η being zero for this particular configuration (z axis coincides with Sn–M bonds; $V_{xx} = V_{yy}$)[9]. The p.q.s. [M] values thus calculated are reported in Table III; the reasonable reliability of data extracted from estimators with low experimental ΔE (those giving $|$p.q.s.$|$ $\gtrsim 0.90$) is deduced from the agreement between p.q.s. of $Co(CO)_4$, $Mn(CO)_5$ and $Fe(CO)_2(\pi\text{-}C_5H_5)$ in the literature[12,14,21] and values obtainable from experimental ΔE of corresponding Ph_3Sn^{IV} derivatives[12,14], the differences being mostly well below the upper limit of ±0.2 mm s^{-1} [21]. It then appears that our Cd and Zn "ligands" insert as follows in Bancroft's order of *p* donor ability toward tetrahedral Sn^{IV} [12,14]:

$Cl,Br < I < Fe(PR_2R'_2)(\pi\text{-}C_5H_5) \sim Zn(Ph_3Sn)\cdot TMED \sim ZnCl\cdot TMED \sim Co(CO)_4 < CdCl\cdot TMED \sim Cd(Ph_3Sn)L_2 < Re(CO)_5{}^{21} < Fe(CO)(\pi\text{-}C_5H_5)L < Mn(CO)_5 < Fe(CO)_2(\pi\text{-}C_5H_5) < Ph < Me$.

Acknowledgement

The financial support by NATO (Grant N. 480), CNR (Roma) and International Tin Research Council (London) is gratefully acknowledged.

References

1 F.J.A. Des Tombe, G.J.M. van der Kerk, H.M.J.C. Creemers, N.A.D. Carey and J.G. Noltes, *J. Organometal. Chem., 44* (1972) 247.

2 F.J.A. Des Tombe, G.J.M. van der Kerk and J.G. Noltes, *J. Organometal. Chem., 43* (1972) 323.

3 F.J.A. Des Tombe, G.J.M. van der Kerk and J.G. Noltes, *J. Organometal. Chem., 51* (1973) 173.

4 P.G. Harrison, J.J. Zuckerman and J.G. Noltes, *J. Organometal Chem., 31* (1971) C23.

5 R. Barbieri, G. Alonzo, A. Silvestri, N. Burriesci, N. Bertazzi, G.C. Stocco and L. Pellerito, *Gazz. Chim. Ital., 104* (1974) 885.

6 V.I. Gol'danskii and E.F. Makarov, "Fundamentals of Gamma-resonance Spectroscopy", in V.I. Gol'danskii and R.H. Herber Eds., "Chemical Applications of Mössbauer Spectroscopy", Academic Press, New York, 1968, Ch. 1.

7 W.R. Cullen, J.R. Sams and J.A.J. Thompson, *Inorg. Chem., 10* (1971) 843.

8 B.V. Liengme, M.J. Newlands and J.R. Sams, *Inorg. Nucl. Chem. Letters, 7* (1971) 1223.

9 G.M. Bancroft, K.D. Butler and A.T. Rake, *J. Organometal. Chem., 34* (1972) 137.

10 C. Wynter and L. Chandler, *Bull. Chem. Soc. Japan, 43* (1970) 2115.

11 S. Onaka, Y. Sasaki and H. Sano, *Bull. Chem. Soc. Japan, 44* (1971) 726.

12 G.M. Bancroft, K.D. Butler, A.T. Rake and B. Dale, *J. Chem. Soc. Dalton,* (1972) 2025 and references therein.

13 S.R.A. Bird, J.D. Donaldson, A.F. LeC. Holding, B. Ratcliff and S. Cenini, *Inorg. Chim. Acta, 6* (1972) 379.

14 G.M. Bancroft and K.D. Butler, *J. Chem. Soc. Dalton,* (1973) 1694.

15 A.N. Karasev, N.E. Kolobova, L.S. Polak, V.S. Shpinel and K.N. Anisimov, *Teor. Eksp. Khim. Akad. Nauk Ukr., 2* (1966) 126.

16 S.R.A. Bird, J.D. Donaldson, A.F.LeC. Holding, S. Cenini and B. Ratcliff, *Inorg. Chim. Acta, 8* (1974) 149.

17 S.R.A. Bird, J.D. Donaldson, S.A. Kepple and M.F. Lappert, *J. Chem. Soc.(A),* (1971) 1311.

18 H.A. Bent, *J. Inorg. Nucl. Chem., 19* (1961) 143.

19 B.A. Goodman, R. Greatrex and N.N. Greenwood, *J. Chem. Soc. (A)* (1971) 1868 and references therein.

20 S.R.A. Bird, J.D. Donaldson, A.F. LeC. Holding, B.J. Senior and M.J. Tricker, *J. Chem. Soc. (A), (1971)* 1616.

21 M.G. Clark, A.G. Maddock and R.H. Platt, *J. Chem. Soc. Dalton,* (1972) 281.

22 R.V. Parish, *Progress Inorg. Chem., 15* (1972) 101.

23 G.M. Bancroft, *Coord. Chem. Rev., 11* (1973) 247.