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A Mössbauer Study of the Tin-Manganese Bond

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The nature of the tin-manganese bond in the series of compounds of formula $[Mn(CO)_5]_nSnR_{4-n}$ *(*$n = 1$*,* $R = Cl, Br, I, C_2H_5, C_6H_5$*;* $n = 2$*,* $R = Cl, Br, C_6H_5$*)* $Mn(CO)_5SnR_{3-n}X_n$ *(*$n = 1, 2$*) (*$X = Cl, Br, I$*;* $R = C_6H_5$*), and* trans–$PPh_3Mn(CO)_4SnR_3$ *(*$R = Cl, C_6H_5$*) where R and X groups have been systematically altered was studied by means of the 119m Sn Mössbauer Effect. The importance of the tin-manganese bond in determining the values of the chemical isomer shift and quadrupole parameters has been emphasised. The effects of bond lengths and bond polarities on the quadrupole splitting parameters are discussed.*

Introduction

Of all the tin-transition metal bonds, the tin-manganese bond has probably been the most studied.[1] Particularly extensive i.r. studies have been carried out on derivatives of the type $Mn(CO)_5SnR_3$[2,3] usually starting from the Cotton Kraihanzel approach to the band assignment and force constant calculations.[4]

Apart from early papers by Karasev et el.[5] and by Goldanskii[6] and a more recent paper by Fenton and Zuckerman,[7] there are no reports of systematic Mössbaure studies on tin-transition metal compounds. This is especially true for compounds containing tin-manganase bonds. Since the earlier studies[6,5] the sign of $\Delta R/R$ has been established[8] and the orgins of the electric field gradient are more fully understood.[9]

In a study concurrent with the present work Donaldson et al.[9] have found that the trends in chemical isomer shifts and quadrupole splittings in the series of compound $[\pi\text{–}C_5H_5Fe(CO)_2]_2SnX_2$ and $\pi\text{–}C_5H_5Fe(CO)_2SnX_3$ ($X = Cl, Br, I, NCS, HCO_2, CH_3CO_2$) can be explained with reference to the very short Sn–Fe bonds. They have also discussed the values of the quadrupole splittings in these series in terms of known crystal structures and have shown how the observed positive sign for e^2qQ in $\pi\text{–}C_5H_5Fe(CO)_2SnCl_3$ can be explained in terms of a high *p*-electron density on the tin atom in the direction of the Sn–Fe bond.

A number of X-ray crystallographic studies have been carried out on tin-manganese derivatives[10-14] and it has been shown that the Sn–Mn bond in all of them is very short. The known bond lenghts for the compounds studied in this work are included in Table I. The character of the Sn–Mn bond, although probably weaker,[15] is not dissimilar to that of the Sn–Fe bond in the $\pi\text{–}C_5H_5Fe(CO)_2SnX_3$ compounds.*

Results and Discussion

The Mössbauer parameters for sixteen tin-manganese compounds are given in Table I, eleven of them for the first time. The data for the other compounds are in fair agreement with the literature values.[5] Compounds 3, 7, and 11 are new and their preparation and i.r. data are described in the experimental section.

For compounds 1-3, 6-7, 9-11, and 12-13 the chemical isomer shift(δ) relative to barium stannate increases in the order Cl<Br<I as would be expected on bond polarity arguments.[16,17] Thus, the Sn–I bond being the most covalent is most like the Sn–Mn bond. A similar relationship between the covalency of halogen and metal-metal bonds has been suggested for Au–Mn componuds.[18] Any $d_\pi\text{–}d_\pi$ bond formation between manganese and tin in these halogen derivatives

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(*) The metal-metal distance in Sn-Mn[12] compounds is usually longer than in similar Sn-Fe materials and this is consistent with the i.r. data

	νSn-Cl	δSn-Cl	νSn-Cl	δSn-Cl	νSn-M (cm⁻¹)
$\pi\text{-}C_5H_5Fe(CO)_2SnCl_3$[9]	346	144	322	118	222
$Mn(CO)_5SnCl_3$[27]	345	134	—	113	201

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Table I.

Compound	d(Sn—Mn)	Mn—$\widehat{Sn}$—X	mm. s^{-1} δ^a	 Δ^a	 Γ^b	ref.
1) $Mn(CO)_5SnCl_3$			1.66	1.50	—	*c*
			1.73	1.56	—	*d*
2) $Mn(CO)_5SnBr_3$			1.71	1.40	—	*c*
			1.84	1.44	—	*d*
3) $Mn(CO)_5SnI_3$			1.95	1.32	—	*c*
4) $Mn(CO)_5Sn(C_2H_5)_3$			1.49	0.88	—	*c*
5) $Mn(CO)_5Sn(C_6H_5)_3$	2.674[11]	112.7°	1.37	—	1.45	*c*
			1.45	—	—	*d*
6) $[Mn(CO)_5]_2SnCl_2$			1.98	2.15	—	*c*
7) $[Mn(CO)_5]_2SnBr_2$			2.04	2.12	—	*c*
8) $[Mn(CO)_5]_2Sn(C_6H_5)_2$	2.70[12]	Mn'—Sn—Mn''117° C'—Sn—C''100°	1.66	—	1.63	*c*
9) $Mn(CO)_5Sn(C_6H_5)Cl_2$			1.74	2.47	—	*c*
10) $Mn(CO)_5Sn(C_6H_5)Br_2$			1.76	2.68^e	—	*c*
11) $Mn(CO)_5Sn(C_6H_5)I_2$			1.80	2.19	—	*c*
12) $Mn(CO)_5Sn(C_6H_5)_2Cl$			1.55	2.64	—	*c*
			1.62	2.60	—	*d*
13) $Mn(CO)_5Sn(C_6H_5)_2Br$			1.59	2.40	—	*c*
14) *trans*-$PPh_3Mn(CO)_4Sn(C_6H_5)_3$	2.627[10]	114.3°	1.49	—	0.82	*c*
15) *trans*-$PPh_3Mn(CO)_4SnCl_3$			1.70	1.87	—	*c*
16) $[Mn(CO)_5]_3SnCl$	2.737[9]	101.0°	1.92	1.55	—	*d*

^{a} Samples at 80°K vs. $BaSnO_3$ at 80°K. Estimated error ± 0.05 mm. s^{-1}. ^{b} Line width at half peak height ± 0.10 mm. s^{-1}. ^{c} This work. ^{d} Reference 5. ^{e} This series subject to disproportionation and rearrangements, hence this result may be anomalous.

Table II.

Compound	d(Fe-Sn)	Compound	δmm. s^{-1}
π-$C_5H_5Fe(CO)_2SnCl_3$ [21]	2.467(1)	$Mn(CO)_5SnCl_3$	1.66
π-$C_5H_5Fe(CO)_2SnCl_2Ph$ [21]	2.468(3)	$Mn(CO)_5SnCl_2Ph$	1.74
π-$C_5H_5Fe(CO)_2SnClPh_2$ [21]	2.504(3)	$Mn(CO)_5SnClPh_2$	1.55
π-$C_5H_5Fe(CO)_2SnPh_3$ [23]	2.533	$Mn(CO)_5SnPh_3$	1.37

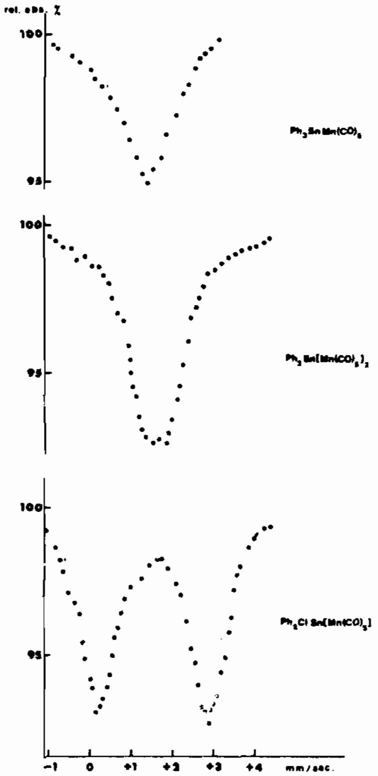

Figure 1. The ^{119}Sn Mössbauer spectra of $Ph_3SnMn(CO)_5$; $Ph_2Sn[Mn(CO)_5]_2$, and $Ph_2ClSn[Mn(CO)_5]$.

would result in an increase in the shielding of the tin *s*-electrons and to a decrease in the chemical isomer shift and would also favour an increase in the shift in the order $SnCl_3 < SnBr_3 < SnI_3$.

The chemical isomer shifts for the orgation derivatives 4.5 and 8 are lower than those of the corresponding halogen compounds. This is contrary to the expected trend on bond polarity arguments, although the correct order is maintained for the phenyl and ethyl derivatives. A similar trend has however, been found for the series of compounds[19] π–$C_5H_5Fe(CO)_2$-SnR_3 (R = Cl, δ = 1.90; R = Et, δ = 1.74; R = Ph, δ = 1.43). This trend is due[9] probably to differencies in the Sn–Fe bond lengths. It is reasonable to suppose that the trends found for the Mn compounds in the present work are also due mainly to differences in the Sn–Mn bond lengths which are a consequence of the replacement of the halogen atoms by organic groups in the SnR_3 moiety. If the longer bonds in the organotin derivatives were due to a weakening of the π-bonding between Sn and Mn, the tin *s*-electrons would be deshielded and a higher chemical isomer shift would be expected. The Mössbauer chemical shifts for these materials therefore confirm that the longer bonds in organotin derivatives are due to variations of the σ-rather than of any

(19) R. H. Herber and A. Hoffman, see « Applications of the Mössbauer Effect in Chemistry and Solid-state Physics », International Atomic Energy Agency, Vienna, pp. 132 (1966).

possible π-interaction between the two metals.[20] Mössbauer[7] and i.r.[2] data have previously been used to suggest that π-interactions in similar metal-metal bonded compounds are less important than the σ-interactions.

Replacement of halogen atoms by phenyl groups in compounds 1-3 affects the chemical isomer shift in two opposite ways: (i) the replacement of the halogen by the less electronegative substituent raises the shift, and (ii) any lengthening of the dominant Sn–Mn bond results in a lowering of the shift. The Mössbauer shift data for the chloride series (Table II) suggest that replacement of one Cl atom in $SnCl_3$ by Ph has no appreciable effect on the length of the Sn–Mn bond but that replacement of more than one Cl produces a weakening of that bond. The Sn–Mn bond lengths for this series are not known but the data are entirely consistent with the trends in the series $\pi-C_5H_5Fe(CO)_2SnCl_{3-n}R_n$ for which bond lenghts are known (Table II). The data for the Br series of Sn–Mn compounds (2, 10, 14) are similar, but it does appear that weakening of the Sn–Mn bond occurs on replacement of only one I in compound 3 by Ph to give compound 11.

The increase in chemical isomer shift in the pairs of compounds 1 and 6, 2 and 7, 5 and 8, shows how the localisation of the *s* electrons on the tin is favoured by the metal-metal bonds as Cl, Br, or Ph are replaced by $Mn(CO)_5$ groups. In the chloride series replacement of a second Cl by $Mn(CO)_5$ does not have a marked effect on the shift (see compounds 6 and 16). This means that the increase in the number of Sn–Mn bonds in compound 16 must have been compensated for by a weakening of the Sn–Mn bonds and certainly the Sn–Mn bond length in this material is one of the longest known tin-manganese bonds (Table I).

The substitution of CO by the more basic PPh_3 ligand *trans* to the tin atom has very little effect on the Mössbauer chemical shift (see compounds 5 and 14, and 1 and 15). In both sets the shift is raised slightly and the main effect of the substitution is seen in the quadrupole splitting or line width parameters. The Mössbauer data for compounds of this type will be discussed in greater detail elsewhere.[22]

The quadrupole splittings (Δ) of the Mössbauer resonance lines for the materials studied in this work are in agreement with previous work[5,6,7,9,19] in that the halogen derivatives have relatively large splittings while those for the organotin derivatives are small or zero. The magnitude of the quadrupole splitting in these materials depends upon the size of the electric field gradient at the tin atom and this can be affected by three main factors, (i) any *p*-electron imbalance due to differences in the use of the tin bonding electrons in forming σ-bonds, (ii) any *d*-electron imbalance caused by the population of Sn *d*-orbitals by π-interactions, (iii) any gross deviation from the ideal tetrahedral angle. Since we have shown that the chemical isomer shifts of the Sn–Mn compounds are best explained in terms of σ-interactions, it is reasonable to suppose that any electric field gradient in these materials would also be produced by differences in the σ-interactions in the four bonds formed by tin. In the manganese derivatives which contain only Sn–Mn and Sn–X bonds (1,2,3,6,7,16), the presence of a field gradient can easily be explained in terms of differences in the use of the tin *p*-electrons in the short Sn–Mn bonds and the more polar Sn–X bonds. The gradual decrease in Δ in the order Cl > Br > I is the expected result on bond polarity arguments,[23] although the magnitude of the splitting could also be affected by the angular displacement of the bonds[9] about the direction of the principal component (V_{zz}) of the field gradient.

Parish and Platt[23] have shown, by point-charge calculations, that the contributions of the atoms to V_{zz} in groups such as $MnSnX_3$ and Mn_2SnX_2 which have ideal tetrahedral structures is identical and equal to 2[Mn]–2[X] where [Mn] and [X] are the contributions of Mn and X respectively to the field gradient. In the ideal case the quadrupole splitting for the $MnSnX_3$ would be smaller than that for Mn_2SnX_2 because of the non-zero asymmetry parameter (η) in the latter case. The difference in the values of η, however, could only account for an increase of about 15% and the observed differences (compounds 1 and 6, and 2 and 7) are much greater than this. The high splittings for the $[Mn(CO)_5]_2SnX_2$ compounds can thus be better explained either by a considerable shortening of the Sn–Mn bonds or by a distortion of the tetrahedral bond angles in these materials compared to the corresponding $Mn(CO)_5SnX_3$ derivatives. The magnitude of similar quadrupole splittings in the related compounds $\pi-C_5H_5Fe(CO)_2SnX_3$ and $[\pi-C_5H_5Fe(CO)_2]_2SnX_2$ has been rationalised[9] on the basis of the known bond angles in these compounds.

The sign of V_{zz}, the principal component of the field gradient, in $\pi-C_5H_5Fe(CO)_2SnCl_3$ is positive and it is probable that the sign of V_{zz} in compounds 1-3 is also positive. The sign of V_{zz} in compound 16 would then be negative because V_{zz} would lie along an Sn–Cl rather than along an Sn–Mn bond.

Small or unresolved quadrupole splittings for the organotin derivatives 4,5 and 8, are expected in view of the greater covalent similarity between Sn–Mn bond and the Sn–C bonds. It is interesting that the ethyl derivative (4) does have a resolved splitting and this presumably means a shorter Sn–Mn bond in this material than in the phenyl derivatives. The Mössbauer quadrupole splitting data for the organotin derivatives are consistent with the low values for the dipole moment found for their metal-metal bonds.[2]

The splittings for the derivatives which contain both Sn–X and Sn–C bonds lie in the expected region[23] for organotin compounds of the type R_nSnX_{4-n} (n = 1-3, R = alkyl or aryl groups, X = halogen). Again these splittings can be rationalised on σ-bonding arguments alone, although the magnitude of the parameters may be affected by the details of the bond angles in the tin environments.

The quadrupole splitting data also seem to be consistent with recent observations on the heterolytic

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(20) P. T. Greene and R. F. Bryan, *J. Chem. Soc. (A)*, 1696 (1970).
(21) R. F. Bryan, *J. Chem. Soc. (A)*, 192 (1967).
(22) S. R. A. Bird, S. Cenini, J. D. Donaldson, and B. Ratcliff, to be published.
(23) R. V. Parish and R. M. Platt, *Inorg. Chim. Acta*, *4*, 65 (1970).

cleavage of metal-metal bonds. These observations[24] suggest that while the strong bond polarity is $Mn^{\delta+}$—$Sn^{\delta-}$ in the halide derivatives,[2] the polarity in the organotin compounds could be $Mn^{\delta-}$—$Sn^{\delta+}$. Similar results on the polarity of the metal-metal bonds in the alkyl and aryl derivatives have also been obtained from dipole moment and infrared data.[25]

Interestingly this inversion in the bond polarity could also account for the anomalous (on the grounds of bond polarity arguments) isomer shift of the organic tin-manganese derivatives.

Conclusions

The Sn-119 Mössbauer parameters on a number of compounds containing the Sn–Mn bond show how the use of the tin bonding electrons is dominated by this metal-metal bond. The rends in the chemical isomer shift and quadrupole splitting parameters can be explained with reference to the expected length of the Sn–Mn bonds in the series of compounds. The data are also consistent with the suggestion that σ-interactions are more important in these metal-metal bonds than are π-interactions.

Experimental Section

The details of the Mössbauer apparatus have been reported previously.[26]. The infrared spectra were recorded on a Perkin-Elmer 621 grating spectrometer. The percentage resonance dip for these compounds was 5-10% when 100,000 to 500,000 counts per channel had been accumulated. The spectra were obtained on 256 and 512 channel analysers calibrated for velocity with the natural iron spectrum. The Mössbauer parameters were obtained graphically although some of the data were checked by computer curve fitting. Typical spectra are shown in the Figure. Starting materials were prepared by standard methods and the known Sn–Mn compounds prepared by literature methods,[2] and identified by elemental analyses, melting points and infrared spectra.

$Mn(CO)_5SnI_2Ph$. A solution of $Mn(CO)_5SnPh_3$ (1.0 g) in dichloromethane (40 ml) was stirred with a solution of iodine (1.0 g) in dichloromethane (60 ml) for 3 hr, until the solution was yellow. The dichloromethane was removed *under vacuum* and the residue extracted with warm n-pentane. Cooling the solution to −80°C gave yellow crystals of the product which was dried *in vacuo* (0.25 g, 21%, m.p. 84°). (Found: C, 20.6; H, 0.9; Calcd for $C_{11}H_5MnSnO_5I_2$: C, 20.5; H, 0.8%) $\nu_{co}(CHCl_3)$: 2112(w), 2026(s).

$Mn(CO)_5SnI_3$. A solution of $Mn(CO)_5SnPh_3$ (1.0 g) in dichloromethane (40 ml) was stirred for 72 hr, under a nitrogen atmosphere, with a solution of iodine (1.5 g) in dicholoromethane (100 ml). The solvent was then completely removed *under yacuum* and the crude yellow product recrystallised twice from n-pentane (0.25 g; 20%, m.p. 72.-4°). (Found: C, 9.1; Calcd for $C_5MnSnO_5I_3$: C, 8.6). $\nu_{co}(CHCl_3)$: 2118(w), 2035(s).

$[Mn(CO)_5]_2SnBr_2$. A stream of hydrogen bromide* was passed through a solution of $[Mn(CO)_5]_2SnPh_2$ (1.0 g) in dichloromethane (40 ml) for 45 min. The solvent was then completely removed *under vacuum* and the crude product recrystallised from ethanol to give fine needles which were dried *in vacuo* (0.7 g, 70%; decomposed at 159°). (Found: C, 18.0%; Calcd for $C_{10}Mn_2SnO_{10}Br_2$: C, 18.4%). $\nu_{CO}(CHCl_3)$: 2120(w), 2096(s), 2055(m,sh), 2029(vs), 2001(m,sh).

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