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MÖSSBAUER SPECTRA OF SOME LOW SYMMETRY COMPOUNDS CONTAINING A TIN MANGANESE BOND

B. MAHIEU, D. APERS

Laboratoire de Chimie Inorganique et Nucléaire, Université Catholique de Louvain, B-1348 Louvain-La-Neuve (Belgium)

I. VANDEN EYNDE * and M. GIELEN

Vrije Universiteit Brussel, T.W.-AOSC, Pleinlaan 2, B-1050 Brussel (Belgium)

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Summary

Tin-119 Mössbauer spectra are reported for five tetrahedral organotin compounds having the general formula $RR'R''SnMn(CO)_5$. These results, combined with earlier information from the literature, provide data for three series of compounds in which the three R groups are progressively substituted by three R″ groups. The changes in the isomer shift and quadrupole splitting are discussed as a function of the degree of such replacement.

Introduction

Recent preparations of the relevant organotin compounds [1] have provided three series of $RR'R''SnMn(CO)_5$ species: (a) $RR'R'' = Ph_3$, Ph_2Me, Me_3; (b) $RR'R'' = Ph_2Cl$, $PhMeCl$, Me_2Cl; (c) $RR'R'' = Ph_2Mn(CO)_5$, $PhMeMn(CO)_5$, $PhMeFe(CO)_2(Cp)$, $Me_2Mn(CO)_5$. We have determined the Mössbauer spectra for some of these compounds (see Tables) in order to complement the isomer shift and quadrupole splitting data for the other Sn–Mn compounds in these series [2–7].

The synthesis of four of the five compounds studied in this paper were described previously [1]. The synthesis of the fifth $MePhSn[Fe(CO)_2Cp][Mn(CO)_5]$ followed the sequence;

$$\begin{tikzcd}
MePh_2SnFe(CO)_2Cp \arrow[r, "HCl", "Et_2O,\ 4\ h"'] & MePhSn[Fe(CO)_2Cp]Cl \arrow[d, "Na^+Mn(CO)_5^-,\ THF,\ 3\ h"] \\
 & MePhSn[Fe(CO)_2Cp][Mn(CO)_5]
\end{tikzcd}$$

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* Present address: U.C.B., Rue d'Anderlecht. B-1620 Drogenbos (Belgium).

TABLE 1

MÖSSBAUER PARAMETERS OF ORGANOTIN COMPOUNDS OF THE TYPE Ph_nMe_{3-n}-$SnMn(CO)_5$

Compound	IS [a]	QS [a]	Ref.
$Ph_3SnMn(CO)_5$	1.41	0	2,3
	1.37	(Γ 1.45)	4
	1.35	0.41	5
	1.38	(Γ 1.09)	This work
	1.51	0	7
$Ph_2MeSnMn(CO)_5$	1.40	0.61	2,3
$Me_3SnMn(CO)_5$	1.33	0.61	2,3
	1.41	0.82	6
	1.46	0.81	7

[a] IS = isomer shift with respect to a $Ca^{119m}SnO_3$ source, QS = Quadrupole Splitting; Γ = line width.

TABLE 2

MÖSSBAUER PARAMETERS OF ORGANOTIN COMPOUNDS OF THE TYPE Ph_nMe_{2-n}-$ClMn(CO)_5$

Compound	IS	QS	Ref.
$Ph_2ClSnMn(CO)_5$	1.57	2.49	2,3
	1.55	2.64	4
	1.61	2.50	5
$PhMeClSnMn(CO)_5$	1.51	2.42	This work
$Me_2ClSnMn(CO)_5$	1.54	2.66	3
	1.52	2.60	5,6

TABLE 3

MÖSSBAUER PARAMETERS OF ORGANOTIN COMPOUNDS OF THE TYPE Ph_nMe_{2-n}-$Sn(Mn(CO)_5)_m(Fe(CO)_2Cp)_{2-m}$

Compound	IS	QS	Ref.
$Ph_2Sn(Mn(CO)_5)_2$	1.66	(Γ 1.63)	4
$PhMeSn(Mn(CO)_5)_2$	1.60	0.73	This work
$PhMeSnFe(CO)_2(Cp)Mn(CO)_5$	1.60	0.68	This work
$Me_2Sn(Mn(CO)_5)_2$	1.68	0.92	7
	1.60	0.68	This work

Experimental

Mössbauer spectra

A constant acceleration spectrometer Elscint MVT4 Promeda was used with a moving $Ca^{119m}SnO_3$ source. All measurements were made with the source at room temperature and the absorber at liquid nitrogen temperature. The experimental data were fitted by an iterative least square computer program to a sum of Lorentzian peaks.

Synthesis of MePh[Fe(CO)$_2$Cp]SnCl

5.1 ml of 0.984 *M* HCl in Et_2O is added dropwise to a solution of 2.35 g (0.005 mol) $Ph_2MeSnFe(CO)_2Cp$ in a mixture of 50 ml dry Et_2O and 10 ml benzene saturated with nitrogen. After 3 h stirring the mixture is evaporated under vacuum to yield 2.2 g of an orange oil.

Synthesis of MePhSn[Fe(CO)$_2$Cp][Mn(CO)$_5$]

The crude chloride described above is dissolved in dry THF and 5 mmol $NaMn(CO)_5$ in 80 ml THF is added under N_2 at room temperature. After 3 h stirring the mixture is evaporated and the residue chromatographed on SiO_2 (Ø 20 mm, *l* 400 mm) using benzene/petroleum ether (40–60°) 40/60 as an eluent. A first yellow band is identified as $Mn_2(CO)_{10}$; a second band, after evaporation of the solvent, yields 750 mg (26%) of a yellow-orange oil, which crystallizes under refrigeration. After recrystallization from petroleum ether 40–60° (30 ml) it has a melting point of 94–95°C (60 MHz, 0.4 *M* in CS_2, MeSn: δ 0.86 ppm; $^2J(^{117/119}Sn\text{–}C\text{–}^1H)$ 34–35 Hz; CpSn: 4.77 ppm; C_6H_5: 7.15–7.65 ppm vs. TMS; IR: 2080 and 1995 cm^{-1} ($Mn(CO)_5$); 1940 cm^{-1} with shoulder at 1990 cm^{-1} ($Fe(CO)_2Cp$).

The mass spectrum shows the molecular ion (*m/e* 584, 0.15%) and other ions at *m/e* 569 (*M* – Me, 1.7%), 542 (*M* – Me – CO, 1.1%), 513 (*M* – Me – 2CO, 1.9%), 507 (*M* – C_6H_5, 0.2%), 500 (*M* – 3CO, 0.3%), 472 (*M* – 4CO, 0.4%), 457 (*M* – Me – 4CO, 0.3%), 444 (*M* – 5CO, 15%). Other important ions are $PhMe[Mn(CO)_5]Sn$ (7%), $PhMe[Fe(CO)_2Cp]Sn$ (100%, base peak), $PhMe[Mn(CO)_4]Sn$ (7%), PhMe[Fe(CO)Cp]Sn (0.9%), $PhMe[Mn(CO)_3]Sn$ (9%), PhMe(FeCp)Sn (82%), Ph(FeCp)Sn (24%), $SnFe(CO)_2Cp$ (49%), PhSn (25%), CpSn (63%), CpFe (9%), Sn (12%), Fe (5%) and Mn (14%).

Results

Tables 1, 2, 3 summarize the experimental Mössbauer data for the organotin compounds.

Discussion

Isomer shift

In each of the three series, the isomer shifts lie in a narrow range, but an appreciable change is observed from one series to another.

Replacement of one of the R ligands (R = Ph or Me) by X (X = Cl) or M (M = $Mn(CO)_5$ or $Fe(CO)_2(Cp)$) markely increases the isomer shift, and thus the density of *s*-electron at the tin nucleus. This effect is readily understood if it is assumed that the Sn–M bond has a pronounced *s*-character while the Sn–X bond has a pronounced *p*-character [5]. Thus in compounds involving tin bonded to a transition metal, a Sn–Cl bond increases $[\Psi(O)_s]^2$ by reducing the *p*-electron density and deshielding the tin nucleus, while a Sn–M bond increases $[\Psi(O)_s]^2$ by reinforcing the *s*-density at the tin atom.

Within series a–c progressive replacement of phenyl groups by methyl ligands does not change the isomer shift significantly when account is taken of the rather large discrepancies between the published values. Within series c, the replacement of one $Mn(CO)_5$ by $Fe(CO)_2(Cp)$ does not change the isomer shift. Comparison of related compounds, which differ from each other by only one ligand, such as: $M'Ph_2SnMn(CO)_5$: M' = Ph, Me, Cl, $Mn(CO)_5$; $M'PhMeSnMn(CO)_5$: M' = Ph, Cl, $Fe(CO)_2(Cp)$, $Mn(CO)_5$; and $M'Me_2SnMn(CO)_5$: M' = Me, Cl, $Mn(CO)_5$, shows the order of increasing *s* electron density at the tin atom to be the following: $Ph \cong Me < Cl < Mn(CO)_5 \cong Fe(CO)_2(Cp)$. This order is different from that established elsewhere [8], and shows how much care must be excercised when extrapolating from one to another series.

Quadrupole splitting

The quadrupole splitting of the Mössbauer spectra reflects the electric-field gradient at the tin nucleus. This gradient is essentially produced by a *p*-electron imbalance in the 5*p* orbital of the tin atom. Thus in tetrahedral compounds with four identical bonds, the splitting is generally zero, except for severely distorted molecules *; in structures containing one tin-metal bond, however, quadrupole splitting should be observed. In series 1 and 3, a small doublet is indeed present, well resolved for the methyl compounds and badly resolved or unresolved for the phenyl compounds (which accounts for the value of QS = 0 quoted by some authors).

In series 2, there is a large quadrupole splitting, reflecting the local asymmetry in the electron shells produced by the different modes of bonding of the halogens. The small influences of methyl and phenyl are masked in this case. The best explanation for the lowering of the splitting by phenyl ligands seems to lie in their ability to delocalize π electrons and so reduce the *p*-electron imbalance in the molecule.

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* For example, we have observed a value of 1.1 mm/s for the splitting in the octaphenyl-1,1'-spirobistannole [9]; this compound has a highly distorted structure around the tin nucleus [10].