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Mössbauer Spectroscopic Studies of Clusters $Mn_2(CO)_8[\mu\text{-}Sn(hal)Mn(CO)_5]_2$ (hal = Cl, Br) and Related Mn and Re Compounds

R. BARBIERI and G. ALONZO
Istituto di Chimica Generale, Università di Palermo, 90123 Palermo, Italy
H.-J. HAUPT and H. PREUT
Lehrstuhl für Anorganische Chemie, Universität Dortmund, 46 Dortmund 50, BRD

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In order to be acquainted with the nature of bonds at Sn involved in the title compounds, as well as to get information on the configuration of the strictly related derivatives $I_2Sn_2Mn_4(CO)_{18}$ and $Cl_2Sn_2Re_4(CO)_{18}$, the Mössbauer spectroscopic investigation reported in this paper has been carried out. The experimental parameters (isomer shifts, δ; nuclear quadrupole splittings, ΔE; for the bromide derivative only, the asymmetry parameter η and the sign of the nuclear quadrupole coupling constant e^2qQ) have been discussed in connection with data concerning compounds with tin–transition metal bonds, mainly $hal_2Sn[Mn(CO)_5]_2$ (hal = Cl, Br) and $ClSn[Mn(CO)_5]_3$. Rationalizations of ΔE and η have been effected by the point-charge model formalism. Deductions derived from Mössbauer–Zeeman spectral parameters have been interpreted in the light of informations extracted from the molecular structures and the application of the second-order hybridization concept. A s character sequence has been proposed for Sn–Mn and Sn–hal bonds, as well as self-consistent sets of calculated absolute partial quadrupole splitting values, for the title compounds and quoted halotin–manganese pentacarbonyls.

Introduction

It has been recently determined (by H.-J. H. and H. P.) that compounds of analytical formula $hal_2Sn_2Mn_4(CO)_{18}$ (hal = Cl, Br) are clusters where two $Mn(CO)_4$ units are bridged by two $Sn(hal)Mn(CO)_5$ groups, forming a four- membered ring (Sn_2Mn_2 atoms) where there is a strong indication of the occurrence of Mn–Mn bonds [1]. In principle, the rationalization of structural parameters (Table I) for bonds at Sn in these clusters, $Mn_2(CO)_8[\mu\text{-}Sn(hal)Mn(CO)_5]_2$, I (hal = Cl) and II (hal = Br), would be feasible in connection with data concerning the related compounds $hal_2Sn[Mn(CO)_5]_2$, III (hal = Cl) and IV (hal = Br), and hal Sn $[Mn(CO)_5]_3$, V (hal = Cl) and VI (hal = Br). The interpretation could be effected in the light of the isovalent rehybridization concept, which states, *inter alia*, that increments of s character provoke shortening of bond distances and increase of bond angles [6]. It could be also assumed that structural parameters of solids correspond to those of free molecules, ignoring, to our purposes, crystal packing requirements which may be essential in dictating solid state structures.

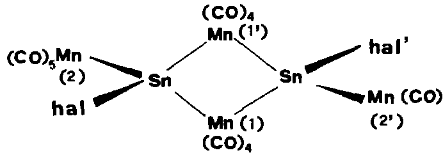
On these grounds, it is observed (from data in Table I) that rationalizations fail. The orders of magnitude of Sn–Mn distances would in fact suggest that s character (which predominates in tin–transition metal bonds in this class of compounds, other bonds in the molecule having mainly p character [7]) would be nearly invariant in Sn–Mn linkages in I, II, III and IV (slightly larger in I, II than in III, IV), while lesser in V, VI; Sn–hal distances would imply that s-character of these bonds decreases in the series III, IV > I, II > V, VI. Angles at Sn would instead dictate the following sequences of s character, referred to individual bonds: i) Sn-Mn: I, II(Sn–Mn(2)) > III, IV > V, VI > I, II(Sn–Mn(1)); ii) Sn–hal: (I, II, angle Mn(1)–Sn–hal) > III, IV (>I, II, angle Mn(2)-Sn–hal) > V, VI. It is evident that deductions are fully satisfactory for III, IV, V and VI, while contrasting and uncertain for I, II. The latter is easily attributed to the peculiar nature of bonds in clusters I, II, where the four-membered rings with Mn(1)–Mn(1′) bonds impose very acute Mn(1)–Sn–Mn(1′) angles, whose physical significance cannot be interpreted in terms of qualitative hybridization rules commonly used by experimentalists.

In order to possibly clarify the situation, and gain a deeper insight in the nature of bonds at the tin atom in I, II and related compounds, we carried out the work reported in this paper, using Mössbauer effects in possibly determining the electrical features of Sn environments.

TABLE I. Structural Parameters Discussed in the Text.

Compound	Code No.	d(Sn–Mn) (pm)	d(Sn–hal) (pm)	Mn–Sn–Mn (°)	Mn–Sn–hal (°)	Ref.
$Cl_2Sn[Mn(CO)_5]_2$[a]	III	263.5 (av.)	238.5 (av.)	126.25(4)	107.58(9) (av.)	2
$Br_2Sn[Mn(CO)_5]_2$[b]	IV	264.2 (av.)	254.8 (av.)	125.88(6)	107.25(9) (av.)	2
$Mn_2(CO)_8[\mu\text{-}Sn(Cl)Mn(CO)_5]_2$[c]	I	262.4(1) (Sn-Mn(2))	240.3	132.75(2) (Mn(1)-Sn-Mn(2))	102.62(3) (Mn(2)-Sn-Cl)	1
		262.3(1) (av.) (Sn-Mn(1))		72.17(2) (Mn(1)-Sn-Mn(1'))	108.24(3) (Mn(1)-Sn-Cl)	
$Mn_2(CO)_8[\mu\text{-}Sn(Br)Mn(CO)_5]_2$[c]	II	263.4(1) (Sn-Mn(2))	255.4	132.22(3) (Mn(1)-Sn-Mn(2))	102.72(2) (Mn(2)-Sn-Br)	1
		262.7(1) (av.) (Sn-Mn(1))		71.91(2) (Mn(1)-Sn-Mn(1'))	108.45(2) (Mn(1)-Sn-Br)	
$ClSn[Mn(CO)_5]_3$	V	273.7 (av.)	243.1	116.5 (av.)	101.0 (av.)	3
$BrSn[Mn(CO)_5]_3$	VI	274.0(2) (av.)	258.8(1)	116.41(5) (av.)	101.05(5)	2
				Mn-Sn-C (°)	C-Sn-C (°)	
$Ph_3Sn[Mn(CO)_4PPh_3]$	IX	262.7		114.(3) (av.)	104.(6) (av.)	4
$Ph_3Sn[Mn(CO)_5]$	X	267.4 (av.)		112.7 (av.)	106.0 (av.)	5

[a] Cl–Sn–Cl, 95.80°. [b] Br–Sn–Br, 98.44°.
[c] Code No.'s of atoms according to the scheme:



Experimental

The Mössbauer parameters at liquid N_2 temperature, reported in Table II, have been determined on thin absorbers using essentially the apparatus and procedures of data reductions described elsewhere [12] (Elscint-Laben spectrometer; constant acceleration of source, held at RT; sawtooth waveform; sources from R. C., Amersham; phototube Na(Tl) I from Nuclear Enterprises, Edinburgh). The quality of the spectra is shown in Fig. 1, a.

Parameters ΔE and η for II at 4.2 °K (Table II; footnote e) have been determined by P.C.M.U., Harwell; the resulting Mössbauer–Zeeman spectrum is shown in Fig. 1, b.

Experimental ΔE's (Table II) have been rationalized by point charge model [9–11] calculations, which have been carried out by using a computer program written by T. C. Gibb (Leeds) and made suitable to our purposes by G. A. Input data of this program are: i) No. of ligands; ii) polar coordinates (of atoms bound to the Mössbauer atom) referred to a Cartesian system (in our calculations on clusters the input Z was usually coincident with Sn–hal bond direction, hal and Mn of terminal $Mn(CO)_5$ being in the XZ plane); iii) partial quadrupole splitting [9, 10] (p.q.s.) values. Outputs are: i) director cosinus of the new Cartesian system which diagonalizes the electric field gradient (e.f.g.) tensor [8, 10, 11]; ii) values of V_{zz} (the component of the e.f.g. along the z axis [10, 11]), ΔE and η, the first two with their proper sign. The positions of atoms around Sn in the diagonalized structure have been visualized from output director cosinus and input axes referred to above. In the more involvec cases concerning compounds I and II (and also VII–VIII by assuming that their structures correspond to those of I, II; code No.s as in Table II), actual x–z axes after diagonalization were in the input X–Z plane, with peculiar angles (depending on the p.q.s.'s magnitude) with respect to X and Z, while y was usually coincident with Y direction.

In order to facilitate the discussion, some Mössbauer parameters of interesting compounds are reported in Table III, while several sets of data, calculated as described above, are in Table IV.

Discussion

In compounds I–II there are three Sn–Mn and one Sn–hal bonds (see Fig., Table I); it seems reasonable

TABLE II. Experimental Mössbauer Parameters.

Code No.	Compound[a]	δ^b	ΔE^c	Γ_+^d	Γ_-^d
I	$Mn_2(CO)_8[\mu\text{-}Sn(Cl)Mn(CO)_5]_2$	2.08	2.28	1.03	1.04
II	$Mn_2(CO)_8[\mu\text{-}Sn(Br)Mn(CO)_5]_2$	2.10	2.30 $+2.30^e$ $(\eta = 0.23)^e$	0.96	1.04
VII	$I_2Sn_2Mn_4(CO)_{18}$	2.10	1.99	0.94	0.98
VIII	$Cl_2Sn_2Re_4(CO)_{18}$	1.95	2.58	1.03	1.16

[a] Compounds VII and VIII could be also formulated by assuming their structures to correspond to those of I and II, see text. [b] Isomer shift [8], mm s^{-1}, at liquid N_2 temperature, with respect to RT $BaSnO_3$ spectra. [c] Quadrupole splitting [8], mm s^{-1}, at liquid N_2 unless otherwise stated. [d] Full width at half height of the resonant peaks occurring at larger (+) and lesser (–) velocity than the spectrum centroid, mm s^{-1}, at liquid N_2. [e] From measurements at 4.2 °K, in a 6T magnetic field (see text); $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter [8–11];

TABLE III. Mössbauer Parameters Discussed in the Text.

Compound	Code No.	δ	$\Delta E_{exp.}$	Ref.	$\Delta E^a_{calcd.}$	Ref.
$Cl_2Sn[Mn(CO)_5]_2$	III	1.98	2.15	13	2.24 ($\eta = 1$)	14
			2.10	9		
$Br_2Sn[Mn(CO)_5]_2$	IV	2.04	2.12	13	2.24 ($\eta = 1$)	14
$ClSn[Mn(CO)_5]_3$	V	1.92	1.55	15	-1.94^b	14
$ISn[Mn(CO)_5]_3$	XI				−1.60	c
$Ph_3Sn[Mn(CO)_4PPh_3]$	IX	1.49	0.00	13		
		1.42	<0.30	16		
$Ph_3Sn[Mn(CO)_5]$	X	1.37	0.00	13	−0.58	14
		1.35	0.41	17		
$Cl_3Sn[Mn(CO)_4PPh_3]^d$	XII	1.70	1.87	13		
		1.70	1.69	16		
$Cl_3Sn[Mn(CO)_5]^d$	XIII	1.66	1.50	13	+1.94	14
			+1.60	14		
$halSn[Re(CO)_5]_3^e$	XIV	1.82	1.60	15	−1.60	c

[a] Assuming regular tetrahedral structures. P.q.s.'s, ΔE equations and procedures used: Refs. 10, 14, 18. [b] Same value for the Br derivative [17]. [c] This work. [d] From the Eq. [10]: (+) $\Delta E = 2([Mn(CO)_4L] - [X])$, the following p.q.s.'s have been obtained: $([Mn(CO)_4PPh_3] - [X]) = -0.93, -0.84$; $([Mn(CO)_5] - [X]) = -0.75 - -0.80$ mm s^{-1}. [e] hal = Cl, Br.

to assume, as a working hypothesis, that analogous bonds exist also in I_2Sn_2 $Mn_4(CO)_{18}$, VII, and $Cl_2Sn_2Re_4(CO)_{18}$, VIII, in view of similarities of method of synthesis and elemental composition. First attempts of rationalizing Mössbauer parameters of these compounds have then to be logically made by comparison with values pertaining to homologous compounds, *i.e.*, $halSn[M(CO)_5]_3$ (V, XI and XIV, Table III). In this context it is observed that δ and ΔE of I, II, VII and VIII (Table II) are consistently larger than corresponding values of V, XI and XIV.

Increases of δ reflect concomitant increases of total s electron density at the Sn nucleus [8–10]. For cases under discussion this could be mainly ascribed to total s character from Sn–M bonds larger for I, II, VII, VIII than for V, XIV (Sn–hal bonds exhibiting a predominant p character [7]), which is consistent with d (Sn–Mn) of I, II, V and VI (Table I and Introduction, this paper). In fact contributions to the increases of δ due to substitution of $M(CO)_5$ with $M(CO)_4Sn$ "ligands" at Sn (in I, II, and also VII, VIII in the case of similar configurations) seem to be minor effects on the following grounds.

It has been demonstrated that substitution of an efficient π-acceptor (as CO) with a poorer one, linked to a transition metal M bound to Sn, increases M → Snσ donor power, originating a concomitant increase of σ [20–22]. This effect is quite limited in compounds with Sn–Mn bonds (IX–X and XII–XIII, Table III), where substitution of CO with PPh_3 provokes average increments of δ well below those observed in going from V, XIV to I, II, VIII (Tables II, III). In the present context the effect on δ of increased σ donation seems also to be independent of

TABLE IV. Some Examples of Calculated[a] Sets of p.q.s.'s, ΔE and η Related to Sn Environments in Clusters $Mn_2(CO)_8[\mu\text{-}Sn(hal)Mn(CO)_5]_2$ and in Related Compounds

Compound[b] (Code No.)	Set No	$[M(CO)_5]$[c]	$[M(CO)_4Sn]$[c]	[hal][c]	ΔE	η
$Mn_2(CO)_8[\mu\text{-}Sn(Br)Mn(CO)_5]_2$	1	−0.99[e]	−0.70	−0.63[f]	+2.36	0.46
(II)[d]	2	−0.99[e]	−1.00	−0.63[f]	+2.86	0.19
	3	−0.60	−1.00	−0.75	+2.30	0.23
	4	−0.70[g]	−0.90[g]	−0.65[g]	"	"
	5	−0.80	−0.85	−0.55	"	"
	6	−0.90	−0.70	−0.45	"	"
	7	−1.00	−0.55	−0.35	"	"
$Mn_2(CO)_8[\mu\text{-}Sn(Cl)Mn(CO)_5]_2$	8	−0.70	−0.90	−0.55[h]	+2.35	0.15
(I)[d]	9	−0.80	−0.85	−0.55	+2.40	0.21
$Cl_2Sn[Mn(CO)_5]_2$	10	−0.90	–	−0.20	+2.17	0.46
(III)[i]	11	−1.00	–	−0.35	+2.16	0.48
$Br_2Sn[Mn(CO)_5]_2$	12	−0.90	–	−0.20	+2.14	0.45
(IV)[i]	13	−1.00	–	−0.35	+2.11	0.45
$ClSn[Mn(CO)_5]_3$	14	−0.95	–	−0.49	−1.55	0.00
(V)[l]	15	−0.99	–	−0.55	−1.55	0.00
$I_2Sn_2Mn_4(CO)_{18}$	16	−0.70	−0.90	−0.90	+2.18	0.61
(VII)[m]	17	−0.80	−0.80	−0.90	+2.16	0.79
$Cl_2Sn_2Re_4(CO)_{18}$	18	−0.59[o]	−1.00	−0.55	+2.41	0.03
(VIII)[n]		"	"	−0.35	+2.57	0.18
	19	−0.67[o]	−1.00	−0.55	+2.51	0.05
		"	"	−0.45	+2.59	0.05

[a] By the computer program described under Experimental. [b] Code No.s as in Tables I–III and text. [c] M = Mn, except for sets 18–19 where M = Re. [hal]: see individual compounds. Partial quadrupole splittings [18], [Ligand], are absolute values expressed as ½ e|Q| [Ligand] [11, 14], mm s^{-1} units. [d] Bonds angles at Sn used in the calculations: Ref. 1 (see Tabl. I). [e] Related to quotation −0.996, from Ref. 14. [f] Calculated from data of $(\pi\text{-}C_5H_5)(CO)_2FeSnBr_3$: ΔE = (+) 1.63 [14]; valence angles, average [19]: Fe–Sn–Br, 117.6(6)°; Br–Sn–Br, 100.1(6)°. ΔE = 2.000 [Fe] −1.0596 [Br] ($V_{xx} = V_{yy}$; $\eta = 0$; [Fe] = $[(\pi\text{-}C_5H_5)(CO)_2Fe]$ = −1.15 mm s^{-1} [14]. [g] This set of p.q.s.'s produces the following polar coordinates (reported as an example) for atoms bound to Sn, after diagonalization of the e.f.g. tensor: Mn(1,1'): $\theta = 145°\ 02'$, $\phi = 81°\ 54'$, $278°\ 06'$; Mn(2): $\theta = 29°\ 40'$, $\phi = 0°$; Br: $\theta = 73°\ 04'$, $\phi = 180°\ 0'$.
Code No.'s as in Tab. I, footnote c. Equations of $V_{\alpha\alpha}$ are:
$V_{xx} = -0.265\ [Mn(CO)_5] + 2\ (-0.980)\ [Mn(CO)_4Sn] + 1.748\ [Br]$;
$V_{yy} = -1.000\ [Mn(CO)_5] + 2\ (-0.036)\ [Mn(CO)_4Sn] - 1.000\ [Br]$;
$V_{zz} = 1.265\ [Mn(CO)_5] + 2(1.013)\ [Mn(CO)_4Sn] - 0.746\ [Br]$.
[h] Related to quotation from Ref. 14, see text. [i] Bond angles at Sn from Ref. 2 (see Table I); to facilitate calculations, average values of angles Mn–Sn–Cl = 107° 35' and Mn–Sn–Br = 107° 15' have been employed here. In the case of the Cl_2 derivative, the e.f.g. tensor is diagonalized for the following set of polar coordinates: Mn: $\theta = 26°\ 52'$, $153°\ 07'$, $\phi = 0°$; Cl: $\theta = 90°\ 0'$, $\phi = 131°\ 55'$, $-131°\ 55'$.
Related $V_{\alpha\alpha}$ equations are:
$V_{xx} = -0.776\ [Mn(CO)_5] + 0.676\ [Cl]$;
$V_{yy} = -2.000\ [Mn(CO)_5] + 1.318\ [Cl]$;
$V_{zz} = 2.776\ [Mn(CO)_5] - 2.000\ [Cl]$.
Analogous results are obtained for the Br_2 derivative.
[l] Bond angles from Ref. 3 (see Table I). Diagonalization of the e.f.g. tensor gives: Cl: $\theta = 0°$, $\phi = 0°$; Mn: $\theta = 101°\ 0'$, $\phi = 180°\ 0' \pm 60°\ 0'$. $V_{zz} = -2.673\ [Mn(CO)_5] + 2.000\ [Cl]$. Sign of ΔE is negative in agreement with earlier reports [14]. From Ref. 14: $[Mn(CO)_5] = -0.996$; [Cl] = −0.556. [m] Calculations are effected by assuming that VII has the same structure as II; bond angles as in II are then used here. [n] Assumed structure of VIII as that of I; angles of I are used. [o] Trial values of absolute p.q.s. $[Re(CO)_5]$ are estimated by assuming $[Mn(CO)_5]_{rel}/[Mn(CO)_5]_{abs} \cong [Re(CO)_5]_{rel}/[Re(CO)_5]_{abs}$.

the nature of acceptor Sn orbitals: in fact, while coordination polyhedra at Sn in IX–X are not very distorted from tetrahedral geometry (Table I, see bond angles at Sn), a more pronounced s character is predictable for Sn–Mn in XII–XIII.

In any event, apart from the role played in determining δ values, the electron donor power of $Mn(CO)_4Sn$ groups towards Sn is undoubtedly high. This provides a further proof of the large s character of Sn–Mn (1, 1') bonds of I, II (Table I, footnote c),

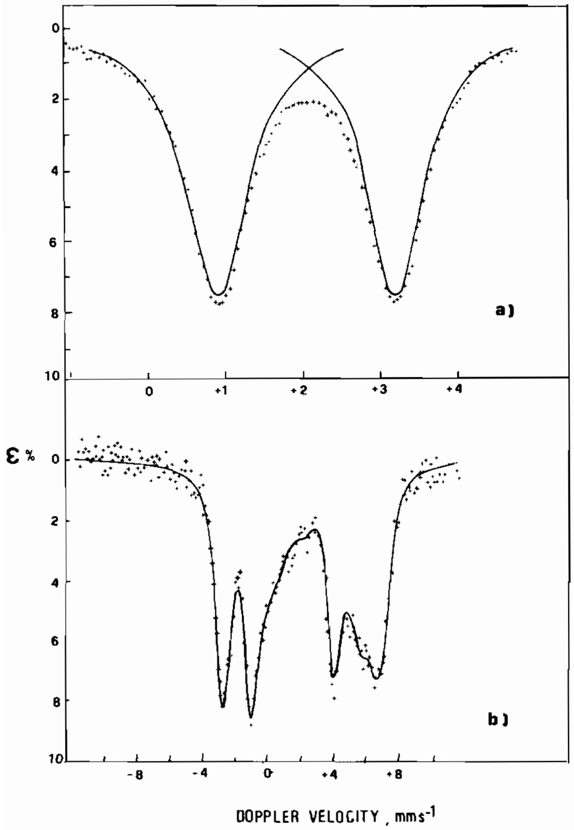


Figure 1. Mössbauer spectra of $Mn_2(CO)_8$ [μ-Sn(Br)Mn-$(CO)_5]_2$. ^{a}At liquid N_2 temperature. Full curves are computed Lorentzians. ^{b}In a magnetic field, 6T, at 4.2 °K. Full curve is computer fitting of experimental data.

since charge donation to eventual Sn hybrids formed mainly by p or d orbitals is expected to shield 5s electron density [9] with a consequent diminution of δ as function of increasing donor power, as has been observed also in tin–transition metal compounds [17]. A consistent Sn p orbital contribution in Sn–Mn (1, 1′) would thus lower δ of, say, I with respect to V, in place of the reverse experimental trend. We may then conclude that total s character of individual Sn–Mn bonds is larger in I, II than in V, which agrees with the sequence inferred from bond distances (I, II $\gtrsim$ III, IV $>$ V, VI, see Introduction). As a consequence, the s character of Sn–hal bonds would be V $>$ I, II, at variance with the trend extracted from d(Sn–hal) (see Introduction).

It is interesting to point out from data in Table II that δ's of I, II and VII are practically invariant for hal = Cl, Br, I, despite the parallel lowering of halogen electronegativity. Invariancy suggests that Sn s–p contribution in Sn–hal bonds in these compounds is such that donation to 5s Sn is counterbalanced by charge donated to shielding 5p orbitals. Instead, substitution of Cl with Br raises δ in the dihalo compounds III, IV (Table III), from which a larger s character in Sn–hal bonds is inferred for III, IV with respect to I, II, VII. We are now allowed to advance the following s character sequence for Sn–hal bonds, according to findings for III, IV, V and VI extracted from structural data (Introduction, this paper) as well as to the preceding discussion: III, IV $>$ V, VI $>$ I, II.

On ending the discussion of δ parameters, it is noticed that what was deduced for I, II apply equally well, to a great extent, to the iodide VII, to the Rhenium derivative VIII and to homologous compounds, from which it could be inferred that VII and VIII are not structurally very much different from I, II.

Taking now into account that partial quadrupole splittings [18] (p.q.s.) are functions of both 5s character of Sn orbitals involved in tin–ligand bonds as well as of the donor power σ of ligand atom (p.q.s. α–σ (1–s) [20]), we would predict, according to the point charge model formalism and the additive p.f.g. concept [9, 10, 18], the following sequence of orders of magnitude of p.q.s.'s: a) [$Mn(CO)_4L$] : V $>$ III, IV ($\gtrsim$ I, II (Mn(1))?) $>$ I, II (Mn(2)); b) [hal] : I, II $>$ V $>$ III, IV. These series obviously reflect the concomitant lowering of p character of acceptor orbitals, proposed earlier. The uncertainty of our tentative assumptions concerning [$Mn(CO)_4Sn$] of I, II arises from effects expected in view of the increment of σ over values of $Mn(CO)_5$. This is briefly discussed in the following.

Assuming that compounds XII and XIII (Table III) have a regular tetrahedral geometry around Sn, from experimental ΔE values it is observed that relative p.q.s.'s [$Mn(CO)_4PPh_3$] increase of about 0.1 mm s^{-1} over [$Mn(CO)_5$] (Table III, footnote d). Bancroft and Sham [23] have estimated an increment of 0.04 mm s^{-1}. This effect is analogous to findings concerning homologous Sn–Co derivatives [20]. In cases of compounds I, II, VII and VIII, considered as regular tetrahedral species (at Sn) halSn [$M(CO)_5$] [$M(CO)_4$-$L]_2$ having ΔE values reported in Table II, we determined (by the computer program described under Experimental) that good fits to ΔE are obtained by using the relative p.q.s. values ([$M(CO)_4$-L] – [X]) = –1.20 for I, II and VII, and –1.40 for VIII [24] (Δ p.q.s. of VIII, ~0.6 mm s^{-1} [24], seems too large, while values for I, II and VII, ~0.2 mm s^{-1} [24], are within observed ranges [20]). It is concluded that, s character of Sn–M bonds being assumed as approximately constant, p.q.s. [$Mn(CO)_4$-Sn] $\cong$ [$Mn(CO)_5$] – (0.1–0.2) in I, II and VII, as a consequence of increments of σ.

It must be noticed that treatment of I, II, VII and VIII as molecules having ideal tetrahedral Sn environments, although useful for the preceding discussion, is unsatisfactory in describing the actual electrical charge distribution around Sn, since it predicts negative ΔE's [24] while the experimental value is positive for II (Table II) (same sign is expected for I in view of strict structural similarities (Table I), and also for VII and VIII whether their structures correspond to those of I and II, as here repeatedly assumed). Equally unsatisfactory there appears to be the "ligand only splitting" [11] treatment of Sn electrical environment in II, using actual bond angles at Sn but "fixed" absolute p.q.s.'s [14] : examples 1 and 2, Table IV, show that this approach, *inter alia*, does not give couples of calculated ΔE and η values in simultaneous agreement with both experimental data (anyhow, the predicted sign of ΔE is now correct).

These failures undoubtedly depend on the severe distortion of our compounds; on one side, this forbids one to employ the approaches so successfully used for quasi regular or slightly distorted bond situations [9, 10, 18], but on the other it seems to permit an accurate delineation of the nature of bonds at Sn, whether all pertinent parameters are made to vary (dependently) in order to produce the best description of experimental data. In this context, being aware of the propositions by La Rossa and Brown [25], we have effected calculations for II by using the "ligand only splitting" concept [11], taking values of input polar coordinates of atoms around Sn from actual bond angles (Table I) (which implies that bonding electron density is presumed to be localized along crystallographic bond directions), and considering p.q.s.'s as variable parameters. The latter means that the p.q.s. of a particular ligand with respect to a given Mössbauer atom is function of the molecular structure (*i.e.*, of the extent of second order hybridization of central atom bonding orbitals) as well as of the nature of other bonded groups (this concept, although concerned with relative p.q.s. values, emerges clearly from papers by Bancroft and Rake [20] and Parish and coworkers [26]). In the calculations, a value in the range –0.40 to –1.20 mm s^{-1} was first selected for the p.q.s. [$Mn(CO)_5$], and then we determined values of [$Mn(CO)_4Sn$] and [Br] fitting ΔE = +2.30 mm s^{-1} and η = 0.23, in related point charge equations; the procedure was repeated with other [$Mn(CO)_5$] values, in increments of 0.10 mm s^{-1}. Some results are reported in Table IV, No.'s 3–7. Sets No. 4–5 agree with deductions reached in the preceding, and we will limit to those data further discussion; on the other hand, sets 3, 6, 7 (and those related to [$Mn(CO)_5$] $>$ 1 and $<$ 0.60) are quite unrealistic, since they would suggest a consistently greater p character in Sn–Mn(2) bonds with respect to Sn–Mn(1) (No.'s 6, 7) and p.q.s. [Br] $>$ [$Mn(CO)_5$] (No. 3).

Sets No. 4, 5, Table IV, work quite well in describing electric field gradients at Sn in I (No.'s 8, 9, Table IV), even using a fixed [hal] value, related to that quoted by Bancroft and Butler [14]. This is not unexpected in view of quasi coincidence of Sn neighbourhood in II and I (Table I). Calculations of p.q.s.'s [$Mn(CO)_5$] and [hal] have been effected in the usual way (as No.'s 3–7) also for III, IV and V, and some sets of data are reported in Table IV.

From the preceding data and discussion on rationalization of ΔE, it is concluded here that the more complicated situation, *i.e.*, that of II, gives the more internally consistent and physically meaningful answers, due to constraints imposed by three dependent p.q.s.'s as well as to the knowledge of sign of the quadrupole coupling constant and value of η; besides, many useful correlations can be deduced from evident electrical peculiarities of atoms linked to Sn, which help considerably in selecting acceptable sets of p.q.s.'s. This allows us to consider sets of p.q.s. in the range roughly corresponding to No.'s 4 and 5, Table IV, as physically significant, and not as mere numerical factors satisfying a series of equations. Instead, the simpler situation of systems with two p.q.s.'s and invariant (or almost invariant) η, such as III, IV and V, produces a much wider sets of (in principle) acceptable data. Anyhow, constraints according to earlier Mössbauer rationalizations and systematics may be imposed: for example, that [$Mn(CO)_5$] pertaining to V must lie around –0.99, which is related to absolute p.q.s.'s of a series of Sn–transition metal compounds [14]. What seems very important, in this context, is the fact that setting the [$Mn(CO)_4L$] predicted sequence as extracted in the preceding, *i.e.*, V $>$ III, IV $\gtrsim$ I, II(Mn(1)) $>$ I, II (Mn(2)), (for example: –0.95, –0.90, –0.85, –0.80, respectively), the consequent [hal] values obey the correlated sequence, *i.e.*, I, II $>$ V $>$ III, IV (respectively, –0.55, –0.49, –0.20) (Table IV).

As far as VII and VIII are concerned, it seems possible to advance a cluster structure of the type of I, II also from the rationalization of their ΔE values (Table IV, No.'s 16–19), but with differences (perhaps consistent) in structural parameters. The latter is inferred from the fact that the p.q.s. of the iodide, needed in conjunction with p.q.s.'s extracted from II in order to fit experimental ΔE, is indeed too large, so that the assumption falls short of correspondence of structures of II and VII; analogously it may be perhaps concluded for VIII, where the difference between p.q.s. of hypothetical groups [$Re(CO)_4Sn$] and [$Re(CO)_5$] seems to be unrealistically large.

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24 Relative p.q.s. (½e/Q/ units, mm s^{-1}) used in the calculations [14, 18]: $[M(CO)_5]$, −0.97(Mn) and −0.80(Re); [I], −0.17; [Cl] = [Br] = 0. The disposition of atoms around Sn (after diagonalization of the e.f.g. tensor) for I, II is as follows (code No.'s: footnote c, Table I): Mn(1, 1′): $\theta = 72° \ 32'$, $\phi = 121° \ 05'$, $238° \ 55'$; Mn(2): $\theta = 66° \ 39'$, $\phi = 0$; hal: $\theta = 176° \ 07'$, $\phi = 0$. Resulting equations of $V_{\alpha\alpha}$ are: $V_{xx} = +1.529([Mn(CO)_5] - [X]) + 2(-0.274)([Mn(CO)_4L] - [X])$; $V_{yy} = -1.000([Mn(CO)_5] - [X]) + 2(+1.000)([Mn(CO)_4L] - [X])$; $V_{zz} = -0.529([Mn(CO)_5] - [X]) + 2(-0.730)([Mn(CO)_4L] - [X])$.
Calculated $\Delta e(\eta)$: −2.29(0.26) (I, II); −1.96 (0.31)(VII); −2.65 (0.59) (VIII).

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