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A Mössbauer Study of the Tin–Cobalt Bond in Compounds Containing Tin–Cobalt Carbonyl Derivatives

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The nature of the tin–cobalt bond in the series of compounds of formula $[Co(CO)_3L]_xSnX_{4-x}$, *(L = CO, PPh_3 or $PBu^n{}_3$; X = Cl, Br, I, Et, or Ph; x = 1 or 2) was studied by means of the 119m Sn Mössbauer effect. The results in the present work extend the information obtained for the related tin–manganese complexes previously studied.*

Results and Discussion

The ^{119}Sn Mössbauer parameters for twenty-one compounds containing the Sn–Co bond have been obtained. The compounds are all of the type $[Co(CO)_3L]_xSnX_{4-x}$, (L = CO, PPh_3 or $PBu^n{}_3$; X = Cl, Br, I, Et or Ph; x = 1 or 2). The Mössbauer data of these, and of five similar compounds from other studies, are given in Table I; $[Co(CO)_3PPh_3]SnMe_3$, reported in the experimental section, decomposed before we could obtain the Mössbauer data.

When X = Cl, Br or I the chemical shifts (δ) of the Sn–Co compounds are in all cases smaller (relative to the source) than those of the corresponding $[Mn(CO)_5]SnX_3$ and $[Mn(CO)_5]_2SnX_2$ derivatives[1], but larger than those of the corresponding tin(IV) halide.[2] These observations are consistent with the $Co(CO)_4$ group being more electronegative than the $Mn(CO)_5$ group.[3–5] Although there have been no crystallographic studies of the comparable Sn–Co and Sn–Mn compounds described in the present work, it has been reported[6] that the Sn–Co bond (2.66Å) is shorter than the Sn–Mn bond (2.73Å) in $Ph_2Sn[Mn(CO)_5][Co(CO)_4]$. The relative magnitudes of these metal–metal bond lengths are contrary to those predicted by Bent's rule[7], which requires that, other things being equal, more *p*-character concentrates in the orbital towards the more electronegative substituent. However, in this molecule, the coordination about each metal atom is severely distorted from a regular symmetry by molecular overcrowding which must place a constraint upon the metal-metal bond distances. Crystallographic structure determinations of compounds of the type $[Mn(CO)_5]SnX_3$ and $[Co(CO)_4]SnX_3$, in which molecular overcrowding would be much reduced, are required in order to establish unperturbed Sn–Co and Sn–Mn bond distances. One possible explanation for the differences in chemical shifts of analogous Sn–Co and Sn–Mn compounds, assuming that the Sn–X bonds do not change in character, is that the Sn–Co bond length is less than that of the Sn–Mn bond, due to increased *s*-electron density from Sn in the former bond. However, this explanation is not entirely substantiated by the i.r. data.

The vibrational stretching frequencies of the metal–metal bond, and of the Sn–X bond of some Sn–Co and Sn–Mn compounds are given in Table II. The Sn–X frequencies in the Sn–Co compounds are substantially larger than those in the corresponding Sn–Mn compounds, suggesting more *s*-character in the Sn–X bonds of the Sn–Co derivatives. It is noteworthy that the frequency of the Sn–Cl deformation mode is lower in $[Co(CO)_4]SnCl_3$ than that in $[Mn(CO)_5]SnCl_3$, suggesting more *s*-character in the Sn–Cl bond of the former compound. The metal-metal bond stretching frequency is slightly greater in the Sn–Co compounds compared to that in the analogous Sn–Mn derivative, and insofar as these frequencies are a measure of metal–metal bond strength, suggest shorter bonds in the Sn–Co compounds. It is possible, however, that the higher Sn–Co stretching frequency is due in part, or wholly, to the lower mass effect of the $Co(CO)_4$ group compared to that of the $Mn(CO)_5$ group.

On balance it would therefore appear that the chemical shifts of the Sn–Co compounds are lower than those of the corresponding Sn–Mn derivative because of the greater electronegativity of the $Co(CO)_4$ group compared to that of the $Mn(CO)_5$ group. This difference in group electronegativities allows more *s*-character in the Sn–X bonds of the Sn–Co compounds, resulting in a further reduction of the chemical shift. In the

TABLE I. The ^{119}Sn Mössbauer parameters for Sn–Co compounds.

No.	Compound	δ* mm × s^{-1}±0.05	Δ mm × s^{-1}±0.05	Γ mm × s^{-1}±0.05	Ref.
1.	$[Co(CO)_4]SnCl_3$	1.35	1.16		a
2.	$[Co(CO_4]SnBr_3$	1.57	1.05		a
3.	$[Co(CO)_4]SnI_3$	1.69	0.64		a
4.	$[Co(CO)_4]SnPh_3$	1.43	1.07		a
		1.50	1.00		b
5.	$[Co(CO)_3PBu^n_3]SnCl_3$	1.59	1.67		a
6.	$[Co(CO)_3PBu^n_3]SnBr_3$	1.76	1.62		a
7.	$[Co(CO)_3PBu^n_3]SnI_3$	1.67	1.24		a
8.	$[Co(CO)_3PBu^n_3]SnPh_3$	1.45	n.r.	1.14	a
9.	$[Co(CO)_3PPh_3]SnPh_3$	1.41	n.r.	1.20	a
10.	$[Co(CO)_3PBu^n_3]SnEt_3$	1.48	0.83		a
11.	$[Co(CO)_4]_2SnCl_2$	1.74	1.42		a
12.	$[Co(CO)_4]_2SnBr_2$	1.73	1.42		a
13.	$[Co(CO)_4]_2SnI_2$	1.93	1.22		a
14.	$[Co(CO)_4]_2SnPh_2$	1.68	1.15		b
15.	$[Co(CO)_3PBu^n_3]_2SnCl_2$	1.86	1.96		a
16.	$[Co(CO)_3PPh_3]_2SnCl_2$	1.84	1.77		a
17.	$[Co(CO)_3PBu^n_3]_2SnBr_2$	1.92	1.93		a
18.	$[Co(CO)_3PPh_3]_2SnBr_2$	1.83	1.79		a
19.	$[Co(CO)_3PBu^n_3]_2SnI_2$	2.04	1.82		a
20.	$[Co(CO)_3PPh_3]_2SnI_2$	2.01	1.63		a
21.	$[Co(CO)_3PBu^n_3]_2SnPh_2$	1.58	n.r.	1.34	a
22.	$[Co(CO)_3PBu^n_3]_2SnEt_2$	1.61	0.97		a
23.	$[Co(CO)_4]SnClPh_2$	1.56	2.22		b
24.	$[Co(CO)_4]_3SnPh$		1.28		c
25.	$[Co(CO)_4]_4Sn$	1.96	n.r.[e]		d

* Relative to $BaSnO_3$ at 80° K. [a] This work. [b] From A. N. Karasev, N. E. Kolobova, L. S. Polak, V. S. Shpinel, and K. A. Anisimov, *Teor. i. eksp. Khim.*, 1966, *2*, 126. [c] From D. E. Fenton and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1968, *90*, 6226. [d] From D. E. Fenton and J. J. Zuckerman, *Inorg. Chem.*, 1969, *8*, 1771. [e] n.r. = not resolvable.

absence of steric effects longer bonds are expected for the Sn–Co compounds, considering the hybridization of the tin bonding orbitals.

The factors affecting quadrupole splittings have already been discussed in detail.[1] Where the data for comparable compounds are available, the splittings for the Co compounds are lower than those for the related Mn derivatives. This could be due either to the fact that the electronegativities of X and $Co(CO)_3L$ are more similar than those of X and $Mn(CO)_4L$ and/or that there is more distortion of the Sn tetrahedron in the Mn compounds. The limited crystallographic data available would be in agreement with this latter suggestion.

For compounds 1–3; 5–6; 15, 17, 19; and 16, 18, 20 the chemical shifts increase in the order $Cl<Br<I$ as would be expected on bond polarity arguments. In those compounds where $x = 2$, the chemical shifts are always greater than where $x = 1$, for the same L and X, in accord with the electronegativity of $Co(CO)_3L<X$. These trends were also found in compounds with Sn–Fe[8] and Sn–Mn[1] bonds. Compounds 11–13 show an overall increase in chemical shift, though the values for 11 and 12 are the same within experimental error. In the series $[Co(CO)_3PBu^n_3]SnX_3$, compounds 5–7, the iodide has an anomalously low shift.

In the compounds where $L = PBu^n_3$ or PPh_3, the phosphine ligand is presumed to be *trans* to the tin atom. $[Co(CO)_3L]_2SnCl_2$ ($L = PBu^n_3$, PPh_3 and $P(OPh)_3$)[9], $[Co(CO)_3PBu^n_3]SnCl_3$[10] and [CO $(CO)_3PPh_3]SnBr_3$[11] have been assigned *trans* structures from i.r. studies, but there is no supporting crystallographic evidence for this assumption in the compounds studied. X-ray crystallographic structure determinations of the analogous compounds, $[Mn(CO)_4PPh_3]SnPh_3$[12] and $[Co(CO)_3PPh_3]GePh_3$[13] have, however, established that the phosphine ligand is *trans* to the group IV atom.

Replacement of the *trans* carbonyl group by a phosphine ligand would make the $Co(CO)_3L$ group a better π-donor towards the tin atom than the $Co(CO)_4$ group. Any increase in the Co→Sn d_π–d_π bonding would result in the shielding of the tin *s*-electrons from the nucleus and to a decrease in the chemical shift. In fact, the replacement of the *trans* carbonyl group by phosphine, assuming a constant Sn–Co bond length,

TABLE II. Far i.r. spectra of Sn–Mn and Sn–Co compounds (cm^{-1}).

x	Sn–X	γ(Sn–X)	δ(Sn–X)	γ(M–M′)	Ref.
$[Mn(CO)_5]_xSnX_{4-x}$					
1	Cl	345	113	201	a
1	Br	250		182	a
1	I	196		154	a
1	Me	517		182	a
		500			
1	Ph			174	a
				199	
2	Cl			170	a
$[Co(CO)_4]_xSnX_{4-x}$					
1	Cl	365	107	204	b
		360			
1	Br	260		188	a
1	I	205		159	a
1	Me	584		176	a
1	Ph			171	c
2	Cl	332		213	a
		322		174	
2	Br	234		210	a
		222		168	
2	I	178		190	a

[a] From T.G. Spiro, *Progr. Inorg. Chem.*, 1970, *11*, 1. [b] From K.L. Watters, J.N. Brittain, and W.M. Risen, *Inorg. Chem.*, 1969, *8*, 1347. [c] This work.

results in an increase of the chemical shift. For the same X, the chemical shifts are greater when L = PBu^n_3 than when L = PPh_3, which corresponds to the order of σ-donor property of the phosphines, and confers an order of softness $Co(CO)_3PBu^n_3 > Co(CO)_3PPh_3 > Co(CO)_4$. From these observations, it is obvious that d_π–d_π bonding between cobalt and tin is of little significance, and that any variation in the chemical shifts of compounds, containing the same X, results from different σ-bond interactions between the two metals, and to some degree between tin and X. These variations can be partly explained by a varying contribution of cobalt electron density to the Sn–Co bond, this being greatest when L = PBu^n_3, thus conserving more *s*-electron density on the tin atom.

Compounds of the type $[Co(CO)_4]_xSnX_{4-x}$, where X = Cl, Br or Me, and x = 1, 2, 3 or 4, have been studied by ^{59}Co nqr in an attempt to ascertain the extent of Co→Sn d_π–d_π bonding.[14] The investigation was inconclusive because the molecular field gradient q_{zz} is oppositely affected by the σ-and π-components of the metal–metal bond.

The chemical shifts of the organotin derivatives, 4, 8–10, 14, 21 and 22 are lower than those of the corresponding halogenotin compounds. This is contrary to the expected trend based on bond polarity arguments since the electronegativities of the ethyl and phenyl groups are smaller than those of the halogens.[2] This apparent anomaly in the magnitude of the chemical shifts can be explained by the greater covalency (and use of tin *s*-orbitals) in the Sn–C bond as compared to the Sn–halogen bond. It is therefore expected that the Sn–Co bond should be longer in the organotin derivatives than in the corresponding halogenotin compounds.[1]

Experimental Section

The details of the Mössbauer apparatus have been reported previously.[15] The spectra were obtained with the source and absorber at 80° K. The percentage resonance dip for these compounds was 5% 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 was checked by computer curve fitting. The errors quoted in Table I are the total experimental errors, not simply the statis-

TABLE III. Analytical data, melting points, colours and yields of new tin–cobalt complexes.

Complex	Colour	M.p. °C	% Calculated		% Found		% Yield (based on cobalt dimer used)
			C	H	C	H	
$[Co(CO)_3PBu^n_3]SnPh_3$	white	133.5–134.5	57.0	6.1	56.91	6.01	71
$[Co(CO)_3PBu^n_3]SnEt_3$	colourless	24	45.7	7.7	46.60	8.00	10
$[Co(CO)_3PBu^n_3]SnCl_3$	lemon–yellow	134–5	31.5	4.8	31.26	4.48	30
$[Co(CO)_3PBu^n_3]SnBr_3$	yellow	115–8 dec.	25.6	3.9	26.63	4.09	34
$[Co(CO)_3PBu^n_3]SnI_3$	orange	116–8 dec.	21.3	3.2	22.14	3.02	10
$[Co(CO)_3PPh_3]SnPh_3$	white	201–6	62.0	4.0	62.87	3.95	38
$[Co(CO)_3PPh_3]SnMe_3$	pale yellow	>130 dec.	50.6	4.3	52.16	3.90	43
$[Co(CO)_3PBu^n_3]_2SnI_2$	orange	112–4	33.9	5.1	34.66	5.11	26
$[Co(CO)_3PPh_3]_2SnBr_2$	orange–yellow	198–200	48.9	2.9	46.25	2.76	37
$[Co(CO)_3PPh_3]_2SnI_2$	orange	>165 dec.	42.6	2.6	42.53	2.54	34

tical accuracy of the computer fit. The infrared spectra were recorded on a Perkin–Elmer 621 grating spectrometer. Starting materials were prepared by standard methods and the known Sn–Co compounds prepared by literature methods,[9,11,16] and were identified by elemental analyses, melting points and infrared spectra. Tetrahydrofuran was dried over sodium in the presence of benzophenone and distilled under nitrogen before use. The analytical data for the new compounds are reported in Table III; other properties are given in the same Table. The infrared spectra have already been reported and discussed.[17]

$[Co(CO)_3PBu^n{}_3]SnPh_3$

A solution of $[Co(CO)_3PBu^n{}_3]_2$ (1.73 g, 0.002 mole) in tetrahydrofuran (30 ml) was reduced using 1% sodium amalgam (2.5 ml) with stirring under nitrogen. After removal of the amalgam, Ph_3SnCl (1.9 g, 0.005 mole) was added and the mixture stirred for 1 h. The solvent was then removed *in vacuo* and the residue extracted thoroughly with petroleum ether. From this extract white needles of product were obtained (2.5 g).

$[Co(CO)_3PBu^n{}_3]SnEt_3$

A solution of $[Co(CO)_3PBu^n{}_3]_2$ (1.0 g, 0.0015 mole) in tetrahydrofuran (20 ml) was reduced using 1% sodium amalgam (2.0 ml) with stirring under nitrogen. The mercury was removed and the solution filtered through paper under nitrogen. Freshly distilled Et_3SnI (0.75 ml *ca.* 1.0 g, 0.004 mole) was added and stirring continued for 1 h. The solvent was then removed *in vacuo* and the residue extracted with methanol. Addition of a little water and partial removal of the methanol gave yellow crystals which were collected and dried *in vacuo*. Recrystallisation from methanol/water gave nearly colourless needles (0.15 g).

$[Co(CO)_3PBu^n{}_3]SnCl_3$

A solution of $[Co(CO)_3PBu^n{}_3]_2$ (1.0 g, 0.0015 mole) in benzene (20 ml) was added dropwise with stirring under nitrogen to a solution of $SnCl_4$ (1.0 g, 0.0038 mole) in benzene (10 ml). Carbon monoxide was evolved and a pale blue gelatinous mixture formed. When the evolution of gas had ceased, the yellow solution was filtered and the solvent removed *in vacuo*. The residue was extracted with benzene and, on adding n-pentane, bright lemon-yellow needles of the product were obtained (0.5 g).

$[Co(CO)_3PBu^n{}_3]SnBr_3$

A solution of $[Co(CO)_3PBu^n{}_3]_2$ (1.0 g, 0.0015 mole) in benzene (20 ml) was added dropwise under nitrogen to a solution of $SnBr_4$ (1.5 g, 0.0034 mole) in benzene (20 ml) over the course of 30 min. The mixture was stirred magnetically under nitrogen until carbon monoxide evolution had ceased. After filtration the solvent was removed from the yellow solution *in vacuo*. The recrystallisation from benzene/n-pentane gave yellow crystals of the product (0.7 g).

$[Co(CO)_3PBu^n{}_3]SnI_3$

A solution of $[Co(CO)_3PBu^n{}_3]_2$ (1.0 g, 0.0015 mole) in benzene (20 ml) was added dropwise under nitrogen to a solution of SnI_4 (2.2 g, 0.0035 mole) in benzene (20 ml) over a period of 30 min. The mixture was stirred magnetically until carbon monoxide evolution had ceased, and the solvent was then removed *in vacuo*. The residue was recrystallised twice from benzene/n-pentane to give orange crystals (0.23 g).

$[Co(CO)_3PPh_3]SnPh_3$

A suspension of $[Co(CO)_3PPh_3]_2$ (1.0 g, 0.0012 mole) in tetrahydrofuran (30 ml) was reduced, using 1% sodium amalgam (2 ml), to the monoanion. The reduction was performed with magnetic stirring under nitrogen for 16 h. After removal of the mercury, Ph_3 $SnCl$ (0.95 g, 0.0027 mole) was added and the mixture stirred for 5 h. The solvent was then removed *in vacuo* and the residue extracted with boiling petroleum ether. Cooling and partial removal of solvent gave white needles of the product (0.7 g). Recrystallisation was effected from dichloromethane/n-pentane with cooling to –80°.

$[Co(CO)_3PPh_3]SnMe_3$

A suspension of $[Co(CO)_3PPh_3]_2$ (1.0 g, 0.0012 mole) in tetrahydrofuran (30 ml) was reduced using 1% sodium amalgam (2 ml) as before. After the mercury had been removed, the monoanion solution was filtered through paper under nitrogen before addition of Me_3SnCl (0.5 g, 0.0025 mole). The mixture was stirred for 2 h and then the solvent was removed *in vacuo*. Extraction of the residue with n-hexane and partial solvent removal from the hexane extract gave a pale yellow solid. The product was recrystallised from n-pentane (0.6 g).

$[Co(CO)_3PBu^n{}_3]_2SnI_2$

A mixture of $[Co(CO)_3PBu^n{}_3]_2$ (1.0 g, 0.0015 mole) and tin(II) iodide (0.64 g, 0.0016 mole) in acetone (80 ml) was stirred magnetically under nitrogen for 64 h. The acetone solvent was then removed *in vacuo* and the residue treated with petroleum ether. The orange solid which resulted was recrystallised from absolute ethanol to give orange crystals (0.45 g).

$[Co(CO)_3PPh_3]_2SnBr_2$

A mixture of $[Co(CO)_3PPh_3]_2$ (1.0 g, 0.0012 mole) and tin(II) bromide (0.42 g, 0.0013 mole) was refluxed in tetrahydrofuran (50 ml) for 3 h under nitrogen. After removal of the solvent *in vacuo* the residue was extracted with dichloromethane. Addition of n-pentane caused the orange-yellow product to separate. The product was recrystallised from dichloromethane/n-pentane (0.5 g).

$[Co(CO)_3PPh_3]_2SnI_2$

A mixture of $[Co(CO)_3PPh_3]_2$ (1.0 g, 0.0012 mole) and tin(II) iodide (0.55 g, 0.0014 mole) was gently refluxed in tetrahydrofuran (50 ml) for 3 h under nitrogen. After removal of the solvent the residue was extracted with dichloromethane. Addition of petroleum ether caused the product to separate as orange crystals (0.5 g). Recrystallisation was effected from dichloromethane/n-pentane.

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