Studies in Mössbauer Spectroscopy. Part 10.[1] Tin-119 Spectra of Compounds containing Tin–Cobalt Bonds, and Comments on the Choice of Partial-quadrupole-splitting Values

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Tin-119 Mössbauer data are reported for compounds of the type $SnX_{4-n}[Co(CO)_3(PR_3)]_n$ (R = Ph or Bu^n; X = H, F, Cl, Br, or I; n = 1—3). New partial-quadrupole-splitting (p.q.s.) values of −0.64(4) and −0.82(3) mm s^{-1} have been obtained for $[Co(CO)_4]^-$ and $[Co(CO)_3(PR_3)]^-$, and a value has been derived for the first time for the hydride ligand of −1.06 mm s^{-1}. Apparent differences between various p.q.s. scales are discussed and shown to be illusory.

MANY studies have been made by ^{119}Sn Mössbauer spectroscopy of compounds containing Sn–M bonds, where M is a transition-metal group. Analysis of these data shows that the donor ability of metal carbonylate groups to tin follows the order of basicities and nucleophilicities.[2] It is generally expected that substitution of carbonyl groups by other neutral ligands, such as tertiary phosphines, should increase the basicity and donor power of the carbonylate, and this has been confirmed by Mössbauer measurements on $SnBu_3[Co(CO)(etpb)_3]$ [3] {etpb = $P[(OCH_2)_3CEt]$}, $SnCl_3[Mn(CO)_4(PPh_3)]$,[4] and some $[Co(CO)_3(PR_3)]^-$ derivatives.[5]

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[1] Part 9, C. A. McAuliffe, R. V. Parish, and P. D. Randall, *J.C.S. Dalton*, 1977, 1426.

[2] R. V. Parish, *Progr. Inorg. Chem.*, 1972, **15**, 101.

[3] R. J. Dickinson, R. V. Parish, P. J. Rowbotham, A. R. Manning, and P. Hackett, *J.C.S. Dalton*, 1975, 424.

[4] S. R. A. Bird, J. D. Donaldson, A. F. Le C. Holding, B. Ratcliffe, and S. Cenini, *Inorg. Chim. Acta*, 1972, **6**, 379.

[5] S. R. A. Bird, J. D. Donaldson, A. F. Le C. Holding, S. Cenini, and B. Ratcliffe, *Inorg. Chim. Acta*, 1974, **8**, 149.

We now report further data for derivatives of monosubstituted cobalt carbonylates, $[Co(CO)_3L]^-$, which complement and extend the previous work.

EXPERIMENTAL

Samples of the compounds were kindly donated by Dr. A. R. Manning;[6] their purity was checked by i.r. spectroscopy. Mössbauer spectra were recorded on Apiezon mulls at 77 K with a $CaSnO_3$ source at room temperature. The velocity scale was calibrated using a natural iron foil with a $^{57}Co/Pd$ source. Spectra were fitted with Lorentzian absorption peaks.

RESULTS AND DISCUSSION

The new data are given in Table 1; agreement with earlier determinations is good. Except as noted below, the usual trends are found: (*a*) increasing isomer shift (i.s.) with decreasing electronegativity of the halogen and increasing number of Co–Sn bonds; (*b*) the quadrupole splitting (q.s.) of compounds of the type $CoSnX_3$ and Co_3SnX are similar and decrease with decreasing electronegativity of the halogen, while the q.s. of compounds of the type Co_2SnX_2 is larger.

TABLE 1

Tin-119 Mössbauer data (mm s^{-1}) at 77 K

Compound	$\delta(BaSnO_3)$ [a]	Δ [a]	Ref.
(1) $SnCl_3[Co(CO)_3(PBu_3)]$	1.68	1.64	*b*
	1.59	1.67	4
(2) $SnBr_3[Co(CO)_3(PBu_3)]$	1.77	1.51	*b*
	1.76	1.62	4
(3) $SnBr_2[Co(CO)_3(PBu_3)]_2$	1.99	1.96	*b*
	1.92	1.93	4
(4) $SnI_2[Co(CO)_3(PBu_3)]_2$	2.05	1.87	*b*
	2.04	1.82	4
(5) $SnH[Co(CO)_3(PBu_3)]_3$	1.71	0.45	*b*
(6) $SnF[Co(CO)_3(PBu_3)]_3$	1.80	1.14	*b*
(7) $SnCl[Co(CO)_3(PBu_3)]_3$	2.05	1.55	*b*
(8) $SnBr[Co(CO)_3(PBu_3)]_3$	2.13	1.49	*b*
(9) $SnI[Co(CO)_3(PBu_3)]_3$	2.11	1.60	*b*
(10) $SnCl_3[Co(CO)_3(PPh_3)]$	1.68	1.66	*b*
(11) $SnCl_3[Co(CO)_3\{PPh_2(C_{10}H_{19})\}]$ [c]	1.68	1.52	*b*
(12) $SnCl_2[Co(CO)_3(AsPh_3)][Co(CO)_3(PPh_3)]$	1.89	1.64	*b*
(13) $SnCl[Co(CO)_3(PBu_3)][Fe(CO)_2(cp)]_2$	2.00	1.87	*b*
(14) $SnCl_2[Co(CO)_3(PPh_3)][Fe(CO)_2(cp)]$	1.80	1.78	*b*
(15) $SnBr_3[Fe(CO)_3(NO)]$	1.63	1.04	*b*

[a] ± 0.02 mm s^{-1}. [b] This work. [c] $C_{10}H_{19}$ = Menthyl.

The q.s. of compound (6), $SnF[Co(CO)_3(PBu_3)]_3$, is lower than that of any of the other monohalides, contrary to expectation, and a similar anomaly was reported[7] for $SnF[Co(CO)_4]_3$ (Table 2). In organotin systems, $SnXR_3$, the fluoride usually gives the largest q.s., owing to the high electronegativity of fluorine.[8] In many cases a further increase in q.s. arises from polymerisation in the solid, giving trigonal-bipyramidal co-ordination of the tin atom with bridging fluorine atoms in the axial positions.[2] The anomalously low q.s. of the Co_3SnF compounds is unlikely to be due to distortion of a monomeric structure, since the q.s. would decrease only if the three metal groups moved closer together and away from the fluoride, which seems improbable on both steric and electronic grounds. It is possible, as suggested by Bancroft,[7] that these compounds are associated by *cis* bridging involving one axial and one equatorial position in a trigonal-bipyramidal $Co_3Sn(\mu\text{-}F)_2$ arrangement.

TABLE 2

Tin-119 Mössbauer data (mm s^{-1}) for Co–Sn compounds at 77 K

Compound	$\delta(BaSnO_3)$	Δ	Ref.
$SnI_3[Co(CO)_3(PBu_3)]$	1.67	1.24	4
$SnPh_3[Co(CO)_3(PBu_3)]$	1.45	n.r.[a]	4
$SnEt_3[Co(CO)_3(PBu_3)]$	1.48	n.r.[a]	4
$SnCl_3[Co(CO)_4]$	1.35	1.16	4
	1.42	1.15	*b*
	1.42	1.20	7
$SnBr_3[Co(CO)_4]$	1.57	1.05	4
	1.49	1.28	*b*
$SnI_3[Co(CO)_4]$	1.69	0.64	4
	1.73	0.71	*b*
$SnPh_3[Co(CO)_4]$	1.43	1.07	4
	1.41	1.20	7
	1.50	1.00	11
$SnMe_3[Co(CO)_4]$	1.39	1.73	7
$SnF[Co(CO)_4]_3$	1.75	0.97	7
$SnCl[Co(CO)_4]_3$	1.83	1.18	*b*
	2.05	1.42	7
$SnBr[Co(CO)_4]_3$	1.97	1.06	*b*
$SnI[Co(CO)_4]_3$	2.03	0.95	*b*
$SnMe[Co(CO)_4]_3$	1.79	1.29	7

[a] n.r. = Not resolved. [b] S. Ichiba, M. Kateda, and H. Negita, *Bull. Chem. Soc. Japan*, 1972, **45**, 1679.

The fitted spectrum for the hydride, $SnH[Co(CO)_3(PBu_3)]_3$ (5), is considerably improved by the inclusion of a second peak. A single-peak fit gave a linewidth of 1.23 mm s^{-1} and a normalised χ^2 of 1.26, which were reduced to 0.82 mm s^{-1} and 0.95 for a doublet. Organotin hydrides do not normally exhibit a resolvable q.s. owing to the similarity in bonding characteristics of organic and hydrido-ligands, but a splitting of 0.67 mm s^{-1} has very recently been reported for $SnH[Mo(CO)_3(cp)][CH(SiMe_3)_2]_2$ (cp = η-cyclopentadienyl).[9]

Isomer Shifts.—Comparison of the data in Tables 1 and 2 reveals that the phosphine-substituted compounds all give substantially greater i.s. than those of the corresponding unsubstituted compounds. This indicates that $[Co(CO)_3(PR_3)]^-$ is a better donor to the tin 5*s* orbital than is $[Co(CO)_4]^-$.[5,10] Such an effect is expected from the increased electron density on the cobalt atom which would result from the replacement of a strongly π-accepting carbonyl group by a tertiary phosphine. The *s*-electron density on the tin atom in series of comparable compounds has been shown to increase as the ligand is changed in the order $Cl^- < Ph^- < Me^- < [Co(CO)_4]^- < [Mn(CO)_5]^- \lesssim [Cr(CO)_3(cp)]^- < [Fe(CO)_2(cp)]^-$. The substituted cobalt carbonylates, $[Co(CO)_3(PR_3)]^-$, are comparable to $[Mn(CO)_5]^-$ or $[Cr(CO)_3(cp)]^-$, but are still less effective donors than $[Fe(CO)_2(cp)]^-$.

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[6] P. Hackett and A. R. Manning, *J.C.S. Dalton*, 1974, 2257.

[7] G. M. Bancroft and K. D. Butler, *J.C.S. Dalton*, 1973, 1694.

[8] R. H. Herber, H. A. Stöckler, and W. T. Reichle, *J. Chem. Phys.*, 1965, **42**, 2447.

[9] J. D. Cotton, P. J. Davidson, M. F. Lappert, J. D. Donaldson, and J. Silver, *J.C.S. Dalton*, 1976, 2286.

[10] G. M. Bancroft and A. T. Rake, *Inorg. Chim. Acta*, 1975, **13**, 175.

When a similar replacement of CO by PPh_3 is made in the six-co-ordinate manganese compounds, *e.g.* $SnCl_3[Mn(CO)_5]$, there is a much smaller increase in isomer shift (from 1.62 to 1.70 mm s^{-1}),[3] consistent with the smaller change in total electron density expected when one ligand of five is changed rather than one of four as in the cobalt case. The replacement of a carbonyl group *trans* to the tin atom could allow greater π donation from the transition metal to *p* or *d* orbitals on the tin atom, which would lower the isomer shift by shielding the *s* electrons. To explain the difference in isomer-shift sensitivity by this mechanism alone would require a much greater increase in π donation in the manganese case than for cobalt, which seems unlikely on geometric and overlap grounds.

On the basis of the single result available, $[Fe(CO)_3(NO)]^-$ [*cf.* compound (15), Table 1] is a significantly weaker donor to the tin 5*s* orbital than $[Fe(CO)_2(cp)]^-$, $[Mn(CO)_5]^-$, or $[Co(CO)_3(PR_3)]^-$, but better than the isoelectronic $[Co(CO)_4]^-$.

Quadrupole Splitting and Partial-quadrupole-splitting (p.q.s.) Values.—The compounds $SnX_3[Co(CO)_3(PR_3)]$ and $SnX[Co(CO)_3(PR_3)]_3$ (X = Cl, Br, or I) all give substantially greater q.s. than their unsubstituted counterparts. The organic derivatives $SnR_3[Co(CO)_3(PR_3)]$ and $SnR[Co(CO)_3(PR_3)]_3$ give no resolvable splitting but the unsubstituted compounds show q.s. of 1.0—1.2 mm s^{-1}. Since the electric-field gradients (e.f.g.s) are expected [2] to be of opposite sign for $MSnX_3$ and $MSnR_3$ and for M_3SnX and M_3SnR, both trends are consistent with greater donation to the tin 5*p* orbital by the phosphine-containing groups.[5,10]

The data are best analysed by the point-charge approach to obtain p.q.s. parameters for the metal groups. Using the values derived previously for the halogens,[3] new values have been calculated for $[Co(CO)_4]^-$, $[Co(CO)_3(PR_3)]^-$, $[Mn(CO)_4(PPh_3)]^-$, and $[Fe(CO)_3(NO)]^-$. These are given in Table 3 together with values previously obtained for other 3*d*-metal groups.[3] Increasingly negative values represent increasing donation to the tin 5*p* orbital. The replacement of one carbonyl ligand by a tertiary phosphine gives a large and significant increase in the donor power of the cobalt group for the reasons outlined above. This trend is continued when further carbonyl groups are replaced, since the compound $SnBu_3[Co(CO)(etpb)_3]$ shows no resolvable splitting.[3] The difference in p.q.s. values for $[Mn(CO)_5]^-$ and $[Mn(CO)_4(PPh_3)]^-$ is much less than for the cobalt compounds, as was noted above for the isomer-shift changes. The nitrosyl, $[Fe(CO)_3(NO)]^-$, is marginally a poorer *p* donor than the isoelectronic $[Co(CO)_4]^-$, which could be attributed to the high π acidity of the $[NO]^+$ group, although the p.q.s. values are not significantly different. The different orderings of p.q.s. values and isomer-shift trends (including halogen and organic ligands) is presumably due to the differing overlaps and energy differences between the donor orbitals and the tin 5*p* and 5*s* orbitals.

TABLE 3

P.q.s. values (mm s^{-1})

X	$(p.q.s.)_X$ [a]
Cl^-	0.0 [b]
Br^-	−0.07(3)
I^-	−0.18(5)
$[Fe(CO)_3(NO)]^-$	−0.59
$[Co(CO)_4]^-$	−0.63(4)
$[Cr(CO)_3(cp)]^-$	−0.72(6)
$[Co(CO)_3(PR_3)]^-$	−0.82(3)
$[Mn(CO)_5]^-$	−0.83(7)
$[Mn(CO)_4(PPh_3)]^-$	−0.89(19)
$[Fe(CO)_2(cp)]^-$	−0.95(14)
Me^-	−1.34(16)

[a] Figures in parentheses are the standard deviations (95% confidence, $\pm tsn^{\frac{1}{2}}$). [b] Arbitrary standard.

Using the p.q.s. values for $[Co(CO)_3(PBu_3)]^-$ and the q.s. for $SnH[Co(CO)_3(PBu_3)]_3$, a p.q.s. value for the hydride ligand becomes available for the first time. Two values may be obtained, depending on the sign assumed for the e.f.g. If the e.f.g. is taken to be positive, a value of −0.62 mm s^{-1} is obtained. Such a value is not sufficiently negative to explain the lack of resolvable q.s. in organotin hydrides. For example, the calculated q.s. for $SnHMe_3$ would be 1.44 mm s^{-1}, which would be readily detectable. The p.q.s. value could be in error if the q.s. of $SnH[Co(CO)_3(PBu_3)]_3$ were increased by distortion of the molecule from the tetrahedral geometry assumed in the point-charge treatment. It is very likely that the bulky $[Co(CO)_3(PBu_3)]$ groups would move apart and towards the small hydride ligand, giving Co–Sn–Co bond angles substantially greater than 109°, which distortion would be expected to augment the q.s. However, by analogy with transition-metal systems, and assuming that the apparent correlations [2,11] of p.q.s. values with nucleophilicities and basicities are valid, it is unlikely that the hydride would be a poorer donor to tin than the metal groups. The alternative assumption, that the hydride is the better donor and the e.f.g. therefore negative, leads to a p.q.s. value of −1.06 mm s^{-1}. This value seems much more in keeping with the large negative values for the organic groups, and leads to an expected q.s. for organotin hydrides of $\leqslant 0.5$ mm s^{-1}, and is therefore the preferred value.

P.Q.S. Scales.—The above p.q.s. values were obtained by averaging values derived from the data for all the compounds containing the appropriate group for which a q.s. has been reported.[2] They are thus representative values, applicable to the whole range of tin compounds, and include the effects of distortions, *etc.* Since the prime use of the values is to obtain calculated q.s. values to aid structural diagnoses, this procedure seems reasonable. Other workers have expressed disapproval of this technique,[12] preferring to derive values from data only for those compounds which are known or are likely to have closely regular structures and in which the (Sn) *s–p* character of the four tin–ligand bonds is likely

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[11] A. N. Karasev, N. E. Kolobova, L. S. Polak, V. S. Shpinel, and K. N. Anisimov, *Teor. i eksp. Khim.*, 1966, **2**, 126.

[12] G. M. Bancroft and T. K. Sham, *J.C.S. Dalton*, 1976, 467.

to be similar. Values derived from other compounds can then, it is thought, be interpreted in terms of distortions and rehybridisation at the tin atom.[10] The claim has been made that these 'best' values give significantly better correlations between calculated and observed q.s. values and between p.q.s. values for octahedral and tetrahedral co-ordination. Such concern is unnecessary and appears to be based on an unrealistic refinement of a simple model, oversimplified assumptions, and a lack of appreciation of the statistical limitations of the data, as will now be demonstrated.

First, to derive p.q.s. values from data for compounds with regular structures implies that the q.s. values used are small, and may therefore be subject to considerable error, and that only a very few such values are used in the derivation. Normally, uncertainties of ± 0.02 mm s^{-1} are quoted for individual q.s. values, although these are usually the errors of the fitting procedure for one spectrum rather than replication errors, and values obtained in different laboratories often differ by considerably more than this (*cf.* Tables 1 and 2). For compounds with poorly resolved q.s. uncertainties as great as ± 0.1 mm s^{-1} are often quoted.[10] It thus seems likely that the uncertainties associated with p.q.s. values derived by the 'better' procedure may be $\pm(0.05—0.1)$ mm s^{-1}, *i.e.* comparable to the standard deviations obtained by averaging data for all the compounds.[3] It is therefore pointless to attempt the interpretation of differences in p.q.s. values less than *ca.* 0.15 mm s^{-1} unless better defined values can be obtained, as for the cobalt-containing groups treated above.

Secondly, it is now well established that p.q.s. values are not precisely constant and independent of the other ligands present,[3,13] and attempts have been made to take the p.q.s. values derived for one metallo-group from data for different compounds and interpret them in terms of changes in the hybridisation at tin.[10] Quite apart from the statistical weakness of this procedure, outlined above, it makes the unjustified assumption that the only changing value is the p.q.s. value of the group concerned while those of the other ligands retain their previously calculated values. It is not unreasonable to expect metal carbonyl groups to be highly polarisable and to adopt varying charge density according to the nature of the other substituents on the tin atom and, indeed, there is a large quantity of i.r. data to suggest that this does occur. There is also, however, considerable evidence from halogen n.q.r. and ^{129}I Mössbauer data[13-15] that similar changes occur in the charge distribution on halide ligands, and there is no reason to believe that such changes will not also apply to organic ligands. If it is accepted that p.q.s. values, and ligand donor strengths, vary from compound to compound, it must be accepted that values for *all* the ligands will change. There is then no possible way of calculating any p.q.s. values at all, unless a method could be devised to standardise the values for one particular ligand in different environments; *e.g.* it might be assumed that the p.q.s. value of a chloride ligand is related to the e.f.g. at the chlorine nucleus (*i.e.* to the n.q.r. frequency).

Thirdly, the suggestion[12] that the 'best' values give better correlations than the scale derived above and previously[3] is not statistically justified. The relevant figures are given in Table 4, from which it is obvious that the differences between the values compared are not statistically significant; in most cases the values differ from each other and from the theoretical value by no more (and often by considerably less) than three standard deviations. While it may seem preferable to present a figure which appears to be close to the theoretical value, proper account must be taken of the statistical meaning of the uncertainties.

TABLE 4

Comparison of statistical parameters (ref. 12)

Metallo-tin compounds:	
Octahedral *versus* tetrahedral p.q.s. values (gradient, theory *ca.* 0.67)	
'Best' values	0.73 ± 0.04
Parish values	0.77 ± 0.04
Calculated *versus* observed q.s. (gradient, theory 1.00)	
'Best' values	0.97 ± 0.14
Parish values	0.92 ± 0.10
Calculated *versus* observed q.s. (intercept, theory 0.00)	
'Best' values	0.01 ± 0.08
Parish values	-0.15 ± 0.20
Organotin compounds:	
Calculated *versus* observed q.s. (gradient, theory 1.00)	
'Best' values	0.96 ± 0.02
Parish values	0.90 ± 0.02

In conclusion, it is now felt, as was stated earlier,[3] that the point-charge model is too simple to withstand further refinement and it should be accepted that the information derived from its application will embody certain inaccuracies inherent in the data used. While the order of, say, p.q.s. values obtained for metal-carbonyl groups accords nicely with chemical expectation, it must be reiterated[3] that the actual differences are in many cases considerably less than the statistical errors. In order to improve the use of the model and the interpretation of the data, Mössbauer parameters of considerably greater precision will be required and a method devised to take account of the variations of the p.q.s. values.

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[13] A. P. Marks, R. S. Drago, R. H. Herber, and M. J. Potasek, *Inorg. Chem.*, 1976, **15**, 259.

[14] B. J. Dale, R. J. Dickinson, and R. V. Parish, *J.C.S. Chem. Comm.*, 1974, 35.

[15] B. J. Dale, R. J. Dickinson, and R. V. Parish, *Chem. Phys. Letters*, 1974, **24**, 286.