Studies in Mössbauer Spectroscopy. Part VII.[1] Tin-119 and Iron-57 Spectra of Compounds involving Tin bonded to Chromium, Molybdenum, Tungsten, Manganese, Iron, or Cobalt

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New ^{119}Sn and ^{57}Fe Mössbauer data for the compounds $[SnX_3\{M(CO)_3(cp)\}]$, $[SnX_2\{M(CO)_3(cp)\}_2]$, and $[SnX_2\{M(CO)_3(cp)\}\{Fe(CO)_2(cp)\}]$ (M = Cr, Mo, or W; X = Cl, Br, or I) are presented. The quadrupole splitting (q.s.) data for these and other tin–transition metal compounds are analysed by the point-charge method to obtain partial quadrupole splitting values for the halide and metal groups in tetrahedral co-ordination to tin, and the causes of the, sometimes large, discrepancies between calculated and observed q.s.s for the dihalides are examined. It is concluded that further refinement of the model is not justified.

TIN-119 Mössbauer data have been reported for many series of compounds containing tin–transition metal bonds and analysed in terms of the point-charge (donated-charge) model [2,3] to obtain partial quadrupole splitting (p.q.s.) values for the various metal groups.[4,5] However, with the exception of $[SnMe_3\{M(CO)_3(cp)\}]$ (M = Cr, Mo, or W; cp = η-cyclopentadienyl),[6] no data are available from which all three transition metals of any one Group can be examined. We now report new data for the systems $[SnX_3\{M(CO)_3(cp)\}]$, (I), $[SnX_2\{M(CO)_3(cp)\}_2]$, (II), and $[SnX_2\{M(CO)_3(cp)\}\{Fe(CO)_2(cp)\}]$, (III) (M = Cr, Mo, or W; X = Cl, Br, or I),[7] together with measurements for iron, manganese, and cobalt compounds, some of which have been examined by other workers. Analysis of these data by the point-charge method reveals some hitherto unsuspected anomalies, and the value of further refinement of the model is discussed. Some ^{57}Fe data are also presented.

RESULTS AND DISCUSSION

^{119}Sn *Mössbauer Spectra.—Compounds* (I). Mössbauer data for compounds (I) are presented in Table 1. The isomer shift (i.s.) and quadruple splitting (q.s.) values for M = Cr, Mo, or W are similar to those observed for other tin–transition metal systems and show similar trends; *viz.* the i.s. increases and the q.s. decreases with increasing atomic number of the halogen. Both parameters increase slightly with increasing atomic number of the transition metal. This observation, coupled with a corresponding decrease in the q.s. values for the compounds in which X = Me, indicates that the $M(CO)_3(cp)$ groups become better donors both to tin 5*s* and 5*p* orbitals as the Group is descended. As Bancroft has shown [4] the large decrease in i.s. from X = Cl, Br, or I to X = Me indicates a high degree of tin 5*s* character in the Sn–M bond. The high donor strength of the $Cr(CO)_3(cp)$ group is confirmed by the observation that V_{zz} is negative for (I; M = Cr, X = Cl).

Previous analysis of q.s. data in terms of the point-charge model has established that different scales are required for four-, five-, and six-co-ordinate tin systems.[2,3] At that time, insufficient data were available for unambiguously four-co-ordinate compounds to allow separate p.q.s. values to be given to chloride and bromide ligands. However, in each of the three series examined here, and in other tin–transition metal systems, distinct and systematic differences in q.s. are observed with change in the halogen. It therefore seemed worthwhile to analyse the data for compounds (I) more fully.

TABLE 1

^{119}Sn Mössbauer data (mm s^{-1}) for compounds (I)

Compound	$\delta(SnO_2)$	Δ	Ref.
$[SnCl_3\{Cr(CO)_3(cp)\}]$	1·67	1·54 [a]	*b*
$[SnBr_3\{Cr(CO)_3(cp)\}]$	1·77	1·34	*b*
$[SnI_3\{Cr(CO)_3(cp)\}]$	1·80	1·06	*b*
$[SnMe_3\{Cr(CO)_2(cp)\}]$	1·41	1·36	6
$[SnCl_3\{Mo(CO)_3(cp)\}]$	1·69	1·71	*b*
$[SnBr_3\{Mo(CO)_3(cp)\}]$	1·82	1·63	*b*
$[SnI_3\{Mo(CO)_3(cp)\}]$	1·87	1·27	*b*
$[SnMe_3\{Mo(CO)_3(cp)\}]$	1·43	1·25	6
$[SnCl_3\{W(CO)_3(cp)\}]$	1·67	1·77	*b*
$[SnBr_3\{W(CO)_3(cp)\}]$	1·80	1·62	*b*
$[SnI_3\{W(CO)_3(cp)\}]$	1·88	1·35	*b*
$[SnMe_3\{W(CO)_3(cp)\}]$	1·36	0·79	6
$[SnCl_3\{Fe(CO)_2(cp)\}]$	1·71	1·81	13, 20, *b*, *c*
$[SnBr_3\{Fe(CO)_2(cp)\}]$	1·76	1·61	20, *b*
$[SnI_3\{Fe(CO)_2(cp)\}]$	1·97	1·48	20, *b*
$[SnMe_3\{Fe(CO)_2(cp)\}]$	1·41	0·46	13
$[SnCl_3\{Mn(CO)_5\}]$	1·62	1·57	11, 13, *b*
$[SnBr_3\{Mn(CO)_5\}]$	1·78	1·47	8, 11, *b*
$[SnI_3\{Mn(CO)_5\}]$	1·95	1·32	8
$[SnEt_3\{Mn(CO)_5\}]$	1·49	0·88	8
$[SnCl_3\{Co(CO)_4\}]$	1·42	1·20	5
$[SnBr_3\{Co(CO)_4\}]$	1·49	1·30	5, *b*
$[SnI_3\{Co(CO)_4\}]$	1·71	0·81	5, *b*
$[SnBu_3\{Co(CO)(etpb)_3\}]$	1·38	0	*b*
$[Sn(NCS)_2\{Fe(CO)_2(cp)\}_2]$	1·82	2·58	13, 20, *b*
$[Sn(SPh)_2\{Fe(CO)_2(cp)\}_2]$	1·86	1·62	*b*
$[Sn(OS{\cdot}OPh)_2\{Fe(CO)_2(cp)\}_2]$	1·90	2·62	*b*, *d*

[a] e^2qQ is positive. [b] This work. [c] R. H. Herber and Y. Goscinny, *Inorg. Chem.*, 1968, **7**, 1293. [d] F. Bonati, S. Cenini, D. Morelli, and R. Ugo, *J. Chem. Soc.* (*A*), 1966, 1052.

Assuming regular geometry, the p.q.s. value for a ligand X, relative to $(p.q.s.)_{Cl} = 0$, is given by equation (1) where $\Delta' = \frac{1}{2}e^2q|Q|$, *i.e.* the q.s. is given the sign of

$$(p.q.s.)_X = \tfrac{1}{4}[\Delta'(SnCl_3M') - \Delta'(SnX_3M')] \qquad (1)$$

V_{zz} (negative for X = halogen, positive for X = Me). Using q.s. data averaged from all available reports, the p.q.s. values for Br, I, and Me have been derived and are given in Table 2. The p.q.s. values of Me and I

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[1] Part VI, R. V. Parish and P. J. Rowbotham, *J.C.S. Dalton*, 1973, 37.

[2] R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 1970, **4**, 65.

[3] M. G. Clark, A. G. Maddock, and R. H. Platt, *J.C.S. Dalton*, 1972, 281.

[4] G. M. Bancroft, K. D. Butler, A. T. Rake, and B. Dale, *J.C.S. Dalton*, 1972, 2025.

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

[6] S. R. A. Bird, J. D. Donaldson, S. A. Keppie, and M. F. Lappert, *J. Chem. Soc.* (*A*), 1971, 1311.

[7] P. Hackett and A. R. Manning, *J.C.S. Dalton*, 1972, 2434.

agree well with those given previously.[3] The values for the three halogens lie in the expected order, becoming more negative with increasing atomic number, and the differences between the values are significant at a high statistical level (99%). However, as is shown below, such small differences may not be chemically significant.

These p.q.s. values can now be reapplied to the original data to obtain values for the various metal groups, which are shown in Table 3. The values for $Fe(CO)_2(cp)$, $Mn(CO)_5$, and $Co(CO)_4$ are slightly smaller than those derived by Bancroft *et al.*,[5] since these authors used a different selection of data. The increase in donor power $Cr(CO)_3(cp) < Mo(CO)_3(cp) < W(CO)_3(cp)$ is clearly evident in the p.q.s. values, and these groups lie between the extreme values for $Fe(CO)_2(cp)$ and $Co(CO)_4$. It has been noted [8,9] that this order accords with that of the basicities and nucleophilicities of the corresponding anions, but no attempt has been made to explain the trends. It has been suggested that Mössbauer parameters may be correlated with Sn–M bond lengths,[10] but few directly comparable crystallographic data are available; a selection for comparable compounds is shown in Table 4, from which it is evident that no simple correlation is possible. Thus, bonds involving the 3*d* metals decrease in length in the order Sn–Cr > Sn–Mn > Sn–Fe, paralleling the order of charge donation to tin. However, the Sn–Co bond is comparable in length to the Sn–Fe bond, although the Co and Fe groups lie at opposite ends of the range of p.q.s values. In view of the variations in stereochemistry, in formal *d* configuration and, hence, in hybridisation of the transition metals, no simple correlations seem likely. The most comparable pairs are the Fe–Sn and Mn–Sn systems, in both of which the transition metals may be regarded as having d^6 configurations with octahedral or pseudo-octahedral geometry. The high π-acceptor character of carbon monoxide relative to cp would make the $Mn(CO)_5$ group the less basic and a poorer donor to tin, and outweighs the effect of the formal difference in oxidation state. The major factor resulting in high donor power to tin seems to be a relatively low *d* character, or large *s* character, in the transition-metal hybrid orbital (d^2sp^3 in this case). A change to the pseudo-seven-co-ordinate d^4 configuration of $(cp)(OC)_3Cr–Sn$ (d^3sp^3) or to the five-co-ordinate d^8 configuration of $(OC)_4Co–Sn$ (dsp^3, with predominantly *d–p* character in the axial bonds) results in decreased donation to tin.

TABLE 2

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

X	$(p.q.s.)_X$ *
Cl	0
Br	-0.07 ± 0.03
I	-0.18 ± 0.05
Me	-1.34 ± 0.16

* The quoted errors are the 95% confidence limits on the mean, $\pm t.s/\sqrt{n}$.

TABLE 3

P.q.s. values (mm s^{-1}) for the M′ groups

M′	$(p.q.s.)_{M'}$
$Fe(CO)_2(cp)$	-0.95 ± 0.14
$W(CO)_3(cp)$	-0.89 ± 0.05
$Mn(CO)_5$	-0.83 ± 0.07
$Mo(CO)_3(cp)$	-0.82 ± 0.10
$Cr(CO)_3(cp)$	-0.72 ± 0.06
$Co(CO)_4$	-0.61 ± 0.14

TABLE 4

Bond lengths in tin–transition metal compounds

Compound	d(M–Sn)/pm	Ref.
$[SnCl\{Co(CO)_4\}_3]$	260	*a*
$[SnCl\{Mn(CO)_5\}_3]$	274	*b*
$[SnPh_2\{Co(CO)_4\}\{Mn(CO)_5\}]$	266 (Co) 273 (Mn)	*c*
$[SnPh_3\{Fe(CO)_2(cp)\}]$	254	*d*
$[SnPh_3\{Mn(CO)_5\}]$	267	*e*
$[SnPh_3\{Cr(CO)_3(cp)\}]$	285	*f*
$[SnPh_3\{Mo(CO)_3(cp)\}]$	285	*f*
$[SnPh_3\{W(CO)_3(cp)\}]$	281	*f*
$[SnCl\{Fe(CO)_2(cp)\}_2\{Mo(CO)_3(cp)\}]$	259 (Fe) 289 (Mo)	*g*

[a] B. P. Bir'yukov, E. A. Kukhtenkova, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, and V. I. Khandozhko, *J. Organometallic Chem.*, 1971, **27**, 337. [b] J. H. Tsai, J. J. Flynn, and F. P. Boer, *Chem. Comm.*, 1967, 702. [c] B. P. Bir'yukov, Yu. T. Struchkov, K. N. Anisimov, N. E. Kolobova, O. P. Osipova, and M. Ya. Zakharov, *Chem. Comm.*, 1967, 749. [d] R. F. Bryan, *J. Chem. Soc.* (*A*), 1967, 192. [e] H. Weber and R. F. Bryan, *Acta Cryst.*, 1967, **22**, 822. [f] Yu. T. Struchkov, K. N. Anisimov, O. P. Osipova, N. E. Kolobova, and A. N. Nesmeyanov, *Doklady Akad. Nauk S.S.S.R.*, 1967, **172**, 107. [g] J. E. O'Connor and E. R. Corey, *J. Amer. Chem. Soc.*, 1967, **89**, 3930.

An increase in donor power can also be achieved by replacement of a CO group by a less-effective π-acceptor, as has been noted for $[SnCl_3\{Mn(CO)_4(PPh_3)\}]$ {Δ 1·87 mm s^{-1}, *cf.* 1·57 mm s^{-1} for $[SnCl_3\{Mn(CO)_5\}]$}.[11] There is, surprisingly, no change in the Sn–Mn bond length.[12] We find a similar, but much more marked, effect for $[SnBu_3\{Co(CO)(etbp)_3\}]$ [etbp = $\{EtC(CH_2O)_3\}P$], for which no q.s. can be resolved (Γ 1·26 mm s^{-1}), whereas $[SnMe_3\{Co(CO)_4\}]$ shows a large splitting (1·77 mm s^{-1}). In this case, increased donation from the transition metal reduces the q.s. because the other ligand at tin is alkyl rather than halogen [$(p.q.s.)_R < (p.q.s)_{M'} < (p.q.s.)_{Cl}$].* The $Co(CO)(etbp)_3$ group is thus a comparable donor to the $Fe(CO)_2(cp)$ group, *i.e.* the substitution of the three CO groups is sufficient to make the worst donor comparable to the best.

In concluding this section, it might be prudent to point out that, given the statistical uncertainties on the averages, very few of the $(p.q.s.)_{M'}$ values are significantly different.

Compounds (II) *and* (III). Mössbauer data for compounds (II) and (III) are shown in Table 5. As found in many other systems, both the i.s. and q.s. show marked increases over the values for the corresponding

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* M′ = $M(CO)_3(cp)$ (M = Cr, Mo, or W), $Fe(CO)_2(cp)$, $Mn(CO)_5$, or $Co(CO)_4$.

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

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

[10] S. R. A. Bird, J. D. Donaldson, A. F. Le C. Holding, B. J. Senior, and M. J. Tricker, *J. Chem. Soc.* (*A*), 1971, 1616.

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

[12] R. F. Bryan, *J. Chem. Soc.* (*A*), 1967, 172.

trihalides, demonstrating again the relatively high *s* character of the Sn–M bonds. The q.s.s for these compounds can be calculated from the p.q.s. values of Tables 2 and 3 (for the mixed-metal compounds the e.f.g. matrix has been diagonalised), and the calculated values of the splitting and of the asymmetry parameter (η) are also included in Table 5. The calculated values are all lower than those observed, again a familiar phenomenon which is normally attributed to distortion of the dihalides from regular tetrahedral geometry.[10,13] In the cases which have been examined crystallographically, the M–Sn–M bond angles are considerably larger than the tetrahedral value, ranging from 116 to 129°, and such distortion is expected to increase the splitting. The largest q.s. value found here is 2·62 mm s^{-1} for $[\mathrm{Sn\{Fe(CO)_2(cp)\}_2(OS{\cdot}OPh)_2}]$. In this compound the Fe–Sn–Fe bond angle is 129° and the O–Sn–O angle is 81°, severe distortion from tetrahedral geometry.[14] Previously, splitting values as large as this have been found only in mixed compounds of low symmetry of the type $\mathrm{SnABC_2}$.[15]

TABLE 5

Mössbauer parameters (mm s^{-1}) for compounds (II) and (III)

	$\delta(\mathrm{SnO_2})$	Δ	$\Delta_{\mathrm{calc.}}$[a]	$\Delta/\Delta_{\mathrm{calc.}}$	η_{calc}	Ref.
$[\mathrm{SnCl_2\{Cr(CO)_3(cp)\}_2}]$	2·00	1·95	1·67	1·17	1·00	*b*
$[\mathrm{SnCl_2\{Mo(CO)_3(cp)\}_2}]$	2·03	2·39	1·89	1·26	1·00	*b*
$[\mathrm{SnCl_2\{W(CO)_3(cp)\}_2}]$	1·96	2·55	2·06	1·24	1·00	*b*
$[\mathrm{SnCl_2\{Cr(CO)_3(cp)\}\{Mo(CO)_3(cp)\}}]$	1·99	2·09	+1·78	1·17	0·98	*b*
$[\mathrm{SnCl_2\{Cr(CO)_3(cp)\}\{W(CO)_3(cp)\}}]$	1·98	2·15	+1·88	1·14	0·96	*b*
$[\mathrm{SnCl_2\{Cr(CO)_3(cp)\}\{Fe(CO)_2(cp)\}}]$	2·03	2·16	+1·97	1·10	0·93	*b*
$[\mathrm{SnCl_2\{Fe(CO)_2(cp)\}\{Mo(CO)_3(cp)\}}]$	2·01	2·45	+2·06	1·19	0·98	*b*
$[\mathrm{SnCl_2\{Fe(CO)_2(cp)\}\{W(CO)_3(cp)\}}]$	2·10	2·46	+2·13	1·15	1·00	*b*
$[\mathrm{SnCl_2\{Fe(CO)_2(cp)\}}]$	1·95	2·41	2·20	1·10	1·00	10, 13, *b*–*d*
$[\mathrm{SnCl_2\{Mn(CO)_5\}_2}]$	1·90	2·10	1·92	1·09	1·00	11, *b*
$[\mathrm{SnCl_2\{Co(CO)_4\}_2}]$	1·75	1·44	1·40	1·03	1·00	5
$[\mathrm{SnBr_2\{Cr(CO)_3(cp)\}_2}]$	2·10	1·85	1·51	1·23	1·00	*b*
$[\mathrm{SnBr_2\{Mo(CO)_3(cp)\}_2}]$	2·03	2·35	1·73	1·36	1·00	*b*
$[\mathrm{SnBr_2\{W(CO)_3(cp)\}_2}]$	2·01	2·42	1·90	1·27	1·00	*b*
$[\mathrm{SnBr_2\{Cr(CO)_3(cp)\}\{Mo(CO)_3(cp)\}}]$	2·03	2·16	+1·62	1·33	0·98	*b*
$[\mathrm{SnBr_2\{Cr(CO)_3(cp)\}\{W(CO)_3(cp)\}}]$	2·04	2·28	+1·73	1·32	0·95	*b*
$[\mathrm{SnBr_2\{Fe(CO)_3(cp)\}_2}]$	1·85	2·13	2·04	1·04	1·00	10, *b*
$[\mathrm{SnBr_2\{Mn(CO)_5\}_2}]$	2·04	2·12	1·76	1·20	1·00	11, *b*
$[\mathrm{SnBr_2\{Co(CO)_4\}_2}]$	1·75	1·46	1·24	1·18	1·00	5
$[\mathrm{SnI_2\{Cr(CO)_3(cp)\}_2}]$	2·19	1·80	1·24	1·45	1·00	*b*
$[\mathrm{SnI_2\{Mo(CO)_3(cp)\}_2}]$	2·09	2·06	1·46	1·41	1·00	*b*
$[\mathrm{SnI_2\{W(CO)_3(cp)\}_2}]$	2·11	2·38	1·64	1·45	1·00	*b*
$[\mathrm{SnI_2\{Cr(CO)_3(cp)\}\{Mo(CO)_3(cp)\}}]$	2·10	2·00	+1·36	1·47	0·97	*b*
$[\mathrm{SnI_2\{Cr(CO)_3(cp)\}\{W(CO)_3(cp)\}}]$	2·19	1·80	+1·46	1·23	0·93	*b*
$[\mathrm{SnI_2\{Fe(CO)_3(cp)\}_2}]$	2·00	2·24	1·78	1·26	1·00	10, *b*
$[\mathrm{SnI_2\{Co(CO)_4\}_2}]$	1·86	1·07	0·98	1·09	1·00	5
$[\mathrm{SnPhCl_2\{Fe(CO)_2(cp)\}}]$	1·71	2·65	+2·40	1·10	0·98	*b*, *e*
$[\mathrm{SnMeCl_2\{Mn(CO)_5\}}]$	1·66	2·56	+2·64	0·97	0·82	13
$[\mathrm{SnPhCl_2\{Mn(CO)_5\}}]$	1·71	2·42	+2·29	1·06	0·92	8, 11
$[\mathrm{SnBr_2Me\{Mn(CO)_5\}}]$	1·69	2·51	2·49	1·01	0·80	11
$[\mathrm{SnBr_2Ph\{Mn(CO)_5\}}]$	1·75	2·70	+2·13	1·27	0·91	11, *b*

[a] The signs given are those of e^2qQ. [b] This work. [c] V. I. Gol'danskii, B. V. Borshagovskii, E. F. Makarov, R. A. Stukan, K. N. Anisimov, N. E. Kolobova, and V. V. Skripkin, *Teor. i eksp. Khim.*, 1967, **3**, 478. [d] R. H. Herber and Y. Goscinny, *Inorg. Chem.*, 1968, **7**, 1293. [e] B. V. Liengme, M. J. Newlands, and J. R. Sams, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 1223.

In the data for the Group 6 metal derivatives, a hitherto unnoticed trend may be discerned. In each series the discrepancy between calculated and observed q.s. increases markedly as the halogen is changed from chloride to bromide to iodide. In several cases the discrepancies are considerably greater than the 0·4 mm s^{-1} suggested as acceptable by Clark *et al.*[3] Similar trends occur in data for other systems (also included in Table 5) but have not previously been noticed, presumably because few iodo-compounds had been measured. In view of the large discrepancies involved, amounting to 40—45% in some cases, it is worthwhile examining the possible causes more closely.

Two approaches have been adopted in allowing for the effects of distortion in the point-charge treatment of four-co-ordinate systems. In the literal point-charge model, the ligands are treated as donating fixed amounts of charge regardless of the geometry, *i.e.* rehybridisation of the tin atom is ignored (*cf.* crystal-field theory).[2,10,16,17] In this case, the components of the e.f.g. tensor are those shown in Table 6. It is evident that no simple relation exists between the degree of distortion and the q.s., and actual p.q.s. values, or at least the ratio $(\mathrm{p.q.s.})_{\mathrm{M'}} : (\mathrm{p.q.s.})_{\mathrm{X}}$, must be inserted before comparison can be made. Thus, the precise calculated value of the q.s. depends on the p.q.s. scale selected; for example, with $\mathrm{X} = \mathrm{Cl}$ and $(\mathrm{p.q.s.})_{\mathrm{Cl}} = 0$, the splitting for compounds (I; $\mathrm{X} = \mathrm{Cl}$) appears to be independent of distortion, an unrealistic result. We have therefore compared two cases, $(\mathrm{p.q.s.})_{\mathrm{X}} = 0$ and $(\mathrm{p.q.s.})_{\mathrm{X}} =$

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[13] B. A. Goodman, R. Greatrex, and N. N. Greenwood, *J. Chem. Soc.* (*A*), 1971, 1868.

[14] R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1220.

[15] G. M. Bancroft, K. D. Butler, and A. T. Rake, *J. Organometallic Chem.*, 1972, **34**, 137.

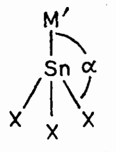
[16] R. V. Parish and C. E. Johnson, *J. Chem. Soc.* (*A*), 1971, 1906.

[17] R. A. Mazak and R. L. Collins, *J. Chem. Phys.*, 1969, **51**, 3220.

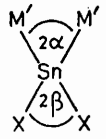
$(\text{p.q.s.})_{\text{M}'}/10$, and the results are shown in Figure 1. For both (I) and (II) the q.s. increases with increasing distortion. The bond-angle ranges observed experimentally are those to the right of the broken vertical line in both diagrams. It will be observed that the calculated splitting values increase more rapidly for (II) than for (I), corresponding to the observed trend, and this is the model implicitly used in the earlier discussions. Discrepancies between calculated and observed q.s.s of 10—20% could easily be accounted for on this basis.

TABLE 6

Components of the e.f.g. tensor for the literal point-charge model



$$V_{zz}^{(1)} = 2(\text{p.q.s.})_{\text{M}'} + 3(\text{p.q.s.})_{\text{X}}\,(3\cos^2\alpha - 1)$$
$$V_{xx}^{(1)} = V_{yy}^{(1)} = -(\text{p.q.s.})_{\text{M}'} + 3(\text{p.q.s.})_{\text{X}}\,(\tfrac{3}{2}\sin^2\alpha - 1)$$



$$V_{zz}^{(2)} = 2(\text{p.q.s.})_{\text{M}'}\,(3\cos^2\alpha - 1) + 2(\text{p.q.s.})_{\text{X}}\,(3\cos^2\beta - 1)$$
$$V_{yy}^{(2)} = -2(\text{p.q.s.})_{\text{M}'} + 2(\text{p.q.s.})_{\text{X}}\,(3\sin^2\beta - 1)$$
$$V_{xx}^{(2)} = 2(\text{p.q.s.})_{\text{M}'}\,(3\sin^2\alpha - 1) - 2(\text{p.q.s.})_{\text{X}}$$
$$\cot^2\beta = 1 - \cot^2\alpha$$

The alternative approach is that of Clark *et al.*,[3] and is based on a hybridisation scheme, *i.e.* each ligand makes a fixed contribution but the *p* character of the orbital involved is taken to be that appropriate for sp^3 hybrids directed towards the ligands. In this case the calculated q.s. is proportional to that for the undistorted case and the scale factors are simple functions of the distortion:

$$\Delta_{\text{hyb}}^{(1)} = f_1\Delta_{\text{tet}}^{(1)},\ f_1 = 4(1 - \cot^2\alpha)/3$$
$$\Delta_{\text{hyb}}^{(2)} = f_2\Delta_{\text{tet}}^{(2)},\ f_2 = 2(\cot^4\alpha - \cot^2\alpha + 1)^{\frac{1}{2}}/\sqrt{3}$$

These functions are plotted in Figure 2. Now, it is $\Delta^{(2)}$ which is almost independent of distortion while $\Delta^{(1)}$ drops very sharply. Obviously, p.q.s. values calculated using $\Delta^{(1)}$ without correcting for the distortion will again be underestimates, and substantial discrepancies will be possible.

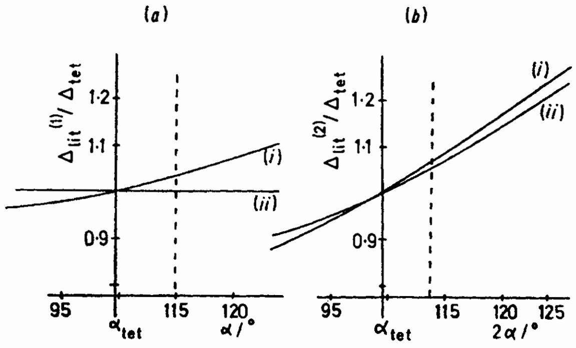


FIGURE 1 Variation of q.s. with distortion according to the literal point-charge model: (*a*), for compounds (I); (*b*), for (II). $(\text{p.q.s.})_{\text{X}} = (\text{p.q.s.})_{\text{M}'}/10$ (*i*), 0 (*ii*)

Thus, both approaches can account for the 'anomalously' large q.s. of (II), although in rather different ways. However, neither model will account for the trend observed on changing the halogen. This trend would seem to imply increasing distortion from regular tetrahedral geometry in the order X = Cl < Br < I. Such a trend is unlikely on either steric or electronic grounds. Since iodide is the largest of the halides, steric effects would be expected to produce a return towards regular geometry. Iodine is also the least-electronegative halogen and would therefore command the most *s* character in the tin hybrid orbitals, again forcing an approach to the regular sp^3 situation. Another possibility is that the $(\text{p.q.s.})_{\text{M}'}$ values are not independent of the other ligands present. I.r. data suggest that as the halogen becomes heavier more electron density resides on the transition-metal group (see below). The M′ group must therefore become a less-effective donor to tin (tin is a less-effective acceptor) as the halogen becomes less electronegative. This effect would make the actual $(\text{p.q.s.})_{\text{M}'}$ value less negative and hence the calculated q.s. would be too large, the reverse of the observed trend.

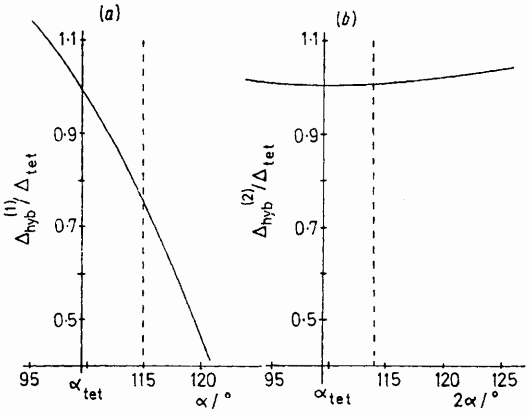


FIGURE 2 Variation of q.s. with distortion according to the hybridisation model: (*a*), for compounds (I); (*b*), for (II)

A reasonable explanation of the data can be found in the rehybridisation argument mentioned above. As the halogen becomes less electronegative, the tin hybrid orbital used in bonding to it will contain more *s* character and, presumably, less *p* character (this effect will operate independently of distortion). Presumably, therefore, the M–Sn bond will increase in tin 5*p* character. Since the M′ group may be expected to make the largest contribution to the e.f.g. (by placing most charge in the valence shell of the tin atom), an increase in *p* character is tantamount to an increase in the $(\text{p.q.s.})_{\text{M}'}$ value. The same effect will operate in series (I), but will be absorbed in the calculation of the p.q.s. values. That such rehybridisation can occur is shown by the n.m.r. coupling constants of the dimethyltin halides, where

^2J(Sn–H) decreases in the order $SnCl_2Me_2 > SnBr_2Me_2 > SnI_2Me_2$.[18] The C–Sn bonds are the most covalent, like the M–Sn bonds in (II), and show loss of *s* character as the halogen becomes heavier.

It therefore appears that p.q.s. values are not independent of the other ligands present, *i.e.* one of the major basic assumptions of the point-charge treatment [9] is no longer valid. In view of the unknown magnitude of the distortion effect, it does not seem worthwhile to attempt to assess the degree of inconstancy. It would seem, then, that further refinement of the point-charge model is profitless, and to attempt to give chemical significance to small differences in p.q.s. values is unwise. Thus, while the model has considerable utility, it is condemned to a crudity of application commensurate with its simplicity.

Correlations with i.r. data. Good linear correlations are found between the e.f.g. at the tin nucleus of (I) and the carbonyl-stretching frequencies of the M′ group (Table 7). In each case the correlation is negative, *i.e.* the highest stretching frequencies correspond to the most-negative e.f.g. values. Carbonyl-stretching frequencies are usually interpreted in terms of the extent of back donation from transition metal to carbonyl group, a high frequency indicating little back donation. The extent of back donation, in turn, depends on the electron density on the metal atom and the number of CO groups. The correlations thus show, as expected, that in the compounds with the most negative e.f.g.s (*i.e.* X = halogen), the transition metal is most positively charged, *i.e.* is functioning as the most-effective donor to tin. The changes involved are, however, quite small, but increase as the number of CO groups decreases. For $Mn(CO)_5$ the correlations for the two A_1 modes have very similar gradients. These two modes correspond to stretching of the axial and equatorial carbonyl groups and their similar dependence on X implies that the Mn–Sn bond is primarily a σ-bond. If there were pronounced π-character in this bond, the axial group *trans* to it would be expected to be more sensitive to change in X than the equatorial group, as in the Cotton–Krainhanzel–Graham technique for separation of σ- and π-effects.[19] When applied to tin compounds, Graham's σ-factor varies smoothly with changing electronegativity of the groups bound to tin, whereas the variation in the π-factor is much smaller and somewhat erratic.

TABLE 7

Linear correlations between carbonyl-stretching frequencies and q.s. for compounds (I; X = Cl, Br, I, or Me). $\bar{\nu}/cm^{-1} = A + B(\Delta'/mm\ s^{-1})$ *

M′	Mode	A	B	r †
$Mn(CO)_5$	A_1^{ax}	2 101·5	−14·4	0·996
	E	2 010·6	−22·3	$0{\cdot}999_9$
	A_1 eq	2 012·7	−16·7	$0{\cdot}999_9$
$Fe(CO)_2(cp)$	A'	1 996·0	−27·9	0·986
	A''	1 944·7	−32·6	0·991
$Cr(CO)_3(cp)$		2 001·3	−17·8	$0{\cdot}999_6$
		1 941·8	−24·4	$0{\cdot}999_1$
		1 918·2	−28·3	0·995
$Mo(CO)_3(cp)$		2 012·6	−18·0	$0{\cdot}999_6$
		1 945·3	−23·2	0·999
		1 922·6	−24·9	0·998
$W(CO)_3(cp)$		1 996·6	−24·7	$0{\cdot}999_9$
		1 928·2	−26·1	0·997
		1 903·4	−30·2	0·998

* $\Delta' = \frac{1}{2}e^2q|Q|$. † r = Correlation coefficient.

Finally, it may be noted that the value of the q.s. interpolated for $[SnPh_3\{Mn(CO)_5\}]$ is 0·54 ± 0·33 mm s^{-1} which compares very favourably with 0·61 mm s^{-1} calculated from the p.q.s. values.

^{57}Fe *Mössbauer Spectra.*—^{57}Fe Mössbauer data for several compounds are presented in Table 8; where comparisons can be made, agreement with previous reports is generally good. For compounds of the type $[Fe(CO)_2(cp)Y]$, the i.s. reflects the σ–π-character of Y, good donor–acceptors giving the lower i.s.s. It is noticeable that the tin-containing compounds give lower i.s.s than the halides, demonstrating as expected that $:SnX_3^-$ is a better donor to iron than X^- (assuming, as indicated above, that π-bonding is negligible). Consistent with this, the lowest i.s.s are found for the dihalides, (III). The q.s.s. in these compounds are also smaller than for $[Fe(CO)_2(cp)Y]$, suggesting that increased donation from tin to iron decreases the e.f.g. at iron; this is consistent with the reported positive sign of the e.f.g. in $[SnPh_3\{Fe(CO)_2(cp)\}]$.[20]

TABLE 8

^{57}Fe Mössbauer data (mm s^{-1}) for $Fe(CO)_2(cp)$ derivatives

	δ(Fe)	Δ
$[Fe(CO)_2(cp)(SnPh_3)]$	0·08	1·75
$[Fe(CO)_2(cp)(SnI_3)]$	0·15	1·74
$[Fe(CO)_2(cp)(SnBr_3)]$	0·10	1·80
$[Fe(CO)_2(cp)(SnCl_3)]$	0·14	1·80
$[\{Fe(CO)_2(cp)\}_2SnCl_2]$	0·12	1·57
$[\{Fe(CO)_2(cp)\}\{Cr(CO)_3(cp)\}SnCl_2]$	0·13	1·71
$[\{Fe(CO)_2(cp)\}\{Mo(CO)_3(cp)\}SnCl_2]$	0·12	1·54
$[\{Fe(CO)_2(cp)\}\{W(CO)_3(cp)\}SnCl_2]$	0·11	1·69
$[\{Fe(CO)_2(cp)\}_2Sn(NCS)_2]$	0·12	1·57
$[\{Fe(CO)_2(cp)\}_2Sn(SPh)_2]$	0·07	1·61
$[\{Fe(CO)_2(cp)\}_2Sn(OS{\cdot}OPh)_2]$	0·09	1·68
$[Fe(CO)_2(cp)Cl]$	0·22	1·89
$[Fe(CO)_2(cp)Br]$	0·22	1·77
$[Fe(CO)_2(cp)I]$	0·20	1·86

EXPERIMENTAL

Mössbauer spectra were obtained as described previously,[21] with absorbers at liquid-nitrogen temperature and Sn–Pd or Co–Pd sources at room temperature. Isomer shifts (i.s.s) are quoted relative to SnO_2 or natural iron at room temperature. Values of the i.s. and quadrupole splitting (q.s.) were reproducible to, at worst, 0·03 mm s^{-1}. The magnetically perturbed spectrum of $[SnCl_3\{Cr(CO)_3(cp)\}]$ was obtained at 4·2 K at P.C.M.U., Harwell.

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