

Synthesis and Mössbauer Spectra of Six-co-ordinate Tin–Metal Compounds: Quotient of the Partial Quadrupole Splittings of the Six- and Four-co-ordinate Species

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Nine new six-co-ordinate tin(IV) compounds have been prepared of the type $[M(SnCl_3L)]$ [$M = Mn(CO)_5$, $Mn(CO)_4(PPh_3)$, $Fe(cp)(CO)_2$; $L = phen$ or $bipy$], $[M(SnXL'_2)]$ ($X = Cl$ or Ph ; $L' = quin$ or pd), and $[M\{SnPhCl_2(phen)\}]$. Structures for these and other similar compounds have been assigned using carbonyl i.r. stretching frequencies and ^{119}Sn Mössbauer quadrupole splittings. Partial quadrupole splittings for six-co-ordinate species, $(p.q.s.)_L^{oct}$, have been calculated from these quadrupole splittings. There is an excellent linear correlation ($R = 0.991$) between the $(p.q.s.)_L^{oct}$ values and previously calculated $(p.q.s.)_L^{tet}$ values: $(p.q.s.)_L^{oct} = 0.73(p.q.s.)_L^{tet} - 0.01$. The gradient of 0.73 is compared with that (0.67) calculated previously from simple molecular-orbital arguments. The relative bonding characteristics for the M groups in six-co-ordination are the same as those evaluated for M groups in four-co-ordinate compounds. Thus, the order of p -donor strength in six-co-ordination is $Mo(cp)(CO)_3 < Mn(CO)_5 < Mn(CO)_4(PPh_3) \approx Fe(cp)(CO)_2 < Ph < Me$, while the M–Sn bonds have substantially higher Sn 5s character than Me–Sn or Ph–Sn bonds.

ALTHOUGH a very large number of four-co-ordinate tin compounds containing a Sn–M bond [$M = Mn(CO)_5$, $Fe(cp)(CO)_2$, $Co(CO)_4$, $Mo(cp)(CO)_3$, etc.; ($cp = \eta$ -cyclopentadienyl)] have been reported,¹ only seven six-co-

¹ E. H. Brook and R. J. Cross, *Organometallic Chem. Rev.*, 1970, **A6**, 227.

ordinate compounds containing such a Sn–M bond have been prepared,^{2,3} often in low yield. Thus, Patmore and

² D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1967, **6**, 1879.

³ F. Bonati and G. Minghetti, *J. Organometallic Chem.*, 1969, **16**, 332.

Graham² first reported three cobalt carbonyl derivatives of six-co-ordinate tin pentane-2,4-dionates. Bonati and Minghetti³ reported another four six-co-ordinate compounds containing a Sn-Fe, Sn-Co, or Sn-Mo bond.

Previous ¹¹⁹Sn Mössbauer results on four-co-ordinate Sn-M compounds⁴⁻⁶ indicated that, for metal groups such as Mn(CO)₅ and Fe(cp)(CO)₂, the Sn-M bond has a larger Sn 5s character than the Sn-Me or Sn-Ph bond, but that the metal groups are comparable donors to Ph and Me. The extensive chemistry of six-co-ordinate tin(IV) compounds containing alkyl or aryl groups⁷ suggested that a large number of six-co-ordinate Sn-M compounds could be prepared. Our report in this paper of a number of new six-co-ordinate Sn-M compounds, mostly with M = Mn(CO)₅, confirms this expectation.

We were particularly interested in six-co-ordinate Sn-M compounds to extend our ¹¹⁹Sn Mössbauer investigations^{4,5} of Sn-M bonds. We wanted to use the ¹¹⁹Sn Mössbauer parameters to compare the bonding of the

bonding properties in both tin co-ordination environments.

EXPERIMENTAL

The compounds in Table 1 were prepared for the first time. The salts Tl[pd] and Tl[quin] (pd = pentane-2,4-dionate and quin = quinolin-8-olate) and the four-co-ordinate M-Sn precursors were prepared by previously published methods.¹⁰⁻¹² Compounds (I), (II), and (VII) were prepared by treating [Mn(CO)₅(SnCl₃)] or [Mn(CO)₅(SnPhCl₂)] with the appropriate thallium salt. The white precipitates of TlCl were discarded and the filtrates were evaporated to dryness. The crude products were recrystallized from n-hexane. The yields were ca. 40%. The products are slightly light sensitive and decompose in air. The 2,2'-bipyridyl (bipy) and 1,10-phenanthroline (phen) adducts were obtained by pipetting benzene solutions of the ligand into a benzene solution of the corresponding [M(SnCl₃)] or [M(SnPhCl₂)] [M = Mn(CO)₅, Mn(CO)₄(PPh₃), or Fe(cp)(CO)₂]. Precipitates formed immediately. The solids

TABLE I
Analytical data

Compound	M.p. (θ _e /°C)	Analysis (%)			
		Found		Calc.	
		C	H	C	H
<i>cis</i> -[Mn(CO) ₅ {SnCl(pd) ₂ }] (I)	128—130	32.9	2.60	33.0	2.50
<i>cis</i> -[Mn(CO) ₅ {SnCl(quin) ₂ }] (II)	122 (decomp.)	45.2	2.30	43.35	1.90
<i>fac</i> -[Mn(CO) ₅ {SnCl ₃ (bipy)}] (III)	134—135 (decomp.)	31.25	1.40	31.3	1.35
<i>fac</i> -[Mn(CO) ₅ {SnCl ₃ (phen)}] (IV)	132—154 (decomp.)	34.4	1.25	33.2	1.31
<i>fac</i> -[Mn(CO) ₄ (PPh ₃){SnCl ₃ (bipy)}] (V)	120—122 (decomp.)	48.55	3.15	47.4	2.85
<i>fac</i> -[Mn(CO) ₄ (PPh ₃){SnCl ₃ (phen)}]·C ₆ H ₆ (VI)	126—128 (decomp.)	52.35	3.15	52.65	3.20
<i>cis</i> -[Mn(CO) ₅ {SnPh(pd) ₂ }] (VII)	141 (decomp.)	42.8	3.25	45.3	2.40
<i>trans</i> -[Mn(CO) ₅ {SnPhCl ₂ (phen)}] (VIII)	139—140 (decomp.)	42.9	1.90	43.05	2.05
<i>fac</i> -[Fe(CO) ₂ {SnCl ₃ (phen)}]·C ₆ H ₆ (IX)	141—142	45.7	2.95	45.45	2.90

metal groups in six-co-ordination with the bonding properties deduced earlier^{4,5} from four-co-ordinate compounds of Sn^{IV}. In particular we wanted to confirm the order of partial quadruple splitting (p.q.s.) values derived from four-co-ordinate tin(IV) compounds^{4,5} and to check the theoretical prediction $(p.q.s.)_{L^{oct}}/(p.q.s.)_{L^{tet}} = 0.67$.⁸ Now that it has been shown by several groups that the p.q.s. values depend on the other ligands bonded to Sn,^{9,6} it is also important to establish the best 'working values' for the M groups. Our values for $(p.q.s.)_{L^{oct}}$ indicate that the $(p.q.s.)_{L^{tet}}$ values derived previously^{4,5} from relatively undistorted R₃SnM compounds wherever possible are probably better working values than those obtained by Dickinson *et al.*⁶ from mostly highly distorted X₃SnM compounds (X = Cl, Br, I, and Me). We also show that the $(p.q.s.)_{L^{oct}}$ values follow the same trend as $(p.q.s.)_{L^{tet}}$ for different M groups, strongly suggesting that the M groups have consistently different

were washed with benzene and then centrifuged. The yield was not less than 90%. These adducts are slightly soluble in non-polar solvents, but moderately soluble in acetone.

The melting points and chemical analyses of the new compounds are listed in Table 1. Satisfactory purity was not obtained for two compounds [(II) and (VII)] which decompose readily on standing at room temperature. However, the Mössbauer spectra gave narrow lines and no indications of Mössbauer impurities. In some cases, clathrated benzene molecules were present [compounds (VI) and (IX)], as has been found previously for six-co-ordinate Sn-Co derivatives.³ Other previously prepared six-co-ordinate Sn-M compounds³ were characterized by their m.p.s and i.r. CO stretching frequencies.

Mössbauer spectra were recorded at 110 K using a newly constructed spectrometer similar to that described previously,¹³ a 10 mCi BaSnO₃ source for ¹¹⁹Sn spectra, and a 50 mCi ⁵⁷Co in Cu source for ⁵⁷Fe spectra. The spectrometer was calibrated using a 99.99% Fe foil and the scan-centre

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

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

⁶ R. J. Dickinson, R. V. Parish, P. J. Rowbotham, A. R. Manning, and P. Hackett, *J.C.S. Dalton*, 1975, 424.

⁷ R. C. Poller, 'Chemistry of Organotin Compounds,' Academic Press, New York, 1970.

⁸ M. G. Clark, A. G. Maddock, and R. H. Platt, *J.C.S. Dalton*, 1972, 281.

⁹ G. M. Bancroft and A. T. Rake, *Inorg. Chim. Acta*, 1975, **13**, 175.

¹⁰ W. H. Nelson and D. F. Martin, *J. Inorg. Nuclear Chem.*, 1965, **27**, 87.

¹¹ R. D. Gorsich, *J. Amer. Chem. Soc.*, 1962, **84**, 2456.

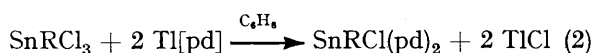
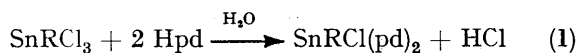
¹² F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 1964, 179.

¹³ G. M. Bancroft, A. G. Maddock, and J. Ward, *Chem. and Ind.*, 1966, 423.

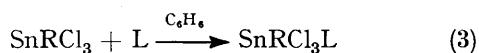
method.¹⁴ All spectra were fitted to Lorentzian line shapes using A. J. Stone's program and techniques previously described.¹⁴ χ^2 Values for all spectra were 500 ± 50 with ca. 500 degrees of freedom. Infrared spectra of Nujol mulls were recorded using a Perkin-Elmer 621 spectrometer.

RESULTS AND DISCUSSION

Method of Preparation.—The reactions of organotin halides with chelating ligands such as pentane-2,4-dionate (pd), quinolin-8-olate (quin), 2,2'-bipyridyl (bipy), and phenanthroline (phen) are well understood.⁷ For example, six-co-ordinate $\text{SnRCl}(\text{pd})_2$ ($\text{R} = \text{Me}$ or Ph) can be formed *via* the routes (1) and (2).^{15,16} Also,



organotin trihalides are known to react directly with neutral ligands such as phen and bipy to give six-co-ordinate $\text{SnRCl}_3(\text{bipy})$ and $\text{SnRCl}_3(\text{phen})$ in a simple addition reaction.^{17,18} Our preparations of $[\text{M}(\text{SnXL}_2)_2]$



and $[\text{M}(\text{SnCl}_3\text{L})]$ compounds were carried out by analogous reactions to those given above. Reaction (2)

$[\text{SnCl}(\text{quin})_2]$ as an isolated product. Our reactions of $[\{\text{Fe}(\text{cp})(\text{CO})_2\}_2\text{SnCl}_2]$ and $[\{\text{Mo}(\text{cp})(\text{CO})_3\}_2\text{SnCl}_2]$ with $\text{TI}[\text{pd}]$ and $\text{TI}[\text{quin}]$ gave products which could not be analyzed and were obviously unstable to both light and air. The Mössbauer and i.r. evidence suggested that the six-co-ordinate $[\text{M}_2(\text{SnL}_2)]$ ($\text{L} = \text{pd}$ or quin) may be present. Because of the previous preparation of *trans*- $[\{\text{Co}(\text{CO})_4\}_2\text{Sn}(\text{pd})_2]$ ² and our preparation of *trans*- $[\text{Mn}(\text{CO})_5\{\text{SnPhCl}_2(\text{phen})\}]$, it seemed likely that the dimetal compounds could be prepared under the proper conditions.

Infrared Spectra and Structure.—The use of CO i.r. stretching frequencies in the $1900\text{--}2200 \text{ cm}^{-1}$ region has greatly facilitated the structural elucidation of metal carbonyl complexes.¹⁸⁻²⁰ Compounds $[\text{Mn}(\text{CO})_5\text{L}]$ ($\text{L} = \text{Cl}$ or Br) have a three-band ($2a_1 + e$) pattern in the carbonyl region corresponding to the C_{4v} local symmetry. If L becomes SnCl_3 or SnR_3 such that the symmetry of the molecule is no longer C_{4v} , the normally i.r.-inactive band b_1 begins to appear [compounds (VII)—(IX), Table 2]. At the same time the e band begins to broaden and eventually splits into a doublet.²⁰

The above variation in i.r. spectra with symmetry is very useful in assigning the structure of many of our $\text{Mn}(\text{CO})_5$ compounds. All compounds showed at least four bands including a b_1 band of appreciable intensity

TABLE 2
CO i.r. stretching bands

Compound	Bands ($\pm 2 \text{ cm}^{-1}$)						
	a_1	b_1	e	a_1'	k_1^e	k_2^e	k_3^e
<i>cis</i> - $[\text{Mn}(\text{CO})_5\{\text{SnCl}(\text{pd})_2\}]$ (I) ^a	2 112 (2 110)	2 055 (2 051)	2 025 (2 022) ^b	1 995 (2 006)	16.20	17.05	0.25
<i>cis</i> - $[\text{Mn}(\text{CO})_5\{\text{SnCl}(\text{quin})_2\}]$ (II)	2 110	2 031	2 016	2 010	16.39	16.66	0.12
<i>fac</i> - $[\text{Mn}(\text{CO})_5\{\text{SnCl}_3(\text{bipy})\}]$ (III)	2 016	2 073	2 021 ^b	2 010	16.58	17.35	0.43
<i>fac</i> - $[\text{Mn}(\text{CO})_5\{\text{SnCl}_3(\text{phen})\}]$ (IV)	2 114	2 070	2 035 ^b	2 010	16.47	17.30	0.29
<i>trans</i> - $[\text{Mn}(\text{CO})_5\{\text{SnPhCl}_2(\text{phen})\}]$ (V)	2 109	2 063	2 012 ^b	2 000	16.41	17.19	0.42
<i>cis</i> - $[\text{Mn}(\text{CO})_5\{\text{SnPh}(\text{pd})_2\}]$ (VI)	2 118	2 068	2 021 ^c	2 001 ^c	16.75	17.27	0.39
$[\text{Mn}(\text{CO})_5(\text{SnCl}_3)]$ (VII) ^d	2 122	2 070	2 043	2 037	16.91	17.31	0.20
$[\text{Mn}(\text{CO})_5(\text{SnPh}_3)]$ (VIII) ^d	2 093	2 027	2 002	2 002	16.34	16.64	0.23
$[\text{Mn}(\text{CO})_5(\text{SnMe}_3)]$ (IX) ^d	2 089	2 021	1 998	1 991	16.29	16.49	0.24
$[\text{Mn}(\text{CO})_4(\text{PPh}_3)(\text{SnCl}_3)]$ (X)	2 090	2 042	1 993			16.81	0.38
$[\text{Mn}(\text{CO})_4(\text{PPh}_3)(\text{SnPh}_3)]$ (XI)	2 049	1 989	1 947			15.98	0.31
<i>fac</i> - $[\text{Mn}(\text{CO})_4(\text{PPh}_3)\{\text{SnCl}_3(\text{bipy})\}]$ (XII)	2 072	2 026	1 974			16.58	0.41
<i>fac</i> - $[\text{Mn}(\text{CO})_4(\text{PPh}_3)\{\text{SnCl}_3(\text{phen})\}]$ (XIII)	2 071	2 027	1 972			16.59	0.44

^a Values in parentheses were obtained from the spectrum in cyclohexane solution. Doublets. ^c Broad. ^d Ref. 24.
^e cm^{-1} .

rather than (1) was used because the $[\text{M}(\text{SnCl}_3)]$ compounds tend to decompose in aqueous solution.

The analogous reactions for SnR_2Cl_2 compounds readily yield the expected six-co-ordinate compounds, $\text{SnR}_2(\text{pd})_2$, $\text{SnR}_2(\text{quin})_2$, $\text{SnR}_2\text{Cl}_2(\text{phen})$, and $\text{SnR}_2\text{Cl}_2(\text{bipy})$. However, the reactions of $[\text{M}_2(\text{SnCl}_2)]$ compounds and the above ligands are not clearly understood at the present time. For example, the reaction of $[\{\text{Fe}(\text{cp})(\text{CO})_2\}_2\text{SnCl}_2]$ and quin³ gives $[\text{Fe}(\text{cp})(\text{CO})_2-$

(Table 2 and Figure 1). In $[\text{Mn}(\text{CO})_5\{\text{SnCl}(\text{pd})_2\}]$ the broad e band in Nujol [Figure 1(a)] split in cyclohexane solution [Figure 1(b)] to give a total of five bands. These similar spectra strongly suggest that the symmetry of the molecule is the same in both solid and solution, and that the local symmetry of all our $\text{Mn}(\text{CO})_5$ compounds is lower than C_{4v} .

For the pd and quin compounds [(I), (II), and (VI),

¹⁴ G. M. Bancroft, 'Mössbauer Spectroscopy: An Introduction for Inorganic Chemists and Geochemists,' McGraw-Hill, London, 1973, and Wiley, New York, 1974.

¹⁵ K. Kawasaki, R. Veeda, T. Tanaka, and R. Okwara, *J. Organometallic Chem.*, 1966, **5**, 194.

¹⁶ G. M. Bancroft and T. K. Sham, unpublished work.

¹⁷ D. Blake, G. E. Coates, and J. M. Tate, *J. Chem. Soc.*, 1961, 756.

¹⁸ J. E. Ferguson, W. R. Roper, and C. J. Wilkins, *J. Chem. Soc.*, 1965, 3716.

¹⁹ W. A. G. Graham, *Inorg. Chem.*, 1968, **7**, 315.

²⁰ L. M. Haines and M. H. B. Stiddard, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 53.

Table 2], the C_{4v} *trans* structure can be ruled out, leaving us with the *cis* structure, (A) (Figure 2), for all three compounds. It seems likely that the previously prepared

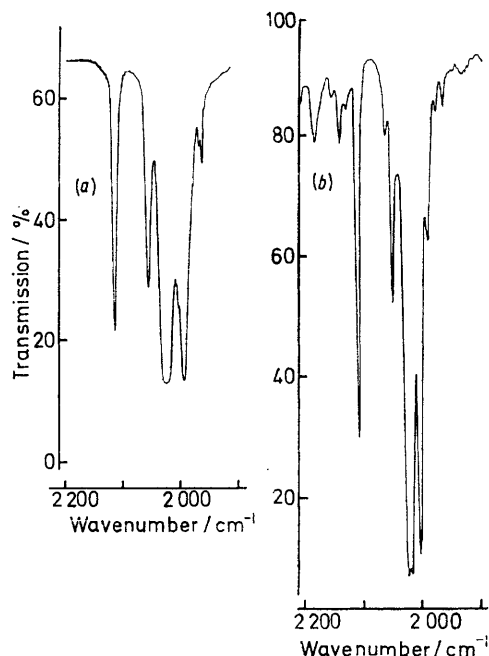


FIGURE 1 Infrared spectra of $[\text{Mn}(\text{CO})_5\{\text{SnCl}(\text{pd})_2\}]$ in the CO stretching-frequency region: (a) in Nujol mull; (b) in cyclohexane solution

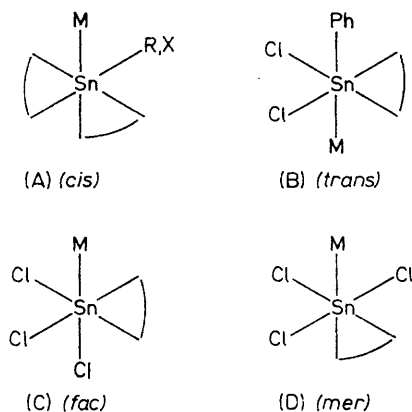


FIGURE 2 Structures for six-co-ordinate tin(IV)-metal compounds

analogues, $[\text{M}\{\text{SnCl}(\text{quin})_2\}]$ [$\text{M} = \text{Fe}(\text{cp})(\text{CO})_2$ or $\text{Mo}(\text{cp})(\text{CO})_3$]³ and $[\text{Co}(\text{CO})_4\{\text{SnCl}(\text{pd})_2\}]$ ² also have the *cis* configuration. These structures are consistent with the Mössbauer quadruple splittings (see below) and the *cis* structure for the $\text{SnRCl}(\text{pd})_2$ compounds.²¹ The Mössbauer quadruple splitting (see below) shows that compound (V) (Table 2) has the *trans* structure, (B) (Figure 2). The five i.r. bands are consistent with this structure.

²¹ N. Serpone and K. A. Hersh, *Inorg. Chem.*, 1974, **13**, 2901.

²² P. G. Harrison, T. J. King, and J. A. Richards, *J.C.S. Dalton*, 1974, 1723.

Once again, the analogous Ph compound, $\text{SnPh}_2\text{Cl}_2(\text{bipy})$, has been shown by X-ray diffraction to have the same structure.²² The other phen and bipy adducts [compounds (III) and (IV)] can have either *fac*, (C), or *mer* structures, (D) (Figure 2). Because both structures have lower than C_{4v} symmetry, it is not possible to distinguish these structures on the basis of the i.r. data. The Mössbauer quadruple splittings (see below) suggest that these compounds, together with the other analogous $\text{Fe}(\text{cp})(\text{CO})_2$ complexes and the Ph and Me analogues,²¹ all have the *fac* structure.

The force constants k_1 , k_2 , and k_i have been calculated using the Cotton-Kraihanzel²³ method. They are compared with those calculated previously for the four-co-ordinate compounds $[\text{Mn}(\text{CO})_5(\text{SnCl}_3)]$ and $[\text{Mn}(\text{CO})_5(\text{SnR}_3)]$ ($\text{R} = \text{Me}$ or Ph).²⁴ There are no discernable trends in the i.r. stretching frequencies or the k values in the six-co-ordinate compounds. The k values and stretching frequencies for the six-co-ordinate compounds nearly all lie between those for the four-co-ordinate $[\text{Mn}(\text{CO})_5(\text{SnCl}_3)]$ and $[\text{Mn}(\text{CO})_5(\text{SnMe}_3)]$. Considering the axial CO a_1' band, it is apparent that this band in the six-co-ordinate compounds lies close to that for $[\text{Mn}(\text{CO})_5(\text{SnPh}_3)]$. This result is perhaps surprising because, for the six-co-ordinate halide complexes at least, the Cl and O bonding atoms are all electronegative compared to the three Ph in $[\text{Mn}(\text{CO})_5(\text{SnPh}_3)]$. There appears then to be more electron density in the CO antibonding orbitals in the six-co-ordinate complexes than might have been expected.

Mössbauer Quadruple Splittings.—The ¹¹⁹Sn Mössbauer parameters and the ⁵⁷Fe Mössbauer parameters for the $\text{Fe}(\text{cp})(\text{CO})_2$ compounds are given in Table 3. The ⁵⁷Fe centre shifts (c.s.) are very similar to those for four-co-ordinate $\text{SnFe}(\text{cp})(\text{CO})_2$ compounds,⁹ while the quadruple splittings (q.s.) are *ca.* 0.1 mm s⁻¹ smaller than those for the four-co-ordinate compounds. Qualitatively, the ¹¹⁹Sn q.s. and c.s. values for the six-co-ordinate compounds are smaller than those for the corresponding four-co-ordinate $[\text{M}(\text{SnCl}_3)]$ species [compounds (XIII)—(XV), Table 3]. Compared to the six-co-ordinate Ph analogues [(XVII)—(XX), Table 3], the M-Sn compounds have larger c.s. values and lower q.s. values. The above trends in q.s. are due to the fact that $|\text{p.q.s.}|_{\text{L}^{\text{oct}}} < |\text{p.q.s.}|_{\text{L}^{\text{tet}}}$,⁸ and that $|\text{p.q.s.}|_{\text{M}} < |\text{p.q.s.}|_{\text{Ph}}$ in both co-ordinations. The quantitative interpretation of these results is given below, while the trends in c.s. are discussed in the next section of this paper.

The i.r. evidence presented earlier strongly suggests that all the pd and quin derivatives [(I), (II), (VII), (IX), and (XII), Table 3] have the *cis* structure, (A). The large q.s. for compound (VIII) is only consistent with the *trans* structure, (B). The *cis* structure would give a q.s. of less than 2 mm s⁻¹. The phen and bipy $[\text{M}(\text{SnCl}_3)]$ adducts could have either structure (C) or (D), but the

²³ F. A. Cotton and C. S. Kraihanzel, *J. Amer. Chem. Soc.*, 1962, **84**, 4432.

²⁴ W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 2271.

additivity treatment discussed below indicates that these compounds have the *fac* structure (C).

The electric field gradient (e.f.g.) expressions for structures (A), (C), and (D) are given in Table 4. Using previously derived (p.q.s.)_L^{oct} values (in mm s⁻¹) for $\frac{1}{2}$ pd (-0.03),²⁵ $\frac{1}{2}$ bipy (-0.08),⁸ $\frac{1}{2}$ phen (-0.04),⁸ $\frac{1}{2}$ quin (-0.05),²⁶ Ph (-0.95),⁸ and Cl (0),⁸ we can now derive (p.q.s.)_M^{oct} values (Table 5) from our q.s. values in Table 3.

these values is satisfying. For example, the values derived from compounds (VII) and (VIII) with electro-positive Ph groups are very similar to those derived from the halide compounds.

If structure (D) is chosen for the phen and bipy [M(SnCl₃)] adducts, much smaller (p.q.s.)_M^{oct} values are calculated which are not consistent with those derived from the other compounds. For example, the (p.q.s.)^{oct}

TABLE 3

¹¹⁹Sn Mössbauer parameters (± 0.02 mm s⁻¹) at 110 °C for six-co-ordinate tin-metal compounds and related compounds. Values given in parentheses are for ⁵⁷Fe

Compound	c.s.	q.s.	Fav. ^a	Ref.
<i>cis</i> -[Mn(CO) ₅ {SnCl(pd) ₂ }] (I)	1.11	1.49	1.06	<i>b</i>
<i>cis</i> -[Mn(CO) ₅ {SnCl(quin) ₂ }] (II)	1.05	1.33	1.04	<i>b</i>
<i>fac</i> -[Mn(CO) ₅ {SnCl ₃ (bipy)}] (III)	1.40	1.24	0.94	<i>b</i>
<i>fac</i> -[Mn(CO) ₅ {SnCl ₃ (phen)}] (IV)	1.35	1.20	0.99	<i>b</i>
<i>fac</i> -[Mn(CO) ₄ (PPh ₃){SnCl ₃ (bipy)}] (V)	1.51	1.33	1.01	<i>b</i>
<i>fac</i> -[Mn(CO) ₄ (PPh ₃){SnCl ₃ (phen)}]·C ₆ H ₆ (VI)	1.52	1.33	1.01	<i>b</i>
<i>cis</i> -[Mn(CO) ₅ {SnPh(pd) ₂ }] (VII)	0.95	1.72	1.07	<i>b</i>
<i>trans</i> -[Mn(CO) ₅ {SnPhCl ₂ (phen)}] (VIII)	1.70	3.25	1.28	<i>b</i>
<i>fac</i> -[Fe(cp)(CO) ₂ {SnCl ₃ (phen)}]·C ₆ H ₆ (IX)	1.47 (0.35)	1.29 (1.71)	1.05 (0.31)	<i>b</i>
<i>fac</i> -[Mn(cp)(CO) ₂ {SnCl ₃ (bipy)}] (X)	1.53 (0.35)	1.43 (1.70)	1.01 (0.27)	<i>b</i>
<i>cis</i> -[Fe(cp)(CO) ₂ {SnCl(quin) ₂ }] (XI)	1.14 (0.34)	1.31 (1.65)	1.00 (0.30)	<i>b</i>
<i>cis</i> -[Mo(cp)(CO) ₃ {SnCl(quin) ₂ }] (XII)	1.10	1.27	1.01	<i>b</i>
[Mn(CO) ₅ (SnCl ₃)] (XIII)	1.65	1.60		4
[Mn(CO) ₄ (PPh ₃)(SnCl ₃)] (XIV)	1.70	1.69		<i>b</i>
[Fe(cp)(CO) ₂ (SnCl ₃)] (XV)	1.75 (0.32)	1.83 (1.80)		4
[Mo(cp)(CO) ₃ (SnCl ₃)] (XVI)	1.69	1.71		6
SnPhCl ₃ (bipy) (XVII)	0.87	1.50		<i>c</i>
SnPhCl(pd) ₂ (XVIII)	0.61	1.78		25
SnPh ₂ (pd) ₂ (XIX)	0.71	2.07		25
SnPhCl(quin) ₂ (XX)	0.67	1.48		27

^a Line-widths for the two peaks are within 0.03 mm s⁻¹. ^b This work. ^c F. P. Mullins, *Canad. J. Chem.*, 1970, **48**, 1677.

To provide the overall best (p.q.s.)_M^{oct} values, we have averaged all (p.q.s.)_M^{oct} values except for those determined from quin compounds [except for compound (XII)

values for Mn(CO)₅ derived from the q.s. for compounds (III) and (IV) are both -0.58 mm s⁻¹, very much smaller than the -0.71 mm s⁻¹ average given above. The additivity treatment strongly suggests that these adducts all have the *fac* structure.

In Table 5, it is apparent that the (p.q.s.)_L^{oct} values are all substantially smaller than the (p.q.s.)_L^{tet} values. The four-co-ordinate (p.q.s.)_M values in Table 5 were

TABLE 4

Electric field gradient expressions for isomers (A), (C), and (D)

Isomer	Expression
(A)	$V_{zz}/e = 2[M] - [L] - [R]$ $V_{yy}/e = 2[R] - [M] - [L]$ $V_{xx}/e = 2[L] - [R] - [M]$
(C), [Cl] = 0	$V_{zz}/e = 2[M] - 2[L]$ $V_{yy}/e = [L] - [M]$ $V_{xx}/e = [L] - [M]$
(D), [Cl] = 0	$V_{zz}/e = 2[M] - [L]$ $V_{yy}/e = -[M] - 2[L]$ $V_{xx}/e = [L] - [M]$

[L], [M] etc. are partial field gradients.

of course]. The q.s. values for SnR₂(quin)₂ compounds²⁷ vary over a wide range, and the (p.q.s.)_{quin} value seems less well-defined than the other values. For Mn(CO)₅, the (p.q.s.)_M^{oct} values (mm s⁻¹) derived from compounds (I), (III), (IV), (VII), and (VIII) [assuming the *fac* structure for compounds (III) and (IV)] are -0.76, -0.70, -0.64, -0.73, and -0.71 respectively giving an average value of -0.71 \pm 0.05 mm s⁻¹ (where the error reflects the standard deviation of these values). Considering the wide variation in structure and bonding about the Sn in these six compounds, the consistency of

²⁵ G. M. Bancroft and T. K. Sham, *Canad. J. Chem.*, 1974, **52**, 1361.

TABLE 5

Derived octahedral p.q.s. values and previously derived tetrahedral p.q.s. values (mm s⁻¹)

L	(p.q.s.) _L ^{oct}	Estimator ^a	(p.q.s.) _L ^{tet}	Ref.
Cl, Br	0		0	8
I	-0.14		-0.17	8
Mo(cp)(CO) ₃	-0.66	(XII)	-0.75	<i>b</i>
Mn(CO) ₅	-0.71	(I), (III), (IV), (VII), (VIII)	-0.97	4
Mn(CO) ₄ (PPh ₃)	-0.73	(V), (VI)	-1.01	<i>c</i>
Fe(cp)(CO) ₂	-0.74	(IX), (XI)	-1.08	4
Ph	-0.95	Ref. 8	-1.26	8
Me	-1.03	Ref. 8	-1.37	8

^a See compounds in Table 3. ^b K. D. Butler, Ph.D. Thesis, University of Western Ontario, 1974. ^c By interpolation, see text.

derived from the nearly tetrahedral [M(SnR₃)] compounds⁴ wherever possible. Since a q.s. has not been

²⁶ G. M. Bancroft, V. G. Kumar Das, T. K. Sham, and M. G. Clark, *J.C.S. Dalton*, in the press.

²⁷ G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59.

resolved for $[\text{Mn}(\text{CO})_4(\text{PPh}_3)(\text{SnPh}_3)]$, a $(p.q.s.)_{\text{L}}^{\text{tet}}$ value for $\text{Mn}(\text{CO})_4(\text{PPh}_3)$ has not been derived. To obtain a reasonable estimate of this value, we plotted the q.s. values of the $[\text{M}(\text{SnCl}_3)]$ compounds $[\text{M} = \text{Fe}(\text{cp})(\text{CO})_2, \text{Mn}(\text{CO})_5, \text{Co}(\text{CO})_4, \text{Mo}(\text{cp})(\text{CO})_3, \text{and } \text{Mn}(\text{CO})_4(\text{PPh}_3)]$ against the known $(p.q.s.)_{\text{M}}^{\text{tet}}$ values and interpolated a $(p.q.s.)_{\text{L}}^{\text{tet}}$ value for $\text{Mn}(\text{CO})_4(\text{PPh}_3)$ of -1.01 mm s^{-1} . The smaller $(p.q.s.)_{\text{L}}^{\text{oct}}$ values are consistent with previous predictions based on a molecular-orbital treatment⁸ in which the p.q.s. values can be approximated by equations (4) and (5) for sp^3 hybridized Sn^{IV} and d^2sp^3 (or

$$(p.q.s.)_{\text{L}}^{\text{tet}} = -\frac{1}{2}e^2Q\left|\frac{3}{10}\langle r^{-3} \rangle\right| p\sigma^{\text{tet}} \quad (4)$$

$$(p.q.s.)_{\text{L}}^{\text{oct}} = -\frac{1}{2}e^2Q\left|\frac{1}{5}\langle r^{-3} \rangle\right| p\sigma^{\text{oct}} \quad (5)$$

sp) hybridized Sn respectively. In these expressions, the σ parameters describe the involvement of the tin hybrid in the M-Sn bond. As the donor properties of M increase, σ increases. Taking the quotient of the two

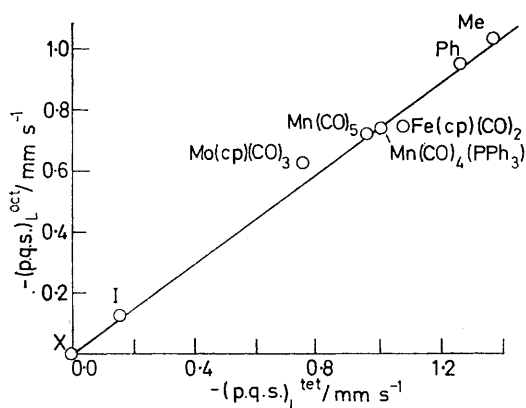


FIGURE 3 Plot of $(p.q.s.)_{\text{L}}^{\text{oct}}$ against $(p.q.s.)_{\text{L}}^{\text{tet}}$ for seven ligands

expressions above, $(p.q.s.)_{\text{L}}^{\text{oct}}/(p.q.s.)_{\text{L}}^{\text{tet}} = 0.67(\sigma^{\text{oct}}/\sigma^{\text{tet}})$. Provided that $\sigma^{\text{oct}} \sim \sigma^{\text{tet}}$, the quotient of the $(p.q.s.)$ values should be *ca.* 0.67.

The quotient of the $(p.q.s.)_{\text{L}}$ values in Table 5 is always *ca.* 0.73, and a plot of $(p.q.s.)_{\text{L}}^{\text{oct}}$ against $(p.q.s.)_{\text{L}}^{\text{tet}}$ (Figure 3) gave a good linear plot according to equation (6). The

$$(p.q.s.)_{\text{L}}^{\text{oct}} = (0.73 \pm 0.04)(p.q.s.)_{\text{L}}^{\text{tet}} - (0.01 \pm 0.04) \text{ mm s}^{-1} \quad (6)$$

intercept was very close to 0 mm s^{-1} as it should be, and the R value (0.991) shows that this is a very good correlation. The gradient of 0.73 is slightly larger than the value of 0.67 for equal σ values. The value of 0.73 could be due to σ^{oct} being larger than σ^{tet} . Another possible reason for the larger value is that the $(p.q.s.)_{\text{L}}^{\text{tet}}$ values were derived from SnR_3X ($\text{R} = \text{Ph}$, or alkyl) and $[\text{M}(\text{SnR}_3)]$ [$\text{M} = \text{Mn}(\text{CO})_5, \text{Fe}(\text{cp})(\text{CO})_2, \text{or } \text{Mo}(\text{cp})(\text{CO})_3$] compounds in which the s character in the Sn-R or Sn-M bond respectively is slightly greater than that expected on the basis of sp^3 hybridization. This greater s character makes the $(p.q.s.)_{\text{L}}^{\text{tet}}$ values less negative

than expected, resulting in an increase in $(p.q.s.)_{\text{L}}^{\text{oct}}/(p.q.s.)_{\text{L}}^{\text{tet}}$. A similar effect could take place to decrease $|(p.q.s.)_{\text{L}}^{\text{oct}}|$, but we feel that this effect should be smaller. The very large structural distortions possible in tetrahedral compared to octahedral compounds is consistent with this argument.

It is interesting to note that the order of $(p.q.s.)_{\text{M}}^{\text{oct}}$ values is identical to the order of $(p.q.s.)_{\text{M}}^{\text{tet}}$ values. The relative bonding properties of the metal moieties are the same in six- and four-co-ordination, and the bonding properties of two metal moieties are consistently different. Thus, as in four-co-ordination, the p -donor ability increases in the order $\text{X} < \text{I} \ll \text{Mo}(\text{cp})(\text{CO})_3 < \text{Mn}(\text{CO})_5 < \text{Mn}(\text{CO})_4(\text{PPh}_3) \leq \text{Fe}(\text{cp})(\text{CO})_2 < \text{Ph} < \text{Me}$. Dickinson *et al.*⁶ recently reported $|(p.q.s.)_{\text{L}}^{\text{tet}}|$ values for metal moieties which are significantly smaller than ours. For example, the $(p.q.s.)_{\text{M}}$ values derived from nearly tetrahedral $[\text{Fe}(\text{cp})(\text{CO})_2(\text{SnBu}_3)]$ and $[\text{Mn}(\text{CO})_5(\text{SnMe}_3)]$ ⁴ are -1.08 and -0.97 mm s^{-1} respectively, while those derived⁶ from $[\text{Fe}(\text{cp})(\text{CO})_2(\text{SnCl}_3)]$ and $[\text{Mn}(\text{CO})_5(\text{SnCl}_3)]$ are -0.95 and -0.83 mm s^{-1} respectively. As has been pointed out,⁹ this variation is largely due to the increase in s character in the Sn-M bond from the $[\text{M}(\text{SnR}_3)]$ to the $[\text{M}(\text{SnCl}_3)]$ compounds. Since the derivation of $(p.q.s.)_{\text{L}}^{\text{tet}}$ [equation (4)] refers to sp^3 hybridization, it seems more reasonable to determine the $(p.q.s.)_{\text{L}}^{\text{tet}}$ values from structures which are closest to tetrahedral whenever possible. Variations in $(p.q.s.)_{\text{L}}^{\text{tet}}$ values can often then be discussed⁹ on the basis of varying s character in the Sn-M bond. When the $(p.q.s.)_{\text{L}}^{\text{tet}}$ values of Dickinson *et al.*⁶ are plotted against $(p.q.s.)_{\text{L}}^{\text{oct}}$, the gradient of the line becomes 0.77 ± 0.04 . This larger value is consistent with our s -character argument used earlier.

Besides the apparent interpretive advantages, our $(p.q.s.)_{\text{L}}^{\text{tet}}$ values usually give significantly better agreement between predicted and observed q.s.²⁸ than those given by Dickinson *et al.*⁶ Thus for 34 dihalide compounds $[\text{M}_2(\text{SnX}_2)]$, $[\text{MR}(\text{SnX}_2)]$, and $[\text{MM}'(\text{SnX}_2)]$ [$\text{R} = \text{Me}$ or Ph ; $\text{M}, \text{M}' = \text{Cr}(\text{cp})(\text{CO})_3, \text{Mo}(\text{cp})(\text{CO})_3, \text{W}(\text{cp})(\text{CO})_3, \text{Mn}(\text{CO})_5, \text{Co}(\text{CO})_4, \text{or } \text{Fe}(\text{cp})(\text{CO})_2$; $\text{X} = \text{Cl}, \text{Br}$, or I], a plot of predicted against observed q.s. gave a gradient of 0.97 ± 0.14 and an intercept of 0.01 ± 0.08 using our $(p.q.s.)_{\text{L}}^{\text{tet}}$ values derived from $[\text{M}(\text{SnR}_3)]$ compounds. Using the values of Dickinson *et al.*,⁶ the gradient and intercept are 0.92 ± 0.10 and -0.15 ± 0.2 respectively. For 67 organometallic tin compounds the correlation coefficient is 0.98 in both cases, but our gradient of 0.96 ± 0.02 is significantly higher than 0.90 ± 0.02 using the values of Dickinson *et al.*⁶ For both theoretical and practical reasons then, our $(p.q.s.)_{\text{L}}^{\text{tet}}$ values seem to be better working values than those given by Dickinson *et al.*⁶

Centre Shifts.—As mentioned earlier, the c.s. values for the six-co-ordinate M-Sn compounds are considerably larger than those for their Ph-Sn analogues [see compounds (I) and (XVIII), (II) and (XX), (III) and

²⁸ G. M. Bancroft and K. D. Butler, *Inorg. Chim. Acta*, 1975, 15, 57.

(XVII)]. As with four-co-ordinate M-Sn and Ph-Sn compounds,⁴ the larger c.s. is due to the larger *s* character in the Sn-M than in the Sn-Ph bond. To compare the *s* characters in Sn-M bonds, we can compare the c.s. values for analogous compounds⁴ [(I)—(XII), Table 3]. The order of increasing *s* character in the L-Sn bond is Cl, Br \ll Ph < Me < Mn(CO)₅ \leq Mo(cp)(CO)₃ < Mn(CO)₄(PPh₃) \leq Fe(cp)(CO)₂. This order is the same as that derived previously from four-co-ordinate struc-

tures [ref. 4 and compounds (XIII)—(XVI)]. Together with the order of (p.q.s.)_L^{tet} values discussed earlier, the *s*-character series shows that the relative bonding properties of the metal groups are very similar in both four- and six-co-ordinate structures.

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