The Correlation between Tin-119 Mössbauer Isomer Shifts and Atomic Charges on Tin in Five-co-ordinated Tin(IV) Derivatives

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Tin-119 Mössbauer isomer shifts, δ, are correlated to partial atomic charges on tin, Q_{Sn}, calculated through a valence state electronegativity equalization procedure, for a number of homologous series of five-co-ordinated Sn^{IV} and $Sn^{IV}R_n$ (n = 1–3) derivatives. Isostructural species are found to be generally described by a single correlation function. The use of δ/Q_{Sn} correlations for structural assignments is proposed.

A satisfactory rationalization of the Mössbauer isomer shift, δ, in tin(IV) derivatives seems to be obtainable through its correlation with partial atomic charges on tin, Q_{Sn}, as extracted by an orbital electronegativity equalization procedure.[1] The relationship δ/Q_{Sn} would mainly give information on the structure of the environment of the tin atoms,[1] thus supplementing the well established procedures based on the nuclear quadrupole splitting.

Our previous work in this field essentially concerned octahedral tin(IV) adducts.[1,2] We report here the results obtained for several homologous series of five-co-ordinated tin(IV) derivatives, representative of complexes and adducts of $Sn^{IV}R_n$ (n = 0—3) with uni- and multi-dentate ligands. These series include the classic halide (X) complexes $[SnR_3X_2]^-$ and $[SnR_2X_3]^-$, the large series of adducts $SnR_3X'(E{=}O)$, $SnR_2X'_2(E{=}O)$, and $[SnR_3(E{=}O)_2]^+$ [X′ = halide or thiocyanate; R = Me, Et, Pr^n, Bu^n, Ph, or n-C_8H_{17}; E=O = various oxygen-containing ligands (see Table 1)], the complexes of $Sn^{IV}R_2$ with quinolin-8-olate, and the complexes of $Sn^{IV}R_2$, $Sn^{IV}R$, and Sn^{IV} with tridentate Schiff-base dianions having ONO and SNO donor atoms.

Experimental

Calculation of Partial Charges; Valence Bond Structures.— Partial atomic charges Q_{Sn} have been calculated according to the principle of orbital electronegativity equalization upon bond formation,[3a-3f] using the semi-empirical approach by Jolly and Perry [3g,3h] and their computer program CHELEQ; these concepts and the related procedures, as applied to our δ/Q_{Sn} correlations, have been amply illustrated earlier.[1] The treatment by Jolly and Perry [3g,3h] is preferred (see ref. 1) in the present context mainly because it implies incomplete equalization of valence state electronegativities, which seems to be physically more correct than complete equalization carried out over all atoms in any given molecule.[1] In our δ/Q_{Sn} correlations, Q_{Sn} data are spread out into larger numerical intervals and yield smoother least-squares fitting lines, which are easier to interpret and discuss.[1]

The assignment of structures, bond orders N_{ij} [for the bond(s) between atoms i and j], and formal charges F to the compounds under study requires particular care (N_{ij} and F values for the environment of the tin atoms, and also for further bonds formed by the atoms directly bound to tin), these greatly influencing charge transfer upon equalization and ultimately the magnitude of the CHELEQ Q_{Sn} data.[1] In this work the five-co-ordinated structures, (I)—(III) (Figure 1), have been assigned as indicated in Table 1, essentially on the basis of X-ray data * as well as spectroscopic investigations.[4-25]

The valence bond formulae (I)—(III) in Figure 1 essenti-

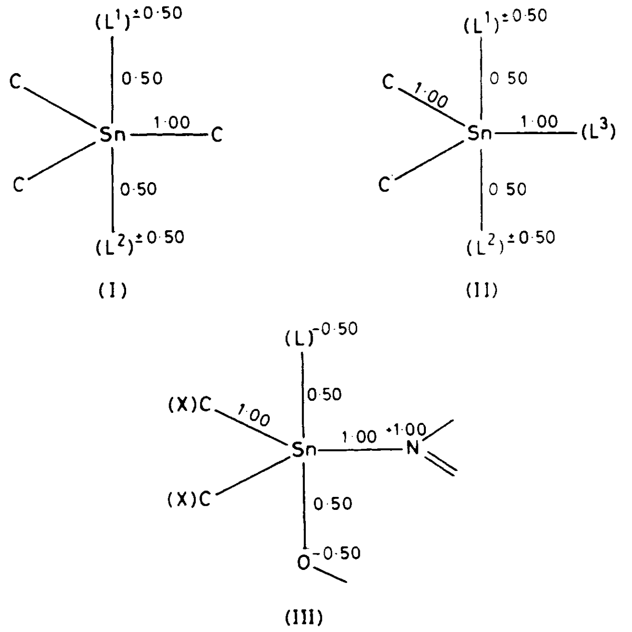

Figure 1. Valence bond structures of tin environments, assumed in the estimation of partial atomic charges by valence state electronegativity equalization. Bond orders, N_{ij}, and formal charges, F (input parameters for the program CHELEQ), are shown for the atoms bound to tin; to the other atoms and bonds in the complex molecules, these parameters have been attributed according to commonly accepted valence bond formulae.[3g,3h] Ligand atoms L, and related F values, are as follows (for equatorial atoms, input F = 0.00 are used unless otherwise stated): axial ligands (atoms $L^{1,2}$ and L) $X^{-0.5}$; $N^{-0.5}$ (of S=C=N); $O^{+0.5}$ (of E=O and H_2O); $O^{-0.5}$ (of pyo, $N^{+1.0}$–$O^{-1.0}$, see text); $S^{-0.5}$ (of S–Ph); $O^{-0.5}$ (of O–Ph)

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* (*a*) $[SnR_3Cl_2]^-$ (R = Me, Bu^n, or Ph): P. J. Vergamini, H. Varenkamp, and L. F. Dahl, *J. Am. Chem. Soc.*, 1971, **93**, 6327; P. G. Harrison, K. Molloy, R. C. Phillips, P. J. Smith, and A. J. Crowe, *J. Organomet. Chem.*, 1978, **160**, 421. (*b*) $[SnMe_3Br_2]^-$, $[SnMe_3(OPR_3)_2]^+$, $SnMe_3Cl(OPR_3)$: L. A. Aslanov, V. M. Attiya, V. M. Ionov, A. B. Permin, and V. S. Petrosyan, *J. Struct. Chem. USSR*, 1977, **18**, 884. (*c*) $[SnMe_2Cl_3]^-$: F. B. W. Einstein and B. R. Penfold, *J. Chem. Soc. A*, 1968, 3019; A. J. Buttenshaw, M. Duchêne, and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1975, 2230. (*d*) $SnPh_3(NO_3)(E{=}O)$ (E = $AsPh_3$ or PPh_3) and related adducts: M. Nardelli, C. Pelizzi, and G. Pelizzi, *J. Organomet. Chem.*, 1976, **112**, 263; 1977, **125**, 161; *Inorg. Chim. Acta*, 1979, **33**, 181. (*e*) $SnPh_3(NO_3)(pyo)$: C. Pelizzi, G. Pelizzi, and P. Tarasconi, *J. Organomet. Chem.*, 1977, **124**, 151 and refs. therein. (*f*) $SnR_2(hpsala)$ (R = Me or Ph) and $SnPh_2(mpsala)$: H. Preut, F. Huber, H.-J. Haupt, R. Cefalù, and R. Barbieri, *Z. Anorg. Allg. Chem.*, 1974, **410**, 88; H. Preut, F. Huber, R. Barbieri, and N. Bertazzi, *ibid.*, 1976, **423**, 75; H. Preut, H.-J. Haupt, F. Huber, R. Cefalù, and R. Barbieri, *ibid.*, 1974, **407**, 257.

Table 1. Partial charges on tin, Q_{Sn}, calculated through an electronegativity equalization procedure (see text), and ^{119}Sn Mössbauer isomer shifts, δ, for homologous series of five-co-ordinated tin(IV) complexes and adducts

Compound [a]	Q_{Sn}	δ^{b}/mm s^{-1}	Ref. for δ
(1) $[NBu^{n}_{4}][SnMe_{3}I_{2}]$	−0.061	1.42	4
(2) $[NEt_{4}][SnMe_{3}Br_{2}]$	−0.033	1.43	5
(3a) $[NEt_{4}][SnMe_{3}Cl_{2}]$	−0.025	1.42; 1.24	5; 6
(3b) $[NMe_{4}][SnMe_{3}Cl_{2}]$		1.27	7
(3c) $[PPh_{3}(CH_{2}Ph)][SnMe_{3}Cl_{2}]$		1.43	*c*
(4a) $[NEt_{4}][SnBu^{n}_{3}BrCl]$	−0.025	1.48	8
(4b) $[NBu^{n}_{4}][SnBu^{n}_{3}BrCl]$		1.46	8
(5) $[PPh_{3}(CH_{2}Ph)][SnEt_{3}Cl_{2}]$	−0.021	1.56; 1.50; 1.42	*c*; 5; 7
(6) $[PPh_{3}(CH_{2}Ph)][SnPr^{n}_{3}Cl_{2}]$	−0.021	1.55	*c*
(7a) $[PPh_{3}(CH_{2}Ph)][SnBu^{n}_{3}Cl_{2}]$	−0.021	1.50	*c*
(7b) $[PPh_{4}][SnBu^{n}_{3}Cl_{2}]$		1.55	*c*
(7c) $[PBu^{n}_{4}][SnBu^{n}_{3}Cl_{2}]$		1.54	*c*
(7d) $[NBu^{n}_{4}][SnBu^{n}_{3}Cl_{2}]$		1.52	8
(8) $[PPh_{3}(CH_{2}Ph)][Sn(CH_{2}Ph)_{3}Cl_{2}]$	−0.017	1.59	*c*
(9) $[NHEt_{3}][SnMePh_{2}ICl]$	0.005	1.45	9
(10) $[NHEt_{3}][SnMePh_{2}BrCl]$	0.020	1.41	9
(11) $[NHEt_{3}][SnMePh_{2}Cl_{2}]$	0.024	1.44	9
(12a) $[NHEt_{3}][SnPh_{3}ICl]$	0.029	1.39	9
(12b) $[NBu^{n}_{4}][SnPh_{3}ICl]$		1.37	8
(13) $[PPh_{3}(n\text{-}C_{10}H_{21})][SnPh_{3}Br_{2}]$	0.039	1.29	10
(14a) $[NHEt_{3}][SnPh_{3}BrCl]$	0.044	1.37	9
(14b) $[NEt_{4}][SnPh_{3}BrCl]$		1.34	8
(14c) $[NBu^{n}_{4}][SnPh_{3}BrCl]$		1.28	8
(14d) $[PPh_{3}(n\text{-}C_{10}H_{21})][SnPh_{3}BrCl]$		1.26	10
(15a) $[NMe_{4}][SnPh_{3}Cl_{2}]$	0.048	1.32; 1.23	5; 7
(15b) $[NBu^{n}_{4}][SnPh_{3}Cl_{2}]$		1.31	8
(15c) $[PPh_{3}(n\text{-}C_{10}H_{21})][SnPh_{3}Cl_{2}]$		1.23	10
(15d) $[PPh_{3}(CH_{2}Ph)][SnPh_{3}Cl_{2}]$		1.34	*c*
(15e) $[AsPh_{3}(CH_{2}COPh)][SnPh_{3}Cl_{2}]$		1.43	*c*
(16) $[NHEt_{3}][SnMePh_{2}FCl]$	0.053	1.31	9
(17) $[NHEt_{3}][SnPh_{3}FCl]$	0.078	1.23	9
(18) $[NBu^{n}_{4}][SnMe_{2}ICl_{2}]$	0.035	1.41	8
(19) $[NBu^{n}_{4}][SnBu^{n}_{2}ICl_{2}]$	0.038	1.58	8
(20a) $[NMe_{4}][SnMe_{2}Br_{3}]$	0.052	1.46	7
(20b) $[NEt_{4}][SnMe_{2}Br_{3}]$		1.52	5
(21a) $[NEt_{4}][SnMe_{2}BrCl_{2}]$	0.060	1.43	8
(21b) $[NBu^{n}_{4}][SnMe_{2}BrCl_{2}]$		1.36	8
(22a) $[NEt_{4}][SnBu^{n}_{2}BrCl_{2}]$	0.063	1.51	8
(22b) $[NBu^{n}_{4}][SnBu^{n}_{2}BrCl_{2}]$		1.55	8
(23a) $[NEt_{4}][SnMe_{2}Cl_{3}]$	0.078	1.48; 1.40; 1.44	5; 6; 11
(23b) $[NBu^{n}_{4}][SnMe_{2}Cl_{3}]$		1.39	8
(23c) $[AsPh_{4}][SnMe_{2}Cl_{3}]$		1.42	5
(24) $[AsPh_{4}][SnEt_{2}Cl_{3}]$	0.081	1.54	5
(25) $[NBu^{n}_{4}][SnBu^{n}_{2}Cl_{3}]$	0.081	1.56	8
(26) $[NBu^{n}_{4}][SnPh_{2}ICl_{2}]$	0.083	1.32	8
(27) $[NEt_{4}][SnMePhCl_{3}]$	0.103	1.28	12
(28a) $[NEt_{4}][SnPh_{2}BrCl_{2}]$	0.109	1.36	8
(28b) $[NBu^{n}_{4}][SnPh_{2}BrCl_{2}]$		1.28	8
(29a) $[NEt_{4}][SnPh_{2}Cl_{3}]$	0.127	1.25	6
(29b) $[NBu^{n}_{4}][SnPh_{2}Cl_{3}]$		1.20	8
(30) $SnMe_{3}Cl(Ph_{3}PO)$	0.146	1.45	13
(31) $SnBu^{n}_{2}PhBr(Ph_{3}PO)$	0.169	1.42	14
(32) $SnBu^{n}_{2}PhCl(Ph_{3}PO)$	0.173	1.41	14
(33) $SnBu^{n}Ph_{2}Br(Ph_{3}PO)$	0.192	1.34	14
(34) $SnPh_{3}Br(Ph_{3}PO)$	0.215	1.29	10
(35) $SnPh_{3}Cl(Ph_{3}PO)$	0.219	1.28; 1.29	10; 15
(36) $SnPh_{3}(NCS)(Ph_{3}PO)$	0.228	1.22	10
(37) $SnBu^{n}_{2}PhBr(Ph_{3}AsO)$	0.167	1.42	14
(38) $SnBu^{n}_{2}PhCl(Ph_{3}AsO)$	0.172	1.37	14

[a] Compounds (1)—(17), (30)—(55), and (62)—(77) have structure (I); compounds (18)—(29) and (56)—(61) have structure (II); compounds (78)—(112) have structure (III): see Figure 1. Ligand abbreviations: dma = *NN*-dimethylacetamide, hmpa = hexamethylphosphoramide, pyo = pyridine *N*-oxide, 4Me-pyo = 4-methylpyridine *N*-oxide, dmf = *NN*-dimethylformamide, quin = quinolin-8-olate, H_2hmbatp = *o*-(3-hydroxy-1-methylbut-2-enylideneamino)thiophenol (SNO donor), H_2mpsala = *N*-(*o*-mercaptophenyl)salicylaldimine (SNO donor), H_2hmppap = *o*-(3-hydroxy-1-methyl-3-phenylprop-2-enylideneamino)phenol (ONO donor), H_2hpsala = *N*-(*o*-hydroxyphenyl)salicylaldimine (ONO donor). [b] At liquid N_2 temperature, relative to room-temperature SnO_2, $BaSnO_3$, or $CaSnO_3$. Values separated by semi-colons are from the corresponding references in the next column. [c] P. G. Harrison, K. Molloy, R. C. Phillips, P. J. Smith, and A. J. Crowe, *J. Organomet. Chem.*, 1978, **160**, 421.

Table 1 (*continued*)

Compound [a]	Q_{Sn}	δ [b]/mm s^{-1}	Ref. for δ
(39) $SnBu^nPh_2Br(Ph_3AsO)$	0.190	1.37	14
(40) $SnPh_3Cl(Ph_3AsO)$	0.218	1.29	15
(41) $SnMe_3Cl(dma)$	0.145	1.50	13
(42) $SnPh_3Cl(dma)$	0.218	1.31	15
(43) $SnMe_3Cl(hmpa)$	0.147	1.44	13
(44) $SnPh_3Br(Me_2SO)$	0.216	1.31	10
(45) $SnPh_3Cl(Me_2SO)$	0.220	1.27; 1.26	10; 15
(46) $SnPh_3Cl(Pr^n{}_2SO)$	0.220	1.28	15
(47) $SnPh_3Cl(Bu^n{}_2SO)$	0.220	1.30	15
(48) $SnPh_3Cl(CH_2CH_2CH_2CH_2-SO)$	0.220	1.29	15
(49) $SnPh_3Cl[(MeO)_3PO]$	0.221	1.31	15
(50) $SnPh_3Cl[(EtO)_3PO]$	0.221	1.30	15
(51) $SnPh_3Cl[(PhO)_3PO]$	0.221	1.31	15
(52) $SnMe_3Cl(4Me\text{-}pyo)$	0.003	1.44	13
(53) $SnPh_3Br(pyo)$	0.072	1.28	10
(54) $SnPh_3Cl(pyo)$	0.076	1.22; 1.30	10; 15
(55) $SnPh_3(NCS)(pyo)$	0.085	1.20	10
(56) $SnPh_2Cl_2(Ph_3PO)$	0.299	1.25; 1.20	16; 17
(57) $SnPh_2Cl_2(Ph_3AsO)$	0.297	1.21	16
(58) $SnPh_2Cl_2(Me_2SO)$	0.300	1.21	17
(59) $SnPh_2Cl_2(Pr^n{}_2SO)$	0.300	1.27	17
(60) $SnPh_2Cl_2(Bu^n{}_2SO)$	0.300	1.25	17
(61) $SnPh_2Cl_2(CH_2CH_2CH_2CH_2-SO)$	0.300	1.23	17
(62) $[SnMe_3(Ph_3PO)_2][BPh_4]$	0.319	1.28	18
(63) $[SnBu^n{}_3(Ph_3PO)_2][BPh_4]$	0.323	1.52	19
(64) $[SnBu^n{}_2Ph(Ph_3PO)_2][BPh_4]$	0.346	1.41	14
(65) $[SnBu^nPh_2(Ph_3PO)_2][BPh_4]$	0.369	1.28	14
(66) $[SnMe_3(Ph_3AsO)_2][BPh_4]$	0.316	1.18	18
(67) $[SnBu^n{}_3(Ph_3AsO)_2][BPh_4]$	0.320	1.45	19
(68) $[SnBu^n{}_2Ph(Ph_3AsO)_2][BPh_4]$	0.343	1.34	14
(69) $[SnBu^nPh_2(Ph_3AsO)_2][BPh_4]$	0.366	1.25	14
(70) $[SnMe_3(dmf)_2][BPh_4]$	0.317	1.34	19
(71) $[SnBu^n{}_3(dmf)_2][BPh_4]$	0.321	1.57	19
(72) $[SnMe_3(Me_2SO)_2][BPh_4]$	0.321	1.30	18
(73) $[SnBu^n{}_3(Me_2SO)_2][BPh_4]$	0.326	1.51	19
(74) $[SnPh_3(Me_2SO)_2][BPh_4]$	0.395	1.27	18
(75) $[SnMe_3(hmpa)_2][BPh_4]$	0.320	1.34	18
(76) $[SnMe_3(OH_2)_2][BPh_4]$	0.275	1.42	6
(77) $[SnBu^n{}_3(pyo)_2][BPh_4]$	0.035	1.54	19
(78) $SnEt_2I(quin)$	0.283	1.43	20
(79) $SnEt_2Br(quin)$	0.298	1.39	20
(80) $SnMe_2Cl(quin)$	0.300	1.26; 1.22	20; 11
(81) $SnEt_2Cl(quin)$	0.303	1.34	20
(82) $SnPr^n{}_2Cl(quin)$	0.303	1.31	20
(83) $SnBu^n{}_2Cl(quin)$	0.303	1.40	20
(84) $Sn(n\text{-}C_8H_{17})_2Cl(quin)$	0.303	1.56	20
(85) $SnEt_2(NCS)(quin)$	0.311	1.31	20
(86) $SnBu^n{}_2(NCS)(quin)$	0.311	1.33	21
(87) $SnBu^nPhCl(quin)$	0.326	1.28	14
(88) $SnPh_2Cl(quin)$	0.349	1.12; 1.07; 1.08	20; 11; 21
(89) $SnPh_2(NCS)(quin)$	0.358	0.98	21
(90) $SnMe_2(hmbatp)$	0.283	1.25	22
(91) $SnMe_2(mpsala)$		1.22	22
(92) $SnPh_2(hmbatp)$	0.332	1.18	22
(93) $SnPh_2(mpsala)$		1.17	22
(94) $SnMeCl(hmbatp)$	0.387	1.00	23
(95) $SnMeCl(mpsala)$		1.03	23
(96) $Sn(n\text{-}C_8H_{17})Cl(mpsala)$		1.06	23
(97) $SnPhCl(mpsala)$	0.411	0.99	23
(98) $SnBr_2(hmbatp)$	0.451	0.86	24
(99) $SnBr_2(mpsala)$		0.73	24
(100) $SnCl_2(mpsala)$	0.491	0.56	24
(101) $SnMe_2(hmppap)$	0.317	1.25	22
(102) $SnMe_2(hpsala)$		1.21; 1.14; 1.13	22; 25; 11
(103) $SnPh_2(hmppap)$	0.366	1.02	22
(104) $SnPh_2(hpsala)$		1.03; 0.99	22; 25
(105) $SnMeCl(hmppap)$	0.422	0.86	23
(106) $SnMeCl(hpsala)$		0.87	23

Table 1 (*continued*)

Compound [a]	Q_{Sn}	δ [b]/mm s^{-1}	Ref. for δ
(107) $Sn(n-C_8H_{17})Cl(hmppap)$	0.423	0.96	23
(108) SnPhCl(hmppap)	0.446	0.82	23
(109) $SnBr_2(hmppap)$	0.486	0.62	24
(110) $SnBr_2(hpsala)$		0.43	24
(111) $SnCl_2(hmppap)$	0.526	0.40	24
(112) $SnCl_2(hpsala)$		0.42	24

ally imply sp^2 hybridized tin and a tin p orbital forming the two axial bonds through three-centre molecular orbitals. The participation of tin 5d orbitals in bonding is not taken into account in this context, in line with earlier general views,[3d] as well as with the circumstance that reliable values of tin 5d-orbital electronegativities are apparently not available.[1] The bonding scheme assumed here is certainly acceptable for (I), but it appears to be rather unrealistic for equatorial halide, or oxygen atoms, in (II), and equatorial halide and heterocyclic nitrogen (or phenol oxygen) in (III). This is the case even if the input values $F = 0.00$ and $+1.00$ for the equatorial atoms shift to equilibrium values more or less consistent with those expected. Anyway, we generally employed the valence bond structures (I)—(III) for all the compounds examined here, for the following reasons: (*i*) to avoid the complications and ambiguities inherent in the use of different N_{ij} and F parameters within given homologous series, and consequently (*ii*) to present to Mössbauer spectroscopists an easy to handle semi-empirical (but working) method of rationalization of δ parameters. By this procedure, Q_{Sn} working values are obtained which are rigorously self-consistent only within any particular set of homologous compounds, so that a given series is expected to be described by a distinct correlation function, analogously to previous findings.[1,2] This is clearly due to the fact that our Q_{Sn} CHELEQ partial atomic charges do not bear any general relationship to s-electron density at the nuclei and to related parameters, which in turn would unequivocally correlate with δ values, possibly yielding a unique function (see ref. 1 and refs. therein). On the other hand, the eventual production of individual δ/Q_{Sn} relationships is of considerable help in structural assignments in the present context (see below).

The input N_{ij} and F values (for Q_{Sn} calculations by the CHELEQ program) of atoms not directly bound to tin have been generally attributed according to the commonly accepted valence bond structures of the individual compound or ligand. In particular, the resonance structure of pyridine N-oxide (pyo), with a single N–O bond (see caption to Figure 1), has been initially chosen on the basis of X-ray diffractometry data, which appear to exclude the relevant involvment of the quinoid form [see section (*e*) of the footnote on the title page].

Values of Q_{Sn} thus obtained are listed in Table 1, in conjunction with the corresponding δ values. Wherever needed and possible, Q_{Sn} data from alternative valence bond formulae, other than those referred to in this work, have been calculated, and related δ/Q_{Sn} data points have been interpreted (see below).

The correlations δ/Q_{Sn} extracted from Table 1 are plotted in Figures 2 and 3. It has been reported that CHELEQ partial atomic charges do not account for inductive effects.[1,3g,3h] In the case of six-co-ordinated $Sn^{IV}R_n$ (R = alkyl) derivatives, Q_{Sn} values are nearly constant and irrespective of the nature of the alkyl radicals for given n and ligands, while δ values vary, apparently as a function of inductive effects.[1,2] The same trend is generally detected for the five-co-ordinated derivatives here investigated (see data of Table 1). Consequently, it has been decided to employ, whenever applicable, the arithmetic mean of δ and Q_{Sn} values of $Sn^{IV}R_n$ (R = alkyl) derivatives as data points in the various δ/Q_{Sn} correlations (Figures 2 and 3).

Results and Discussion

The plots of δ *versus* Q_{Sn} shown in Figure 2 for the four homologous series $[SnR_3X_2]^-$, $[SnR_2X_3]^-$, $SnR_3X'(E{=}O)$, and $[SnR_3(E{=}O)_2]^+$ give the results expected by using our CHELEQ charges program. The Q_{Sn} range for each series is clearly dictated by the valence state electronegativities (or better, by the related parameters inserted into the CHELEQ program [3g,3h]) of the ligand atoms directly bound to tin: Q_{Sn} values become more positive as function of the number of halide atoms, and of halide (or thiocyanate groups) and sp^2 oxygen. Within any individual series, Q_{Sn} consistently vary also according to the different electronegativities of sp^3 and sp^2 carbon atoms (bound to tin). The variation of the parameters δ (which reflect changes of the 5s electron density at the Sn nuclei) generally follows quite satisfactorily the above described trend of Q_{Sn}, as indicated by the values of the correlation coefficients (caption to Figure 2).

The compounds $[SnMe_3I_2]^-$, $[SnMe_3Br_2]^-$, and $[SnMe_3(hmpa)_2]^+$ (data points 1, 2, and 75 of Figure 2) deviate from their respective series apparently due to their low δ values (see above), consistent with the trend detected for six-co-ordinated adducts;[1] the same occurs for $[SnR_3(Ph_3AsO)_2]^+$ [R = Me or Bu^n; data points 66 and 67), the mean δ value being heavily influenced by that of the $Sn^{IV}Me_3$ complex (Table 1).

In the series $[SnR_2X_3]^-$, Q_{Sn} of the mixed complexes $[SnR_2XCl_2]^-$ (X = Br or I), and the corresponding data points in Figure 2, refer to isomers with equatorial Br or I, in line with still accepted views on the location of substituents in five-co-ordinated structures.[26] Values of Q_{Sn} for the isomers with equatorial Cl are slightly shifted to more positive values (*ca.* 0.01—0.03), the correlation coefficient for the whole series being now $r = 0.906$. No assumption is then confidently feasible on the configuration of the mixed complexes on the basis of the present treatment.

Adducts $SnR_3X'(E{=}O)$ (X′ = halide or NCS) show quite interesting features in their δ/Q_{Sn} correlation, Figure 2. The $Sn^{IV}Me_3$ derivatives (data points 30, 41, and 43) insert in an excellent way into the relationship, to which belong also terms containing higher alkyls (Bu^n) in mixed $Sn^{IV}R_3$ species (see Figure 2 and Table 1). Moreover, the parameters δ (and Q_{Sn}) of the terms of the series are independent of the nature of the E=O ligand, as well as of the atoms bound to the P, As, C, or S atom of the ligand, so that only sp^2 oxygen of E=O, linked to Sn, would influence the magnitude of δ. Lastly, all $SnPh_3X(E{=}O)$ species show quite similar δ and Q_{Sn} values. The same occurs also for the adducts $SnPh_2Cl_2(E{=}O)$.

The trends shown by the $Sn^{IV}R_n$ (R = alkyl) adducts along this series are contradictory to earlier assumptions (see above) concerning the dependence of δ values of $Sn^{IV}R_n$ derivatives on inductive effects of the alkyl radicals R, and suggest both

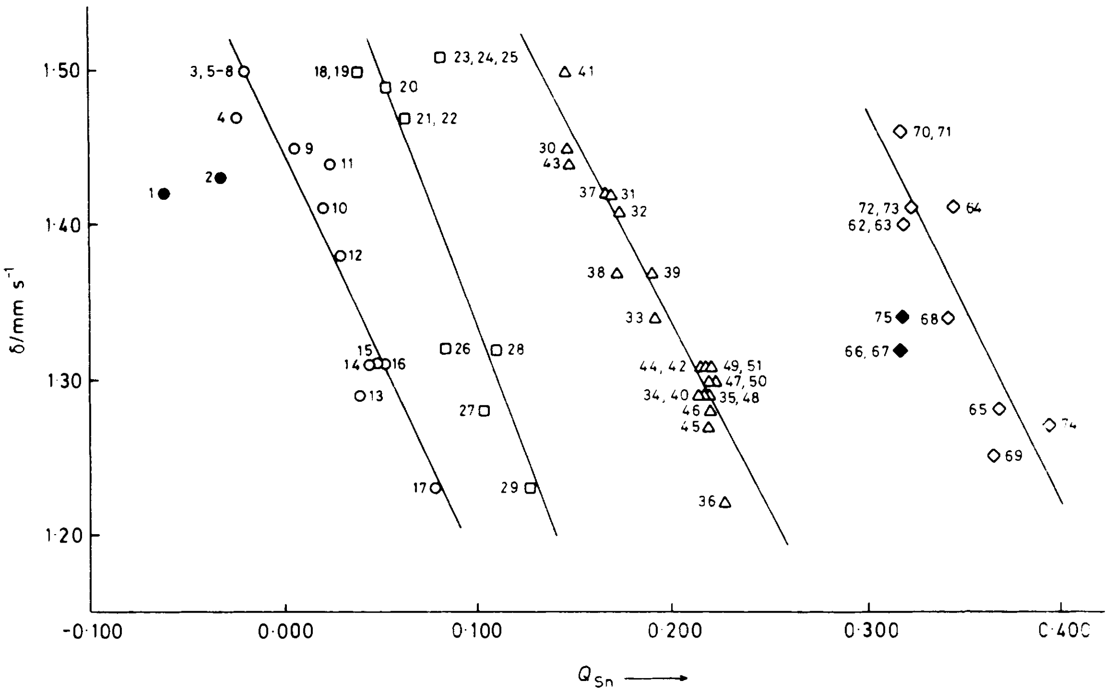

Figure 2. The correlation δ/Q_{Sn} (Mössbauer isomer shift *versus* partial atomic charge on tin) for a number of homologous series of compounds. Numbers refer to the compounds of Table 1. Average Q_{Sn} and δ values are employed whenever applicable. (○) $[SnR_3X_2]^-$; (□) $[SnR_2X_3]^-$; (△) $SnR_3X'(E=O)$; (◇) $[SnR_3(E=O)_2]^+$; (●, ▲) terms out of correlations (see text). Full lines are least-squares fits of data points, the related equations and correlation coefficients are (○) $\delta = 1.44 - 2.64 \times Q_{Sn}$ ($r = 0.939$); (□) $\delta = 1.66 - 3.26 \times Q_{Sn}$ ($r = 0.876$); (△) $\delta = 1.81 - 2.37 \times Q_{Sn}$ ($r = 0.960$); (◇) $\delta = 2.24 - 2.54 \times Q_{Sn}$ ($r = 0.877$)

the general reliability of CHELEQ Q_{Sn} data in the context of the correlations here proposed (*i.e.*, they are practically insensitive to the chain length in $Sn^{IV}R_n$ derivatives) and the need of a different interpretation of the eventual variation of δ values. In fact, the latter could be ascribed to steric effects, in the sense that bulky radicals could force the (equatorial) SnC_n skeletons into increasingly planar configurations, with a consequent increase of the *s* character of these bonds as well as of the *s*-electron density at the Sn nuclei.

The adducts $SnPh_2Cl_2(E=O)$, compounds (56)—(61), where E=O contains P, As, or S and sp^2 oxygen is assumed to be axial,[16,17] are expected to show a δ/Q_{Sn} correlation other than that of $SnR_3X'(E=O)$ species (X' = halide or NCS), according to the preceding discussion on Q_{Sn} ranges. To our knowledge, there are in this series only a few additional adducts $SnMe_2Cl_2(E=O)$,[17] giving presumably almost coincident δ/Q_{Sn} data points, which consequently have not been taken into account in the present context.

The pyridine *N*-oxide adducts $SnR_3X'(pyo)$, (52)—(55), generate a separate δ/Q_{Sn} correlation (not shown in the Figures of the present paper) when the ligand is taken *e.g.* as its ' aromatic ' resonance structure[27] (see the section concerning the calculation of partial charges; also Table 1 and Figure 1). On the other hand, assuming for example the quinoid resonance form for co-ordinated pyo, with sp^2 oxygen in the $N^+=O$ group,[27] the four respective data points insert into the correlation of the series $SnR_3X'(E=O)$, which is consistent with the discussion on the latter adducts [Q_{Sn} are now 0.164, 0.232, 0.237, and 0.245 for compounds (52)—(55) respectively]. In any case, the quinoid and related forms of unsubstituted pyo appear to be unimportant,[28] which again strongly suggests that much care must be exercised in assigning valence bond structures in the present context. Analogously, the adduct $[SnBu^n_3(pyo)_2]^+$ (77) inserts into the $[SnR_3(E=O)_2]^+$ series for quinoid pyo ($Q_{Sn} = 0.358$); instead, the data point of the aqua-cation $[SnMe_3(OH_2)_2]^+$ (76) stands definitely by itself, consistent with the different valence state electronegativities of the co-ordinating oxygens of H_2O and E=O.

The homologous series of complexes (90)—(112) of Table 1, formed by $Sn^{IV}R_2$, $Sn^{IV}RCl$, and $Sn^{IV}X_2$ moieties with the tridentate ' planar ' ligands hmbatp, mpsala (both with SNO donor atoms) and hmppap, hpsala (ONO donor atoms), see Table 1, yield a unique, reasonably good correlation δ/Q_{Sn} which is shown in Figure 3. These compounds generally exhibit a tin environment of type (III), Figure 1 [see section (*f*) of the footnote to the title page];[11,22-25] the values of Q_{Sn}, and in some way also the respective δ values, even in this case are independent of inductive effects of groups bound to the co-ordinating ligand atoms (see Table 1), so that average data points are reported in Figure 3 for equal tin environments. It is remarkable that the present series includes terms with two, one, or no tin–carbon bonds, analogously to earlier findings for octahedral adducts[1,2] and contrary to results for some of the series discussed above {*e.g.*, $[SnR_3X_2]^-$, $[SnR_2X_3]^-$ and $SnR_3X'(E=O)$, $SnPh_2Cl_2(E=O)$ for which independent δ/Q_{Sn} correlations have been established or assumed, see Figure 2}. The reason seems to lie in the valence bond formulae used in this work (Figure 1) where the nature and valence states of the equatorial substituents, as well as their input formal charge, play an essential role in dictating the magnitude of Q_{Sn}. In particular, equatorial sp^2 nitrogen with input $F = +1.00$ dominates in establishing the Q_{Sn} values of the complexes with tridentate ligands, as it appears from the charges transferred from Sn upon electronegativity equalization (Table 2); the occurrence of the δ/Q_{Sn} correlation on changing both the remaining equatorial and one of the axial atoms is consequently understood.

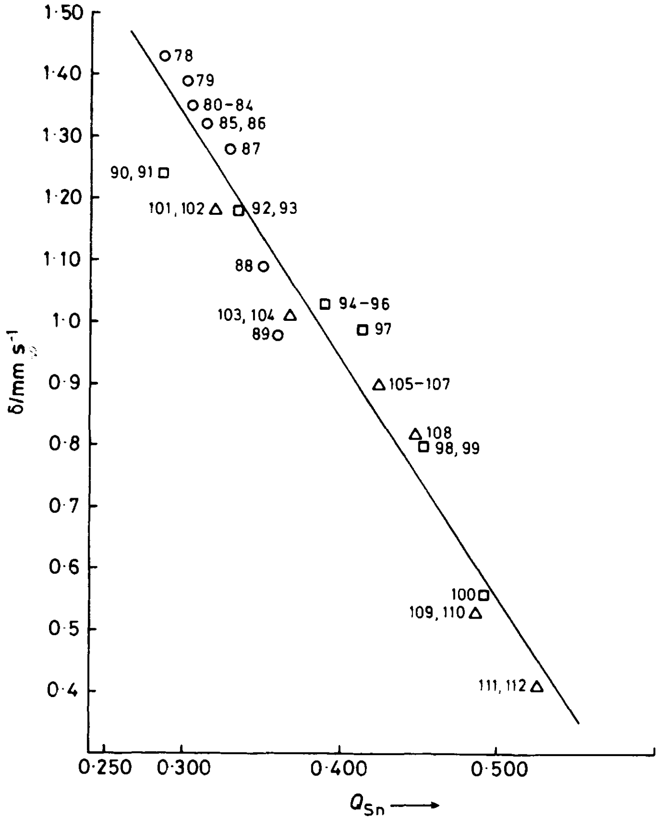

Figure 3. The correlation δ/Q_{Sn} for complexes with (○) quin; (□) hmbatp, mpsala; (△) hmppap, hpsala. Numbers refer to the compounds of Table 1. Average Q_{Sn} and δ values have been employed whenever applicable. The full line is the least-squares fit of all data points, with the equation $\delta = 2.46 - 3.82 \times Q_{Sn}$ (correlation coefficient $r = 0.972$)

The quinolin-8-olate complexes SnR_2X'(quin) (78)—(89) have been assumed as five-co-ordinate compounds on the basis of the point-charge model rationalization of their nuclear quadrupole splittings[18] and of other spectroscopic evidence;[11,14,20,21] it was not possible to determine which of the O or N atoms of co-ordinated quin were axial or equatorial. The amount of CHELEQ charge transferred from Sn upon equalization, Table 2, favours equatorial oxygen and axial nitrogen [input formal charges $F = 0.00$ and $+0.50$ respectively in a structure of type (III), where N and O are interchanged in Figure 1], since the latter is found to be more electronegative.[26] An independent δ/Q_{Sn} line is obtained in this context for compounds (78)—(89). On the other hand, these results are clearly confined to the way in which input CHELEQ parameters are here attributed, and it is hard to say whether they are really correct. If the structure (III) as shown in Figure 1 is instead selected, the quin complexes excellently insert into the correlation of the tridentate ligands (Figure 3; see the value of the correlation coefficient *r*); this is fully consistent with the preceding discussion concerning Q_{Sn} data, since equatorial $N^{+1.00}$ (sp^2) now determines their magnitudes. On the other hand, the insertion of the quin complexes into the correlation depends also on the experimental δ values of the terms of the series, and there may be two interpretations of these facts: (*i*) the insertion is accidental; (*ii*) quin complexes actually have structure (III). We are not sure which it is; it would be interesting to determine the molecular structure of one term of the series in order to determine the potential of our δ/Q_{Sn} correlations for structural assignments.

Table 2. Examples of CHELEQ charges transferred from tin to neighbour atoms upon electronegativity equalization. Input partial charges and bond orders are given in Figure 1

	CHELEQ charge transferred from Sn to:	
Compound	Equatorial substituents	Axial substituents
$SnMe_2$(hpsala)	C, −0.030; N, +0.326	O, +0.025
$SnMe_2Cl$(quin)	C, −0.029; N, +0.329	O, +0.026; Cl, +0.004
$SnMe_2Cl$(quin)	C, −0.027; O, +0.141	N, +0.158; Cl, +0.005

It is concluded that the δ/Q_{Sn} functions here investigated are generally suitable for structural assignments within the various series. In our opinion, the results obtained are surprisingly good, taking into account that individual δ values here employed come from a variety of laboratories over a large period of time; it is evident that in many instances better values are obtained by averaging the data. The reliability of CHELEQ partial atomic charges in relation to the above is also quite clear. In fact, acceptable relationships are obtainable also by correlating δ values with the valence state electronegativities of the (isolated) atoms directly bound to tin[3b–3d] following the same method employed in obtaining, for example, the data in Figures 2 and 3, but without any equalizing procedure; in any case, the respective correlation coefficients (ranging from 0.483 to 0.896) are consistently worse than those of the corresponding δ/Q_{Sn} plots. Moreover, in the case of the series of complexes with ONO and SNO type tridentate ligands, as well as of the full series of complexes with quin, ONO, and SNO ligands, reasonable correlations are feasible by using ground-state (Pauling) electronegativities of free atoms bound to tin, although with poorer correlation coefficients (*e.g.*, $r = 0.791$ for the latter series). Relationships δ/χ (ground state) for the present compounds (Table 1) generally consist of individual plots for organotins having the same organic radicals bound to the metal and varying ligand atoms, in much the same way as those reported by Flinn;[29] the number of data points is drastically reduced due to the many terms showing coincident χ values, and the correlation coefficients are not very satisfactory.

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References

1 R. Barbieri and A. Silvestri, *Inorg. Chim. Acta*, 1981, **47**, 201 and refs. therein.
2 E. Rivarola, A. Silvestri, and R. Barbieri, *Inorg. Chim. Acta*, 1978, **28**, 223.
3 (*a*) R. S. Mulliken, *J. Chem. Phys.*, 1934, **2**, 782; (*b*) J. Hinze and H. H. Jaffé, *J. Am. Chem. Soc.*, 1962, **84**, 540; (*c*) J. Hinze, M. A. Whitehead, and H. H. Jaffé, *ibid.*, 1963, **85**, 148; (*d*) J. Hinze and H. H. Jaffé, *Can. J. Chem.*, 1963, **41**, 1315; (*e*) *J. Phys. Chem.*, 1963, **67**, 1501; (*f*) J. E. Huheey, *J. Phys. Chem.*, 1965, **69**, 3284; (*g*) W. L. Jolly and W. B. Perry, *J. Am. Chem. Soc.*, 1973, **95**, 5442; (*h*) *Inorg. Chem.*, 1974, **13**, 2686.
4 C. H. W. Jones and M. Dombsky, *Can. J. Chem.*, 1981, **59**, 1585.
5 R. V. Parish and R. H. Platt, *Inorg. Chim. Acta*, 1970, **4**, 65.
6 N. W. G. Debye, E. Rosenberg, and J. J. Zuckerman, *J. Am. Chem. Soc.*, 1968, **90**, 3234.
7 R. V. Parish and C. E. Johnson, *J. Chem. Soc. A*, 1971, 1906.
8 J. W. Nicholson, J. A. Douek, and A. J. Crowe, *J. Organomet. Chem.*, 1981, **219**, 309.

9 E. J. Kupchick and G. F. Yamnitsky, *Synth. React. Inorg. Metal-Org. Chem.*, 1979, **9**, 345.

10 J. Ensling, P. Gütlich, K. M. Hassellbach, and B. W. Fitsimmons, *J. Chem. Soc. A*, 1971, 1940.

11 J. N. R. Ruddick and J. R. Sams, *J. Chem. Soc., Dalton Trans.*, 1974, 470.

12 T. K. Sham, J. S. Tse, V. Wellington, and G. M. Bancroft, *Can. J. Chem.*, 1977, **55**, 3487.

13 J. C. Hill, R. S. Drago, and R. H. Herber, *J. Am. Chem. Soc.*, 1969, **91**, 1644.

14 V. G. Kumar Das, N. S. Weng, P. J. Smith, and R. Hill, *J. Chem. Soc., Dalton Trans.*, 1981, 552.

15 R. W. J. Wedd and J. R. Sams, *Can. J. Chem.*, 1970, **48**, 71.

16 F. P. Mullins, *Can. J. Chem.*, 1971, **49**, 2719.

17 B. V. Liengme, R. S. Randall, and J. R. Sams, *Can. J. Chem.*, 1972, **50**, 3212.

18 G. M. Bancroft, V. G. Kumar Das, T. K. Sham, and M. G. Clark, *J. Chem. Soc., Dalton Trans.*, 1976, 643.

19 A. J. Crowe, P. J. Smith, and P. G. Harrison, *J. Organomet. Chem.*, 1981, **204**, 327.

20 R. C. Poller and J. N. R. Ruddick, *J. Chem. Soc. A*, 1969, 2273.

21 F. P. Mullins and C. Curran, *Inorg. Chem.*, 1968, **7**, 2584.

22 R. H. Herber and R. Barbieri, *Gazz. Chim. Ital.*, 1971, **101**, 149.

23 L. Pellerito, R. Cefalù, A. Silvestri, F. Di Bianca, R. Barbieri, H.-J. Haupt, H. Preut, and F. Huber, *J. Organomet. Chem.*, 1974, **78**, 101.

24 R. Barbieri, F. Di Bianca, G. Alonzo, A. Silvestri, L. Pellerito, N. Bertazzi, and G. C. Stocco, *Z. Anorg. Allg. Chem.*, 1975, **411**, 173.

25 J. N. R. Ruddick and J. R. Sams, *J. Organomet. Chem.*, 1973, **60**, 233.

26 E. L. Muetterties and R. A. Schunn, *Q. Rev. Chem. Soc.*, 1966, **20**, 245.

27 R. A. Abramovitch and E. M. Smith, in 'Pyridine and its Derivatives,' ed. R. A. Abramovitch, Wiley, New York, 1974, ch. 4.

28 D. Ülkü, B. P. Huddle, and J. C. Morrow, *Acta Crystallogr., Sect. B*, 1971, **27**, 432 and refs. therein.

29 P. A. Flinn, in 'Mössbauer Isomer Shifts,' eds. G. K. Shenoy and F. E. Wagner, North Holland, Amsterdam, 1978, ch. 9a, p. 595.

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