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A LIGAND'S-EYE VIEW OF COORDINATION

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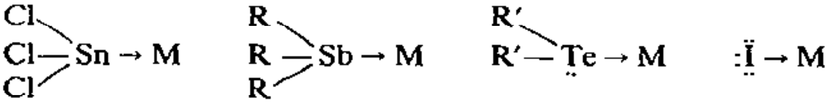
CONTENTS

A. INTRODUCTION

Coordination chemists are normally mainly concerned with the acceptor entity in donor–acceptor systems, very frequently a transition metal atom. Detailed studies have been made of the modification of the properties of the acceptor by coordination to different ligands, e.g. *d–d* spectra, spin states, stereochemistry, redox potentials, etc. The effects which the act of coordination has on the ligand are much less frequently considered, although they are of fundamental importance in determining the way in which ligands react, e.g. in ligand-modification and template reactions, catalysis, etc. This neglect is due principally to the paucity of techniques applicable to the study of coordinated ligands. One technique which has been available for some time is Mössbauer spectroscopy, and there is a small number of non-metals and metalloids which can act as donor atoms in ligands and which have isotopes suitable for this method. A relatively large body of data now exists for compounds of tin, antimony, tellurium, and iodine, and the aim of this review is to examine data for transition metal complexes of the iso-electronic series of ligands Cl_3Sn^-, R_3Sb, R'_2Te, I^- ($R = C_6H_5$, o-$CH_3C_6H_4$, p-$CH_3C_6H_4$; $R' = p$-$C_2H_5OC_6H_4$). These data afford an unprecedented opportunity to obtain a "ligand's-eye" view of coordination, giving information on the nature of the ligand–metal bond and the acceptor ability of different metal atoms in their various oxidation states. It is also possible to probe the way in which the other ligands present influence the acceptor ability of the metal. The discussion is prefaced by an explanation of the chemical significance carried by the parameters of a Mössbauer spectrum.



B. CHEMICAL SIGNIFICANCE OF MÖSSBAUER PARAMETERS [1–3]

Mössbauer spectroscopy is essentially absorption spectroscopy practised with gamma rays. A radioactive source is used which decays to the excited state of the nucleus under study. This then drops to the ground state with emission of a gamma photon. The resulting gamma radiation is passed through the sample to obtain a Mössbauer absorption spectrum. The spectra are characterised by two major parameters, both of which carry chemical information: (a) the isomer shift, IS, which is the overall position of the absorption within the energy spectrum, and (b) the quadrupole coupling constant, QCC, which is a measure of the separation of the absorption peaks in multiplet spectra. Owing to the nuclear spin states, ^{129}I and ^{121}Sb give complex eight (or twelve) line spectra; for ^{119}Sn and ^{125}Te only a doublet is seen, the splitting of which (the quadrupole splitting, QS) is one-half the QCC.

The IS arises from the change in radius of the nucleus on absorption or emission of a gamma photon, but also depends on the electron density at the nucleus (Box A). Thus, for a given isotope, the IS difference between two substances is proportional to the difference in electron densities which, in

BOX A ISOMER SHIFT

$$IS_c = \tfrac{2}{5}\pi e^2 Z\, \delta\langle R^2\rangle [\Psi^2_{cpx} - \Psi^2_{lig}]$$

$\delta\langle R^2\rangle$ = change in mean-square radius of nucleus on absorption (emission) of gamma photon

Ψ^2 = total electron density at nucleus

cpx, lig = complex, ligand

TABLE I

Properties of nuclei

	$10^3\,\delta\langle R^2\rangle$ [a] (fm^2)	eQ [b] (b)	E_γ (keV)	Conversion factors [a] (eV/mm s^{-1})	(J mol^{-1}/mm s^{-1})
^{119}Sn	+3.3	−0.08	23.8	7.97×10^{-8}	7.69×10^{-3}
^{121}Sb	−24.6	−0.26	37.2	1.24×10^{-7}	1.19×10^{-2}
^{125}Te	+2.7	−0.20	35.5	1.18×10^{-7}	1.14×10^{-2}
^{129}I	+18.5	−0.55	27.7	9.25×10^{-8}	8.91×10^{-3}

[a] G.K. Shenoy and F.E. Wagner, Mössbauer Isomer Shifts, North Holland, Amsterdam, 1978.
[b] Ref. 3.

turn, is a measure of the differences in population of the valence-shell orbitals. In the present context, the relevant difference is that between the free ligand and its complexes, i.e. the coordination IS, designated IS$_c$. Since the only electrons with finite probability of occurring at the nucleus are the *s* electrons, other electrons contribute to the IS only indirectly by relatively small shielding effects. (The small positive contribution from relativistic $p_{1/2}$ electrons is usually ignored.) Thus, IS$_c$ measures principally the change in valence-shell *s* electron density on the Mössbauer atom. The sensitivity of IS$_c$ to change in 5*s* population depends on the change in mean-square radius of the nucleus, $\delta\langle R^2\rangle$, values of which are given in Table I with other relevant nuclear parameters. In most cases $\delta\langle R^2\rangle$ is positive, so that a negative value for IS$_c$ indicates loss of 5*s* electrons by the ligand to the acceptor; for ^{121}Sb this correlation is reversed, $\delta\langle R^2\rangle$ being negative.

The QCC arises from the interaction of a quadrupolar nucleus with an electric-field gradient (efg) produced by an asymmetric distribution of charge about the nucleus (i.e. a distribution with less than cubic symmetry). The principal contribution to the efg comes from imbalance in the population of the valence-shell *p* orbitals (Box B). The core electrons have spherical sym-

BOX B QUADRUPOLE COUPLING CONSTANT

QCC $= e^2qQ$
eQ = quadrupole moment of nucleus
eq = electric-field gradient at nucleus
$= \partial^2V/\partial z^2$
$= -\frac{4}{5}e(N_z - \frac{1}{2}N_y - \frac{1}{2}N_x)\langle r^{-3}\rangle_p$
$N_{x,y,z}$ = populations of $p_{x,y,z}$ orbitals
$\langle r^{-3}\rangle_p$ = expectation value of r^{-3} for p orbitals
QCC$_c$ = QCC$_{cpx}$ − QCC$_{lig}$
quadrupole splitting (for ^{119}Sn, ^{125}Te):
QS $= \frac{1}{2}e^2qQ$

metry (in the absence of polarisation effects) and thus contribute nothing to the efg. Charges beyond the valence shell make only small contributions because of the inverse cubic dependence of the efg on distance from the nucleus. Loss of electron density from the $5p_z$ orbital, by donation to the acceptor, would make the efg more positive. However, for all the isotopes under consideration, the quadrupole moment, Q, is negative. Thus, the coordination shift in QCC, QCC_c, would normally be expected to be negative.

C. ENERGY UNITS

The radiation source in a Mössbauer experiment is a fixed-energy (monochromatic) gamma emitter. In order to scan the spectrum, the energy of the source is modulated by the Doppler effect. A velocity, v, is applied to the source so that the energy E of the radiation perceived by the sample is $E = E_\gamma(1 + v/c)$, where E_γ is the gamma energy of the stationary source and c is the velocity of light. The velocities required are usually in the range 1–20 mm s^{-1}, and Mössbauer data are conventionally quoted directly in velocity units. Factors for conversion to more traditional units vary with E_γ, and are given in Table 1.

D. LIGAND BONDING ORBITALS

To a first approximation, IS_c and QCC_c measure the changes in $5s$ and $5p$ electron density on the ligand atom as a result of coordination. It is useful, therefore, to make a preliminary survey of the data available for each ligand with a variety of acceptors, to monitor the contributions of each orbital to the metal–ligand bond. This is conveniently done by plotting QCC_c against IS_c. Such a plot for compounds of iodine is shown in Fig. 1. (All the data for this and subsequent plots are tabulated in the Appendix.) This plot covers the full range of compounds in which iodine is univalent and one-coordinate. The points closest to the origin are for the complexes of transition metals [4–8]. Those farthest away are for I_2, ICl, ICN, etc. [9–12]. Intermediate points correspond to the covalent iodides such as CH_3I, SiI_4 [13–15]. It is evident that there is effectively a linear correlation between the two parameters, with a negative slope. As the group X in I–X becomes more electronegative, QCC_c becomes increasingly negative, reflecting the loss of $5p_z$ electron density from iodine to X. In these terms, the transition metals have a low effective electronegativity, as might be expected. As QCC_c becomes more negative, IS_c becomes increasingly positive, indicating an increase in electron density at the iodine nucleus. Since I^- has a closed-shell electron configuration, $I \rightarrow X$ donation cannot increase the $5s$ population, but an increase in

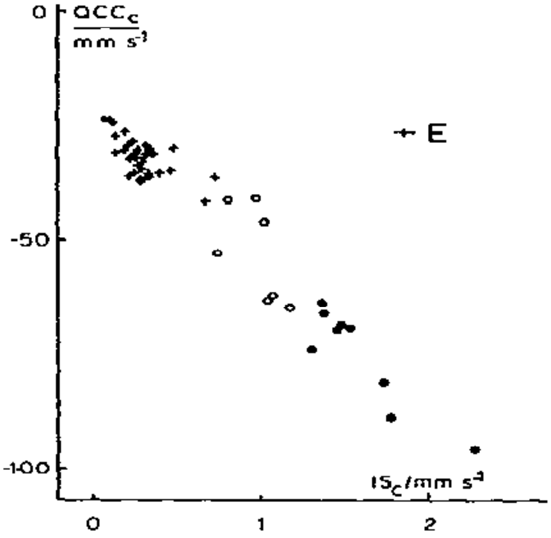


Fig. 1. ^{129}I-Mössbauer parameters for iodine compounds relative to iodide ion. The symbols refer to: + metal complexes, ○ group IVB iodides, ● iodine halides (I_2, IBr, ICl, ICN). The symbol marked E represents the error limits on individual points.

electron density at the nucleus could be caused by a diminution in the shielding effect of the reducing 5*p* population. The linear correlation of QCC$_c$ with IS$_c$ thus indicates use of an unhybridised 5*p* orbital by iodine, and the slope is close to that calculated for pure *p*-bonding [10].

The other ligands under consideration also have closed-shell (octet) configurations, but are not such simple species; all involve other groups bonded to the donor atom. These groups may be expected to influence the hybridisation of the lone pair, and considerable changes in hybridisation are likely on coordination. The situation is particularly complex for R'_2Te, which has two lone pairs only one of which is involved in coordination. The bond angle in diorganotellurides is 95–100°, suggesting that the Te–C bonds are intermediate between pure 5*p* and $5s5p^3$ hybridisation [16]. The pyramidal cations R_3Te^+ show appreciable quadrupole splitting, indicating that the remaining lone pair has hybrid 5*s*–5*p* character [17]. (In the present context, the latter species may be regarded as arising from coordination of R_2Te to an R^+ cation, an extreme acceptor.) However, the difference in IS between R_2Te and R_3Te^+ is very small (0.1–0.2 mm s^{-1}), while the change in QCC is much larger (ca. 9 mm s^{-1}), suggesting that the changes in electron distribution affect mainly the 5*p* electrons, as with iodine. Data for metal complexes are sparse and subject to the considerable uncertainties inherent in the large line widths of ^{125}Te Mössbauer spectra, but do indicate a similar trend to those for iodo-complexes (Fig. 2) [18,19]. With the exception of one

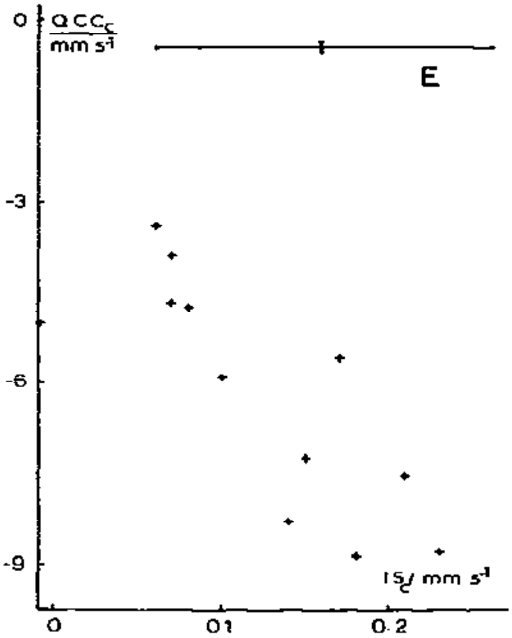


Fig. 2. ^{125}Te coordination shifts in IS and QCC for metal complexes of $Te(C_6H_4OEt)_2$.

point, IS_c and QCC_c are well correlated with a negative slope, indicating that $R'_2Te \rightarrow M$ donation involves primarily the (Te)5*p* orbital, and that changes in IS are due to deshielding.

Tri-organostibines, R_3Sb, are pyramidal molecules with a single lone pair.

TABLE 2

Mössbauer parameters for antimony(III) compounds and metal complexes [a]

	$IS(CaSnO_3)$ ($mm\ s^{-1}$)	QCC ($mm\ s^{-1}$)
$SbCl_3$	−14.1	+12.2
$SbBr_3$	−14.2	9.4
Ph_3Sb	−9.35	16.2
$(o\text{-}CH_3C_6H_4)_3Sb$	−9.77	17.4
$(p\text{-}CH_3C_6H_4)_3Sb$	−9.37	17.0
$[Cu(SbPh_3)_4]ClO_4$	−7.21	13.3
$[Ag(SbPh_3)_4]BF_4$	−7.35	12.4
$IrCl(CO)(SbPh_3)_3$	−6.89	12.5
$IrHCl_2(CO)(SbPh_3)_2$	−6.49	9.5
$IrHCl_2(SbPh_3)_3$	−6.66	12.0

[a] Data from ref. 12; L.H. Bowen, J.G. Stevens and G.G. Long, J. Chem. Phys., 51 (1969) 2010; R.V. Parish and O. Parry, unpublished observations.

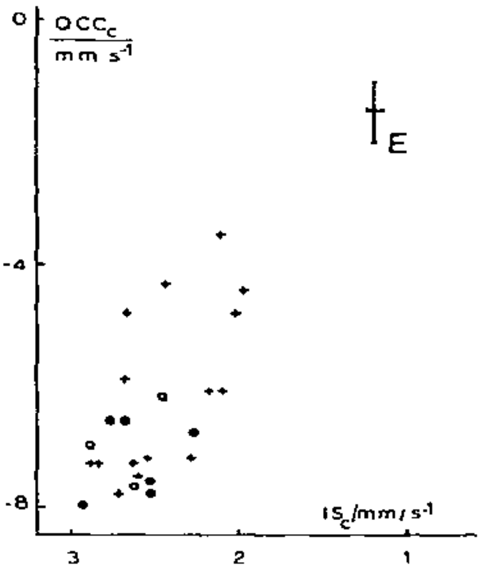


Fig. 3. ^{121}Sb coordination shifts for complexes of R_3Sb (+, R = Ph; ●, R = o-$C_6H_4CH_3$; O, R = p-$C_6H_4CH_3$). Note the reversal of the IS_c scale.

The Mössbauer spectra show substantial quadrupole coupling, and the IS values are at the positive end of the range for antimony(III) compounds (Table 2). Both parameters thus indicate a lone pair with substantial *s–p* hybrid character. Relatively few data are available for complexes: a few iron–carbonyl complexes [21,22] and several palladium(II) and platinum(II) complexes have been examined [20], and unpublished data for other metal complexes are given in Table 2. A plot of QCC_c vs. IS_c is superficially similar to those for iodine and tellurium, showing a reasonably good negative correlation, tending to the origin. The interpretation, however, must be different since $\delta\langle R^2\rangle$ is negative for ^{121}Sb. The increase in IS_c which parallels the decrease in QCC_c now signals a decrease in 5*s* electron density. In this case, the act of coordination involves loss of both 5*p* and 5*s* electron density to the metal atom. For this reason Fig. 3 is drawn with the IS_c scale reversed. Some rehybridisation of the Sb–C bonds would be expected, with reduction in 5*s* character and increase in 5*p* character, but these changes cannot be monitored separately from those accompanying the formation of the Sb → M bond. However, it is clear that the bond to the metal involves considerable 5*s* character and that donation of 5*s* electron density increases approximately proportionately to donation from the 5*p* orbital.

The iso-electronic ligand Cl_3Sn^- appears to behave similarly, provided that only complexes with metal carbonyl groups are considered (Fig. 4) [23–31]. (Note that in previous publications these compounds have been

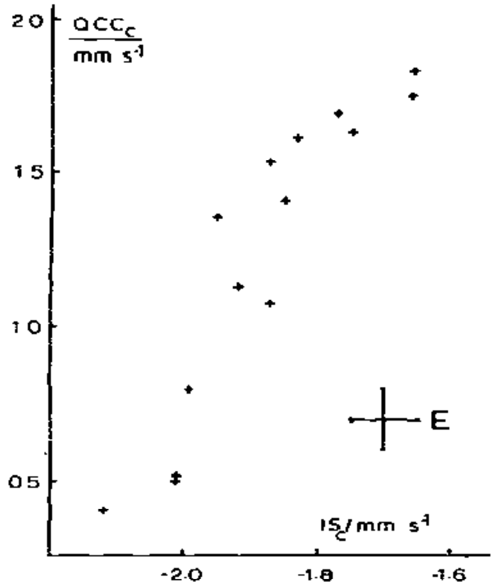


Fig. 4. ^{119}Sn coordination shifts for Cl_3Sn complexes with metal carbonyls.

discussed as derivatives of tin(IV) with metal carbonylate anions as ligands to tin. In the present context, the complementary approach is adopted of treating the compounds as Cl_3Sn^- complexes of metal carbonyl cations.) There is a positive correlation between IS_c and QCC_c, indicating the use of

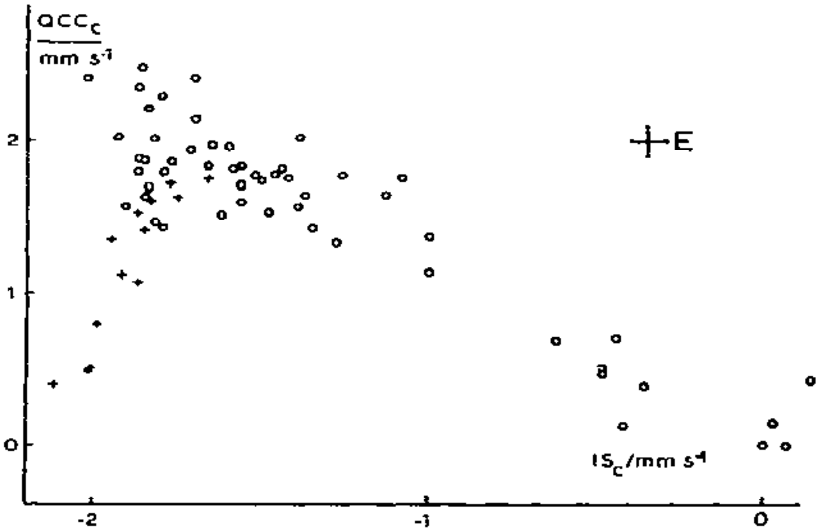


Fig. 5. ^{119}Sn coordination shifts for Cl_3Sn^- salts and metal complexes (carbonyl complexes are marked +).

both 5*p* and 5*s* orbitals by tin, but the trend of points does not extrapolate to the origin. Data for non-carbonyl complexes, mainly those of noble metals [32,33], form a reasonably well correlated band of values which leads towards the origin, but the slope is negative, the IS_c values are negative, and the QCC_c values are positive (Fig. 5). The two sets of data merge with each other and with those for salts of the Cl_3Sn^- anion [32,34–37], giving an almost continuous band of points which, starting from large negative values of IS_c, rise to a maximum QCC_c and then fall away towards the origin. This behaviour has been explained by Mays and Sears [33] in terms of rehybridisation of the tin atom. In the Cl_3Sn^- anion the lone pair has a high 5*s* character [38], shown by the large positive IS values and Cl–Sn–Cl bond angles which are close to 90°. Some 5*p* character is required to account for the moderately small QCC values. Coordination to even the weakest acceptor results in a negative value of IS_c but a positive QCC_c. Rehybridisation decreases the 5*s* character of the lone pair and increases the 5*p* character so that, even after formation of the tin–metal bond, there is greater 5*p* electron density in the lone pair than in the free Cl_3Sn^- ion. This rehybridisation continues as metals of increasing acceptor power are used, i.e. metals with effectively greater electronegativity relative to tin. The rehybridisation is therefore in line with Bent's rule of isovalent hybridisation, in increasing the *p* character of the bond to the more electronegative substituent. Eventually, however, a point is reached at which more *p* electron density is lost by donation than can be gained by rehybridisation. At this stage, increased donation involves the loss of more 5*p* electron density than 5*s*, the rate of change of IS decreases, and the QCC falls sharply.

Thus, for Cl_3Sn^- as a ligand, there is considerable involvement of both 5*s* and 5*p* orbitals in the bonding, and extensive rehybridisation of the tin atom occurs, according to the demands of different acceptors. The organostibines also employ both orbitals, but there is less evidence of great flexibility in hybridisation. Such evidence might be obtained with a wider range of acceptors. Tellurium and iodine ligands appear to use almost entirely the 5*p*

TABLE 3

Calculated orbital energies (MJ mol^{-1}) [a]

	E(5*s*)	*E*(5*p*)	*E*(5*p*) − *E*(5*s*)
Sn	−2.525	−1.405	1.120
Sb	−3.083	−1.774	1.309
Te	−3.713	−1.902	1.811
I	−4.352	−2.137	2.215

[a] G.F. Fischer, The Hartree–Fock Method for Atoms, Wiley, New York, 1977.

orbitals, although again a greater variety of data is desirable. The trend to increased use of the 5*p* orbital with increasing atomic number of the donor atom is consistent with the increased energy separation between the 5*s* and 5*p* orbitals and the rapidly increasing tightness of binding of 5*s* electrons (Table 3).

E. ELECTRON POPULATIONS ON THE DONOR ATOM

Each isotope has a unique set of values for the nuclear parameters (Table 1). The relationship between the IS and QCC and the 5*s* and 5*p* populations is therefore different for each isotope and for each parameter. Fortunately, it is possible to calibrate the IS and QCC scales. In some instances the QCC is known for a system in which the electron configuration is also known. For example the value for atomic iodine is -70.33 mm s^{-1} (for ^{129}I), corresponding to the configuration $5s^2 5p^5$, i.e. one 'hole' in the 5*p* shell [39]. Following Townes and Dailey [40], linear interpolation can be made between this value and that of zero for the iodide ion. Thus, in the present context, the extent of donation from the 5*p* orbital on an iodide ion to an acceptor is given by $\mathrm{QCC_c}/(-70.3\ \mathrm{mm\ s^{-1}})$. Similar calibrations can be derived for the other isotopes. The IS is sensitive to changes in both 5*s* and 5*p* populations, and a linear relationship again holds to a good approximation [2]. Thus, the reductions in populations of the 5*s* and 5*p* orbitals, S_c and P_c, due to coordination of the ligand are related to the Mössbauer parameters by the expressions

$$\mathrm{IS_c} = aS_c + bP_c$$

$$\mathrm{QCC_c} = cP_c$$

The present author has recently reviewed these procedures [41], and a consistent set of calibration constants is given in Table 4. Using the appropriate values of *a*, *b*, and *c*, the equations can be solved to give S_c and P_c. The absolute values thus obtained are probably reliable to not better than ca. 0.05 electrons.

TABLE 4

Constants for conversion of Mössbauer parameters to electron populations (mm s^{-1} e^{-1}) [41]

	a	*b*	*c*
^{119}Sn	-2.7	$+0.15$	-8.0
^{121}Sb	$+15.0$	-0.80	-26
^{125}Te	-2.7	$+0.45$	-15.7
^{129}I	-9.0	$+1.5$	-70.3

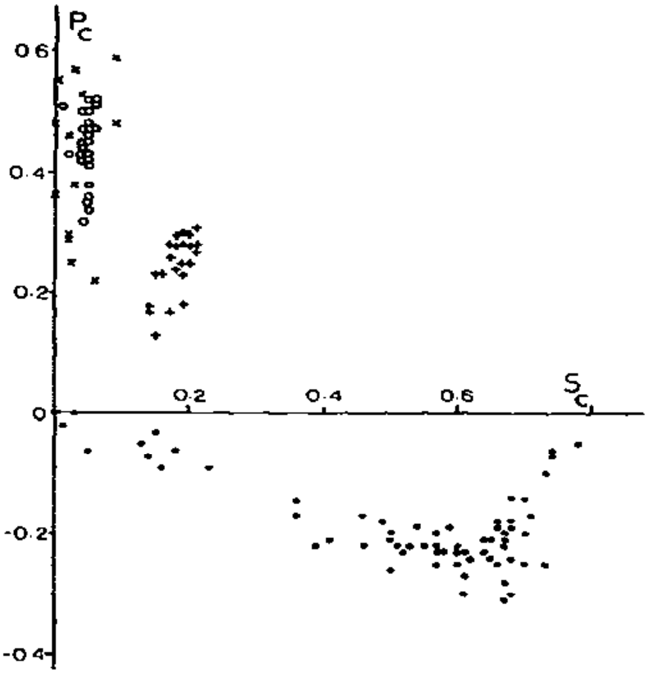


Fig. 6. Extent of donation from 5*s* and 5*p* orbitals by I^- (O), $(EtOC_6H_4)_2Te$ (x), R_3Sb (+), and Cl_3Sn^- (●).

The changes in electron populations thus derived are tabulated in the Appendix, and are plotted on common axes in Fig. 6. This plot emphasizes the differences in hybridisation across the series of ligands. Iodine and tellurium bond principally through the 5*p* orbital, donating 0.3–0.5 electrons, and donation from 5*s* is small, $\lesssim 0.05$ electrons. For antimony, the 5*s* and 5*p* orbitals both participate, with 5*p* making slightly the greater contribution on average. Extensive rehybridisation occurs for tin, with shifting of 5*s* electron density into the lone pair, and the tin–metal bond has considerable 5*s* character. The spread of data for the Cl_3Sn^- ligand reflects the much wider range of compounds for which measurements have been made. It is clearly desirable to extend the ranges for the other ligands.

On a broad basis, the total amount of charge donated by each ligand, $S_c + P_c$, seems to be very similar. The best comparisons can be made for complexes with platinum(II), for which data are available for all the ligands. The figures in Table 5 show that about 0.5 electrons are donated by each ligand to platinum(II). There seems to be a trend towards increasing donation in the order $Cl_3Sn^- < R_3Sb < R'_2Te, I^-$, which might reflect increasing polarisability (softness) along the series. On the other hand, with iron–

TABLE 5

Data for platinum(II) complexes

	S_c	P_c	S_c+P_c	Average S_c+P_c
$(Me_4N)_2[PtCl_2(SnCl_3)_2]$	0.67	−0.28	0.39	0.37
$(Et_4N)_2[PtCl_2(SnCl_3)_2]$	0.70	−0.25	0.45	
$(Ph_3BzP)_2[PtCl_2(SnCl_3)_2]$	0.61	−0.30	0.31	
$(Ph_4As)_2[PtCl_2(SnCl_3)_2]$	0.68	−0.30	0.38	
$PtCl(SnCl_3)(PPh_3)_2$	0.61	−0.27	0.34	
$PtCl_2(SbPh_3)_2$	0.21	0.28	0.49	0.47
$PtI_2(SbPh_3)_2$	0.18	0.28	0.46	
$Pt(NO_2)_2(SbPh_3)_2$	0.19	0.29	0.48	
$PtCl_2(Sbptol_3)_2$	0.21	0.27	0.48	
$PtI_2(Sbptol_3)_2$	0.18	0.24	0.42	
$Pt(NO_2)_2(Sbptol_3)_2$	0.19	0.30	0.49	
$PtCl_2(Sbotol_3)_2$	0.19	0.25	0.44	
$PtI_2(Sbotol_3)_3$	0.20	0.25	0.45	
$Pt(NO_2)_2(Sbotol_3)_2$	0.21	0.31	0.52	
$PtCl_2(TeR'_2)_2$	0.00	0.48	0.48	0.53
$PtCl_2(TeR'_2)_2$	0.09	0.48	0.57	
$PtI_2(PPh_3)_2$	0.05	0.48	0.53	0.53
$PtI_2(PMePh_2)_2$	0.05	0.46	0.51	
$PtI_2(PMe_2Ph)_2$	0.05	0.45	0.50	
$PtI_2(PEtPh_2)_2$	0.05	0.46	0.51	
$PtI_2(PEt_2Ph)_2$	0.05	0.46	0.51	
$PtI_2(PEt_3)_2$	0.04	0.44	0.48	
$PtI_2(PEt_3)_2$	0.07	0.51	0.58	
$PtI_2(PBu_3)_2$	0.06	0.51	0.57	
$PtI_2(PMe_2Ph)_2$	0.06	0.51	0.57	

carbonyl species, $[Fe(CO)_4X]^+$, as acceptors, there is little difference between Cl_3Sn^- and I^- (Table 6). Similarly, Cl_3Sn^- and Ph_3Sb lose comparable amounts of charge to $[Fe(CO)_2cp]^+$, and Ph_3Sb and R'_2Te to $[Fe(CO)_4]^0$. However, it is clear from even these limited comparisons that significant differences can be detected between the acceptor abilities of different metals and even of one metal in different ligand environments. These effects will now be examined more closely.

(i) Acceptor abilities of different metals

As will be apparent from the discussions below, in order to compare the acceptor abilities of two metals it is necessary to examine completely analogous pairs of complexes. The oxidation state, the ancillary ligands, and even the stereochemistry must be the same. With such a severe restriction,

TABLE 6

Data for iron carbonyl complexes

	S_c	P_c	$S_c + P_c$	Average $S_c + P_c$
$Cl_3SnFe(CO)_4Cl$	0.73	−0.10	0.63	0.64
$(Cl_3Sn)_2Fe(CO)_4$	0.74	−0.06	0.68	
$(Cl_3Sn)_2Fe(CO)_4$	0.74	−0.07	0.67	
$Fe(CO)_4I_2$	0.03	0.60	0.63	0.63
$Cl_3SnFe(CO)_2cp$	0.67	−0.20	0.47	0.42
$Cl_3SnFe(CO)(PPh_3)cp$	0.61	−0.22	0.39	
$Cl_3SnFe(CO)(PEt_3)cp$	0.58	−0.23	0.35	
$Cl_3SnFe(CO)[P(OPh)_3]cp$	0.64	−0.21	0.43	
$Cl_3SnFe(CO)[P(OEt)_3]cp$	0.65	−0.21	0.44	
$[Fe(CO)_2(SbPh_3)cp]PF_6$	0.19	0.28	0.47	0.47
$Fe(CO)_4(SbPh_3)$	0.20	0.30	0.50	0.46
$Fe(CO)_3(SbPh_3)_2$	0.19	0.23	0.42	
$Fe(CO)_4(TeR'_2)$	0.03	0.38	0.41	0.41

TABLE 7

Complexes of 4*d* and 5*d* metals [a]

	S_c	P_c	$S_c + P_c$
$Cl_3SnRh(nbd)_2$	0.48	−0.18	0.31
$Cl_3SnIr(nbd)_2$	0.57	−0.22	0.35
$Cl_3SnRh(nbd)(PPh_3)_2$	0.41	−0.21	0.20
$Cl_3SnIr(nbd)(PPh_3)_2$	0.50	−0.21	0.29
$[PdCl_2(SnCl_3)_2]^{2-}$	0.73	−0.30	0.43
$[PtCl_2(SnCl_3)_2]^{2-}$	0.67	−0.29	0.38
cis $Pd(NO_2)_2(SbPh_3)_2$	0.17	0.28	0.45
cis $Pt(NO_2)_2(SbPh_3)_2$	0.19	0.29	0.48
trans $PdCl_2(Sbotol_3)_2$	0.17	0.26	0.43
trans $PtCl_2(Sbotol_3)_2$	0.19	0.25	0.44
trans $PdI_2(Sbotol_3)_2$	0.18	0.30	0.48
trans $PtI_2(Sbotol_3)_2$	0.20	0.25	0.45
$PdCl_2(TeR'_2)_2$	0.00	0.36	0.36
$PtCl_2(TeR'_2)_2$	0.04	0.48	0.52
$PdI_2(pdsa)$ [b]	0.04	0.42	0.47
$PtI_2(pdsa)$ [b]	0.04	0.45	0.49

[a] The stereochemistry of the tertiary stibine complexes is not certain. [b] pdsa = *o*-$C_6H_4(SbPh_2)(AsPh_2)$.

TABLE 8

Complexes of the coinage metals

	S_c	P_c	$S_c + P_c$
$Cl_3SnCu(PPh_3)_3$	0.39	−0.22	0.17
$Cl_3SnAg(PPh_3)_3$	0.36	−0.17	0.19
$Cl_3SnAu(PPh_3)_3$	0.36	−0.15	0.21
$[Cu(SbPh_3)_4]ClO_4$	0.15	0.13	0.28
$[Ag(SbPh_3)_4]BF_4$	0.14	0.17	0.31

very few suitable data are available, but Table 7 shows eight pairs involving complexes of Group VIII metals. In nearly every case, the 5*d* metal acts as a better acceptor than the corresponding 4*d* metal. (In the two exceptional pairs, the stereochemistries are not established with certainty.) Table 8 shows a similar comparison for Cl_3Sn^- and Ph_3Sb complexes of the coinage metals. Here the differences are smaller but in the same direction, and there are indications that the 3*d* metal is the poorest acceptor. The trend is that expected from HSAB theory, in that the 'soft' donors of the 5th Period might be expected to form better complexes with the 'softer' metals. This effect arises from the better overlap of 5*s*, 5*p* donor orbitals with 5*d* (and 6*s*, 6*p*) metal orbitals than with 4*d*(5*s*, 5*p*) and 3*d*(4*s*, 4*p*) orbitals.

The data of Tables 6 and 7 also suggest, as would be expected, that the acceptor ability of a metal increases with increase in oxidation state, from iron(0) to iron(II), from rhodium(I) to palladium(II), and from iridium(I) to platinum(II). Table 9 shows similar data for platinum(II), platinum(IV) and iridium(I), iridium(III) systems.

(ii) Effects of ancillary ligands

A survey of all the data available for complexes of Cl_3Sn^- and R_3Sb shows that metal carbonyl systems are the best acceptors, taking 0.45–0.7 electrons compared to 0.3–0.4 electrons for non-carbonyl-containing acceptors, and this effect is independent of the Period in which the metal lies.

TABLE 9

Effect of change in oxidation state

	S_c	P_c	$S_c + P_c$
$Cl_3SnPtCl(PPh_3)_2$	0.61	−0.27	0.34
$(Cl_3Sn)_2PtCl_2(PPh_3)_2$	0.68	−0.24	0.44
$IrCl(CO)(SbPh_3)_2$	0.17	0.17	0.34
$IrHCl_2(CO)(SbPh_3)_2$	0.20	0.28	0.48

TABLE 10

Effect of replacing carbonyl groups

	S_c	P_c	S_c+P_c
$Cl_3SnMn(CO)_5$	0.70	−0.14	0.56
$Cl_3SnMn(CO)_4(PPh_3)$	0.62	−0.20	0.42
$Cl_3SnCo(CO)_4$	0.78	−0.05	0.73
$Cl_3SnCo(CO)_3(PBu_3)$	0.71	−0.17	0.58
$Cl_3SnFe(CO)_2cp$	0.67	−0.20	0.47
$Cl_3SnFe(CO)[P(OEt)_3]cp$	0.66	−0.21	0.44
$Cl_3SnFe(CO)[P(OPh)_3]cp$	0.64	−0.21	0.43
$Cl_3SnFe(CO)(PPh_3)cp$	0.61	−0.22	0.38
$Cl_3SnFe(CO)(PEt_3)cp$	0.58	−0.23	0.35
$Cl_3SnFe(CO)[P(OPh)_3]cp$	0.64	−0.21	0.43
$Cl_3SnFe[P(OPh)_3]_2cp$	0.60	−0.23	0.37
$Fe(CO)_4(SbPh_3)$	0.20	0.30	0.50
$Fe(CO)_3(SbPh_3)_2$	0.19	0.23	0.42
$IrHCl_2(CO)(SbPh_3)_2$	0.20	0.28	0.48
$IrHCl_2(SbPh_3)_3$	0.19	0.18	0.37
$W(CO)_5(TeR'_2)$	0.02	0.30	0.32
$W(CO)_4(NCMe)(TeR'_2)$	0.02	0.25	0.27

Thus, carbonyl ligands are able to enhance the Lewis acidity of the metal centre, presumably by the synergic effect of back donation from metal to carbon monoxide. Such back donation removes negative charge from the metal atom, allowing a greater degree of ligand-to-metal donation for all the ligands. However, this trend is markedly reversed for R'_2Te, from which carbonyl systems apparently remove only ca. 0.33 electrons (average), while non-carbonyl acceptors take 0.4–0.6 electrons. Of possible significance here could be the fact that R'_2Te possesses an additional lone pair. Thus while Cl_3Sn^- and R_3Sb may, in principle, act as weak π-acceptor ligands, R'_2Te is potentially a π-donor ligand. The effect on QCC_c of loss of $5p_\pi$ electron density from tellurium would be opposite in sign to that of loss of $5p_\sigma$ electron density. Thus, any π-donation would result in QCC_c being less negative than would otherwise be expected. Metal carbonyl groups should be effective π-acceptors, and this may explain the apparently anomalous behaviour of R'_2Te.

Metal centres bearing large numbers of carbonyl groups are strong σ-acceptors. Substitution of the carbonyl groups by other ligands leads to a substantial decrease in acceptor ability towards Cl_3Sn^-, Ph_3Sb and R'_2Te (Table 10). Replacement of CO by a ligand with greater σ-basicity and lower π-acidity would decrease the positive charge on the metal atom, leading to a

TABLE 11

Effect of good σ-donor ligands [a]

	S_c	P_c	S_c+P_c
$Cl_3SnRh(nbd)_2$	0.49	−0.18	0.31
$Cl_3SnRh(nbd)(SbPh_3)_2$	0.50	−0.26	0.24
$Cl_3SnRh(nbd)(AsPh_3)_2$	0.46	−0.22	0.24
$Cl_3SnRh(nbd)(PPh_3)_2$	0.41	−0.21	0.20
$Cl_3SnIr(nbd)_2$	0.57	−0.22	0.35
$Cl_3SnIr(nbd)[PPh(OMe)_2]$	0.53	−0.22	0.31
$Cl_3SnIr(nbd)(PPh_3)_2$	0.50	−0.21	0.29
cis $PtI_2(SbPh_3)_2$	0.06	0.53	0.59
cis $PtI_2(AsPh_3)_2$	0.06	0.52	0.58
cis $PtI_2(PPh_3)_2$	0.05	0.48	0.53
cis $PtI_2(PEt_3)_2$	0.04	0.44	0.48
cis $PtI_2(NH_3)_2$	0.04	0.42	0.46
PtI_2(dcpd)	0.04	0.50	0.54
PtI_2(dppp)	0.05	0.45	0.50
PtI_2(pdsa)	0.04	0.45	0.49
PtI_2(dpae)	0.04	0.45	0.49
PtI_2(dppe)	0.04	0.43	0.47

[a] nbd = norbornadiene, dcpd = dicyclopentadiene, dpae = $Ph_2As(CH_2)_2AsPh_2$, dppp = $Ph_2P(CH_2)_3PPh_2$, pdsa = $o\text{-}C_6H_4(SbPh_2)(AsPh_2)$, dppe = $Ph_2P(CH_2)_2PPh_2$.

decrease in acceptance from Cl_3Sn^-, etc. This trend is well illustrated by the data for $Cl_3SnFe(CO)(L)cp$, where charge donation from tin to iron decreases in the series $L = CO > P(OR)_3 > PR_3$, following the generally accepted trend to greater π-acceptance and lower σ-donation by tertiary phosphites than tertiary phosphines. A further decrease in donation from tin follows substitution of the second carbonyl group.

These effects are also seen in non-carbonyl systems, although rather less markedly. The data of Table 11 show that donation by Cl_3Sn^- to rhodium(I) or iridium(I) in the five-coordinate complexes $M(SnCl_3)(nbd)L_2$ (nbd = norbornadiene) decreases in the order $L = \frac{1}{2}nbd > SbPh_3 > AsPh_3 > PPh_3$ (M = Rh) and $L = \frac{1}{2}nbd > PPh(OMe)_2 > PPh_3$ (M = Ir), which are the orders of increasing σ-basicity of the ligands L. Similar trends are found in square-planar platinum(II) iodo complexes, *cis* PtI_2L_2, where donation by iodide decreases in the order $L = Ph_3Sb > Ph_3As > PPh_3 > PEt_3 > NH_3$. As will be seen below, detailed discussion of these data is complicated by the occurrence of directional effects.

Somewhat surprisingly, in the carbonyl series the substitution effect seems to be rather greater in $Cl_3SnCo(CO)_4$, $Cl_3SnMn(CO)_5$ and $Ph_3SbFe(CO)_4$ than in the cyclopentadienyl–carbonyl complexes. Since the last of these contain fewer carbonyl groups, a proportionately greater effect might have been anticipated. When many CO groups are present, the remaining groups would be expected to buffer the effects of substitution of one of their number by increasing their degree of π-acceptance; such an increase in back-donation is usually inferred from the IR spectra. It therefore seems possible that a directional effect may be operating since, in $Cl_3SnCo(CO)_4$, $Cl_3SnMn(CO)_5$, and $Ph_3SbFe(CO)_4$, the incoming ligand enters *trans* to the Mössbauer ligand. If such a directional effect can be identified, the analyses of IR data for substituted carbonyls in terms of the σ-basicity and π-acidity of the substituents must be re-evaluated. In such treatments it is usually assumed that the effects of σ bonding are passed isotropically to all other ligands [42].

(iii) Cis *and* trans *influences*

The effects discussed above for the carbonyl compounds suggest the possibility of a *trans* influence, a phenomenon which has been studied by a wide variety of techniques [43]. Ligands are rated in a *trans* influence series which represents the extent to which each ligand weakens the bond in the position *trans* to itself in the equilibrium ground-state configuration of the complex [44]. In the present context, a weakening of a metal–ligand bond involving one of the Mössbauer ligands would be manifested as a reduction in donation. The most extensive data are available for the iodide ligand in platinum(II) complexes [4,5]. The lowest extent of donation is found in complexes where iodide is *trans* to a hydride or methyl group, and the highest extent when iodide is *trans* to iodide, which accords with the conventional *trans* influence series [43]. These systems are illustrated in Table 12, which suggests a difference in donation of about 0.2 electrons across the extremes of the series. A further indication that a systematic effect is operating comes from the observation that, when both isomers of PtI_2L_2 are available, less donation by iodide usually occurs in the *cis* complex, and

TABLE 12

Platinum(II) iodo complexes

	S_c	P_c	$S_c + P_c$
trans $PtI_2(PEt_3)_2$	0.07	0.51	0.58
trans $PtI_2(PMe_2Ph)_2$	0.06	0.51	0.57
trans $PtI_2(PBu_3)_2$	0.06	0.51	0.57
trans $Pt(H)I(PEt_3)_2$	0.05	0.34	0.39
trans $Pt(H)I(PPh_3)_2$	0.05	0.35	0.40
trans $Pt(CH_3)I(PMe_2Ph)_2$	0.04	0.32	0.36

TABLE 13

Cis–trans pairs of platinum(II) iodo complexes

	S_c	P_c	S_c+P_c
$PtI_2(PEt_3)_2$ *cis*	0.04	0.44	0.48
trans	0.07	0.51	0.58
PtI_2(β-picoline)$_2$ *cis*	0.06	0.47	0.53
trans	0.05	0.46	0.51
$PtI_2(py)_2$ *cis*	0.05	0.41	0.46
trans	0.05	0.45	0.50
$PtI_2(NH_3)_2$ *cis*	0.04	0.42	0.46
trans	0.05	0.43	0.48

the differences are larger for $L = PEt_3$ than for the N-donor ligands (Table 13), again consistent with the normal *trans* influence series $I^- <$ N-donor $<$ P-donor. Fuller examination can be made with the series of complexes *cis* PtI_2L_2 (Table 14) which indicate the orders $Ph_3Sb < Ph_3As < Ph_3P < Ph_2RP < Ph_2RP < R_3P$ (R = alkyl) and $NH_2R <$ β-picoline $<$ py, NH_3. These series accord well with those derived from other data [43] but, when the two sets of data are combined, NH_3 and py appear to have much greater *trans* influences than is usual. The most likely explanation for this anomaly is that each iodine has, in addition to a ligand L in the *trans* position, another ligand L in the *cis* position. Change of L exerts not only a differing *trans* influence but also, in principle at least, a differing *cis* influence. The *cis* influence is normally dismissed as being insignificant, but this cannot be justified by the present data (vide infra). Bancroft and Butler [5] have eliminated this effect by studying the series *trans* $PtI(L)(PMe_2Ph)_2$, in which the ligands *cis* to iodide remain constant. Their data (Table 15) give the *trans*

TABLE 14

Data for *cis* $PtI_2(L)_2$—the *trans* influence

L	S_c	P_c	S_c+P_c
$SbPh_3$	0.06	0.53	0.59
$AsPh_3$	0.06	0.52	0.58
PPh_3	0.05	0.46	0.51
$PMePh_2$	0.05	0.46	0.51
$PEtPh_2$	0.05	0.46	0.51
PMe_2Ph	0.05	0.45	0.50
PEt_2Ph	0.05	0.46	0.51
PEt_3	0.04	0.44	0.48
NH_2Oct	0.05	0.52	0.57
β-picoline	0.06	0.47	0.53
py	0.05	0.41	0.46
NH_3	0.04	0.42	0.46

TABLE 15

Data for *trans* PtI(L)(PMe$_2$Ph)$_2$ — the *trans* influence

L	S_c	P_c	S_c+p_c
I^-	0.06	0.51	0.57
$AsPh_3$	0.04	0.47	0.51
PPh_3	0.04	0.47	0.51
CNC_6H_4OMe-*p*	0.05	0.44	0.49
CNEt	0.05	0.43	0.48
$PPh(OMe)_2$	0.05	0.43	0.48
$P(OMe)_3$	0.05	0.42	0.47
CF_3^-	0.05	0.36	0.41
CH_3^-	0.04	0.32	0.36

influence series $L = I^- < AsPh_3$, $PPh_3 < CNR$, $PPh(OMe)_2$, $P(OMe)_3 < CF_3^- < CH_3^-$.

The *cis* influence can be directly studied in the series *trans* PtI_2L_2 [4], data for which are shown in Table 16. There is clear evidence for the working of a substantial *cis* influence, comparable in magnitude to the *trans* influence. However, the series obtained is P-donor < S-donor < N-donor, which is the reverse of the conventional *trans* influence series. The earliest theory of the *trans* influence, due to Syrkin [45], agrees with this finding. Syrkin based his arguments on an *s–d* hybridisation scheme and suggested that a ligand which forms a strong bond to the metal would also strengthen the bonds in the *cis* positions. Thus, a ligand which exerts a high *trans* influence has a weak *cis* influence. More modern molecular orbital treatments [46,47] suggest that the two influences should be similar in magnitude but operate in the same direction. Most recently, the calculations of Shustorovich [48] show that the *cis* influence should be the smaller but whether it operates in the same direction as or in opposition to the *trans* influence depends on the relative contributions of the metal *d* and *s* orbitals to the bonding.

TABLE 16

Data for *trans* PtI$_2$(L)$_2$ — the *cis* influence

L	S_c	P_c	S_c+P_c
PEt_3	0.07	0.51	0.58
PBu_3	0.06	0.51	0.57
SMe_2	0.05	0.50	0.55
SEt_2	0.05	0.46	0.51
β-picoline	0.05	0.46	0.51
py	0.05	0.45	0.50
NH_3	0.05	0.43	0.48

F. CONCLUSIONS

The data discussed above allow examination of the way in which the amount of charge removed from a ligand by coordination to a transition metal is affected by the identity of the metal, its oxidation state, and the nature and stereochemical positioning of the ancillary ligands. In many cases the changes observed are very small, close to the uncertainties of the treatment, but it is reassuring that there are usually several sets of data showing similar trends. Most significantly, the same trends are shown by each of the indicator ligands, Cl_3Sn^-, R_3Sb, R'_2Te and I^-, which suggests that fundamental changes are being observed. Such harmony is all the more convincing when the substantial differences in hybridisation of the various ligands are considered. The iodide ion employs principally its $5p$ orbital while Cl_3Sn^- adapts its hybridisation to suit the acceptor, yet both respond in the same ways to the demands of different acceptors.

The general trends which emerge are that, for these ligands:

(i) Similar amounts of charge are donated by each of the indicator ligands;

(ii) $5d$ metals are better acceptors than $4d$ or $3d$ metals;

(iii) carbonyl groups enhance and good σ-donor ligands decrease the acceptor power of the metal;

(iv) the *trans* influence is manifested in a similar way to that shown by other techniques;

(v) the *cis* influence is much larger than that found by other techniques.

In principle, similar data could be provided by NQR measurements, for which there is a wide range of suitable isotopes, e.g. ^{35}Cl, ^{37}Cl, ^{79}Br, ^{81}Br, ^{75}As, as well as ^{127}I and ^{121}Sb. Such data as are available show some of the trends discussed above [49–51]. A serious disadvantage of the NQR method, however, is that it provides only the QCC and no information is obtained about changes in *s* orbital populations. This might be adequate for the halides, which coordinate principally through *p* orbitals, but would give a very incomplete picture for less electronegative ligands such as $^{75}AsPh_3$, where considerable hybridisation of the valence orbitals is expected.

It might be thought that donation to any given metal centre would decrease through the series of Mössbauer ligands from Cl_3Sn^- to I^-, as the donor atom becomes more electronegative. The difference in electronegativity between tin(II) and antimony(III) is offset by the difference in substituents carried by the two atoms; tin bears the more electronegative chlorine and antimony the less electronegative aryl groups. Similarly, for tellurium(II) and iodine(−I), the differences in oxidation state and formal charge outweigh the difference in electronegativity.

It is also worthwhile to ask why the *cis* influence demonstrated by the

Mössbauer (and NQR) data is so different from that indicated by other methods. Most of the other methods, and all of the calculations, monitor some property of the whole metal–ligand bond: bond lengths, stretching force constants, electron densities or populations. However, in the Mössbauer and NQR methods, attention is focussed principally on the ligand donor atom, showing changes in electron density on that atom rather than in the metal–ligand bond as a whole. For instance, the contribution to the QCC of any given element of charge is inversely proportional to the cube of the distance of the charge from the nucleus under examination. Charge density on adjacent atoms thus makes a considerably smaller contribution to the QCC than that in the valence shell of the Mössbauer (NQR) atom. This effect is quite clearly shown in the calculations of Perkins and co-workers [47]. Using the bond-orbital populations as measures of bond strength, these calculations show that the *cis* and *trans* influences should operate in the same direction, in conflict with the results discussed above. However, the calculated 5*p* orbital populations of the iodide ligands in PtI_2L_2 correlate very well with the observed values [4].

The ligand's-eye view is thus a rather myopic, egocentric impression, but it is nonetheless valuable. In many areas of chemistry it is the electronic changes produced within one ligand which are of importance, rather than the distribution of charge over the whole complex. For instance, in catalysis, polarization of a substrate by coordination allows low-energy pathways to desirable reactions. An understanding of this polarization and its dependence on the metal and the ancillary ligands is vital to the development of more effective catalysts. I hope to have shown that the Mössbauer method provides a valuable probe for these and related studies.

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APPENDIX

Collected data for all isotopes

TABLE A1

Data for $SnCl_3^-$ complexes and salts
$P_c = -QCC_c/(8.0\ mm\ s^{-1})$
$S_c = -[IS_c/(mm\ s^{-1}) - 0.15P_c]/2.7$
$QS = \frac{1}{2}QCC$
Error limits are: IS, ±0.05 mm s^{-1}; QCC, ±0.1 mm s^{-1}

	Ref.	IS [a]	QS	IS_c	QCC_c	P_c	S_c	$S_c + P_c$
		(mm s^{-1})						
$CsSnCl_3$	32	3.40	1.22	−0.14	0.44	−0.06	0.05	−0.01
Me_4NSnCl_3	35	3.51	1.08	−0.03	0.16	−0.02	0.01	−0.01
$Et_2OHSnCl_3$	36	3.54	1.00	0	0	0	0	0.00
Et_4NSnCl_3	37	3.47	1.00	−0.07	0.00	0.00	0.03	0.03
$[Co(NO_2)_2en_2]SnCl_3$	33	3.16	1.26	−0.38	0.52	−0.07	0.14	0.07
$[CoCl(dppe)_2]SnCl_3$	33	3.10	1.36	−0.44	0.72	−0.09	0.16	0.07
$[Nicp(PPh_3)]SnCl_3$	[a]	3.18	1.20	−0.36	0.40	−0.05	0.13	0.08
$Cl_3SnAu(CNC_6H_4OMe)_2$	33	3.06	1.24	−0.48	0.48	−0.06	0.18	0.12
$PyHSnCl_3$	34	3.12	1.07	−0.42	0.14	−0.02	0.15	0.13
$Cl_3SnAu(PMe_2Ph)_2$	33	2.92	1.35	−0.62	0.70	−0.09	0.23	0.14
$Cl_3SnCu(PPh_3)_3$	32, 33	2.46	1.88	−1.08	1.76	−0.22	0.39	0.17
$Cl_3SnAg(PPh_3)_3$	32, 33	2.54	1.69	−1.00	1.38	−0.17	0.36	0.19
$Cl_3SnRh(nbd)(PPh_3)_2$	37	2.41	1.83	−1.13	1.66	−0.21	0.41	0.20
$Cl_3SnAu(PPh_3)_3$	32, 33	2.44	1.58	−1.00	1.16	−0.15	0.36	0.21
$Cl_3SnRh(nbd)(SbPh_3)_2$	32	2.15	2.04	−1.39	2.08	−0.26	0.50	0.24
$Cl_3SnRh(nbd)(AsPh_3)_2$	32	2.28	1.89	−1.26	1.78	−0.22	0.46	0.24
$Cl_3SnAu(AsPh_3)_3$	33	2.26	1.67	−1.28	1.34	−0.17	0.46	0.29
$Cl_3SnIr(nbd)(PPh_3)_2$	33	2.16	1.82	−1.38	1.64	−0.21	0.50	0.29
$Cl_3SnIr(cod)(AsMe_2Ph)_2$	33	2.17	1.83	−1.37	1.66	−0.21	0.50	0.29
$Cl_3SnIr(cod)(dpdae)$	33	2.12	1.88	−1.42	1.76	−0.22	0.51	0.29

TABLE A1 (continued)

	Ref.	IS [a]	QS	IS_c	QCC_c	P_c	S_c	S_c+P_c
		(mm s^{-1})						
$Cl_3SnRh(PPh_3)_3$	32	2.10	1.91	−1.44	1.82	−0.23	0.52	0.29
$Cl_3SnIr(cod)(dpae)$	33	2.15	1.79	−1.39	1.58	−0.20	0.50	0.30
$Cl_3SnIr(nbd)[PPh(OMe)_2]_2$	33	2.08	1.89	−1.46	1.78	−0.22	0.53	0.31
cis $(Ph_3BzP)_2[PtCl_2(SnCl_3)_2]$	32	1.84	2.21	−1.70	2.42	−0.30	0.61	0.31
$Cl_3SnRh(nbd)_2$	32, 33	2.20	1.72	−1.35	1.44	−0.18	0.49	0.31
trans $Pt(H)(SnCl_3)(PPh_3)_2$	32	1.94	1.98	−1.60	1.96	−0.25	0.57	0.32
$Cl_3SnIr(cod)[PPh(OMe)_2]_2$	33	2.04	1.87	−1.50	1.74	−0.22	0.55	0.33
trans $PtH(SnCl_3)(PEt_3)_2$	32	2.02	1.89	−1.52	1.78	−0.22	0.55	0.33
$Cl_3SnIr(tfbb)_2$	33	1.98	1.92	−1.56	1.84	−0.23	0.57	0.34
trans $PtCl(SnCl_3)(PPh_3)_2$	32	1.84	2.07	−1.70	2.14	−0.27	0.61	0.34
$Cl_3SnIr(cod)_2$	33	2.06	1.77	−1.48	1.54	−0.19	0.54	0.35
$Cl_3SnIr(nbd)_2$	33	1.98	1.86	−1.56	1.72	−0.22	0.57	0.35
$(Me_4N)_2[RuCl_2(SnCl_3)_2]$	32, 35	1.89	1.99	−1.65	1.97	−0.25	0.60	0.35
$Cl_3SnFe(CO)(PEt_3)cp$	30	1.95	1.91	−1.59	1.82	−0.23	0.58	0.35
$(Et_4N)_2[RhCl(SnCl_3)_2CO]$	32	1.74	2.15	−1.80	2.30	−0.29	0.65	0.36
$(Et_4N)_2[Rh(SnCl_3)_3CO]$	32	1.68	2.25	−1.86	2.50	−0.31	0.67	0.36
$Cl_3SnNi(PPh_3)cp$	[b]	1.85	1.90	−1.69	1.80	−0.23	0.61	0.37
$Cl_3SnFe[P(OPh)_3]_2cp$	30	1.88	1.92	−1.66	1.84	−0.23	0.60	0.37
$Cl_3SnFeCl(pdma)_2$	32	1.98	1.81	−1.56	1.62	−0.20	0.57	0.37
$Cl_3SnFe(CO)(PPh_3)cp$	30 [c]	1.86	1.89	−1.66	1.76	−0.22	0.60	0.38
cis$(Ph_4As)_2[PtCl_2(SnCl_3)_2]$	32	1.67	2.18	−1.87	2.36	−0.30	0.68	0.38
$(Ph_3BzP)_2[RuCl_2(SnCl_3)_2]$	32	1.83	1.97	−1.71	1.94	−0.24	0.62	0.38
cis$(Me_4N)_2[PtCl_2(SnCl_3)_2]$	32, 35	1.70	2.11	−1.84	2.21	−0.28	0.67	0.39
$Cl_3SnFe(dppe)cp$	33	1.92	1.76	−1.62	1.52	−0.19	0.59	0.40
$(Et_4N)_2[RhCl_2(SnCl_3)(CO)]$	32	1.77	1.93	−1.77	1.86	−0.23	0.64	0.41
$(Ph_3BzP)_4[Ir_2Cl_6(SnCl_3)_4]$	32	1.72	2.01	−1.82	2.02	−0.25	0.66	0.41

trans $Cl_3SnMn(CO)_4(PPh_3)$	26, 28	1.70	1.78	−1.84	1.56	−0.20	0.62	0.42
$(Me_4N)_2[PdCl_2(SnCl_3)_2]$	35	1.52	2.21	−2.02	2.42	−0.30	0.73	0.43
$Cl_3SnFe(CO)[P(OPh)_3]cp$	30	1.79	1.82	−1.75	1.64	−0.21	0.64	0.43
$PtCl_2(SnCl_3)_2(PPh_3)_2$	32	1.69	1.94	−1.85	1.88	−0.24	0.68	0.44
$Cl_3SnFe(CO)[P(OEt)_3]cp$	30	1.77	1.85	−1.77	1.70	−0.21	0.65	0.44
cis$(Et_4N)_2[PtCl_2(SnCl_3)_2]$	32	1.61	2.01	−1.93	2.02	−0.25	0.70	0.45
$(Ph_3BzP)_4[Rh_2Cl_2(SnCl_3)_4]$	32	1.67	1.90	−1.87	1.80	−0.22	0.67	0.45
$(Me_4N)_4[Ir_2Cl_6(SnCl_3)_4]$	32	1.67	1.94	−1.87	1.88	−0.23	0.68	0.45
$(Ph_4As)_3[Pt(SnCl_3)_5]$	32	1.69	1.82	−1.85	1.64	−0.21	0.67	0.46
$(Et_4N)_4[RhCl_2(SnCl_3)_4]$	32	1.70	1.85	−1.84	1.70	−0.21	0.67	0.46
$(Ph_3BzP)_3[Pt(SnCl_3)_5]$	32	1.72	1.74	−1.82	1.48	−0.19	0.66	0.47
$Cl_3SnFe(CO)_2cp$	23,24,25, 30,31 [c]	1.71	1.81	−1.83	1.62	−0.20	0.67	0.47
$(Et_4N)_3[Pt(SnCl_3)_5]$	32	1.74	1.72	−1.80	1.44	−0.18	0.66	0.48
$Cl_3SnW(CO)_3cp$	31	1.67	1.77	−1.87	1.54	−0.19	0.68	0.49
$(Me_4N)_3[Pt(SnCl_3)_5]$	32	1.63	1.79	−1.91	1.58	−0.20	0.70	0.50
$Cl_3SnMo(CO)_3cp$	31	1.69	1.71	−1.85	1.42	−0.18	0.68	0.50
$Cl_3SnCr(CO)_3cp$	31	1.67	1.54	−1.87	1.08	−0.14	0.68	0.54
$Cl_3SnMn(CO)_5$	25,26,31	1.62	1.57	−1.92	1.14	−0.14	0.70	0.56
$Cl_3SnCo(CO)_3(PBu_3)$	29	1.59	1.67	−1.95	1.36	−0.17	0.71	0.58
$Cl_3SnFe(CO)_4$	27	1.55	1.40	−1.99	0.80	−0.10	0.73	0.63
trans$(Cl_3Sn)_2Fe(CO)_4$	27	1.53	1.26	−2.01	0.52	−0.07	0.74	0.67
cis$(Cl_3Sn)_2Fe(CO)_4$	27	1.53	1.25	−2.01	0.50	−0.06	0.74	0.68
$Cl_3SnCo(CO)_4$	28,29	1.42	1.20	−2.12	0.40	−0.05	0.78	0.73
$SnCl_4$	1	0.80	0.00	−2.74	2.00	+0.25	1.03	1.28

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[a] Relative to SnO_2. [b] P.A. McArdle and A.R. Manning, Chem. Commun., (1967) 417. [c] W.R. Cullen, J.R. Sams and J.A.J. Thompson, Inorg. Chem., 10 (1971) 843.

TABLE A2

Data for triorganostibines and their metal complexes

$P_c = -\mathrm{QCC}_c/(26\ \mathrm{mm\ s^{-1}})$

$S_c = [\mathrm{IS}_c/(\mathrm{mm\ s^{-1}}) + 0.80\ P_c]/15$

Error limits are: IS, ±0.05 mm s^{-1}; QCC, ±0.5 mm s^{-1}

	Ref.	IS[a]	QCC	IS_c	QCC_c	P_c	S_c	S_c+P_c
		(mm s^{-1})						
L=Ph_3Sb	20[b,c]	−9.33	16.8					
[CuL_4]ClO_4		−7.21	13.3	2.12	−3.5	0.13	0.15	0.28
trans PdI_2L_2	20	−7.23	10.7	2.10	−6.1	0.23	0.15	0.28
[AgL_4]BF_4		−7.35	12.4	1.98	−4.4	0.17	0.14	0.31
trans $PdCl_2L_2$	20	−7.31	12.0	2.02	−4.8	0.18	0.14	0.32
$IrCl(CO)L_2$		−6.89	12.5	2.44	−4.3	0.17	0.17	0.34
$IrHCl_2L_3$		−6.66	12.0	2.67	−4.8	0.18	0.19	0.37
$RhCl_3L_3$	20	−7.14	10.7	2.19	−6.1	0.23	0.16	0.39
$Fe(CO)_3L_2$	21	−6.65	10.9	2.68	−5.9	0.23	0.19	0.42
cis(?)$Pd(NO_2)_2L_2$	20	−7.04	9.6	2.29	−7.2	0.28	0.17	0.45
cis PtI_2L_2	20	−6.78	9.6	2.55	−7.2	0.28	0.18	0.46
[$Fe(CO)_2(L)cp$]PF_6	22	−6.7	9.5	2.63	−7.3	0.28	0.19	0.47
$IrHCl_2(CO)L_2$		−6.49	9.5	2.84	−7.3	0.28	0.20	0.48
cis $Pt(NO_2)_2L_2$	20	−6.73	9.3	2.60	−7.5	0.29	0.19	0.48
cis $PtCl_2L_2$	20	−6.44	9.5	2.89	−7.3	0.28	0.21	0.49
$Fe(CO)_4L$	21	−6.62	9.0	2.71	−7.8	0.30	0.20	0.50
L′=Sb(tol-*p*)$_3$	20	−9.37	17.0					
cis $PtI_2L'_2$	20	−6.91	10.8	2.46	−6.2	0.24	0.18	0.42
cis $PtCl_2L'_2$	20	−6.48	10.0	2.89	−7.0	0.27	0.21	0.48
cis $Pt(NO_2)_2L'_2$	20	−6.75	9.3	2.62	−7.7	0.30	0.19	0.49
L″=Sb(tol-*o*)$_3$	20	−9.77	17.4					
trans $PdCl_2L''_2$	20	−7.40	10.6	2.37	−6.8	0.26	0.17	0.43
trans $PtCl_2L''_2$	20	−7.09	10.8	2.68	−6.6	0.25	0.19	0.44
trans $PtI_2L''_2$	20	−7.00	11.0	2.77	−6.4	0.25	0.20	0.45
trans(?) $Pd(NO_2)_2L''_2$	20	−7.24	9.8	2.53	−7.6	0.29	0.18	0.47
trans $PdI_2L''_2$	20	−7.24	9.6	2.53	−7.8	0.30	0.18	0.48
cis(?) $Pt(NO_2)_2L''_2$	20	−6.84	9.4	2.93	−8.0	0.31	0.21	0.42

[a] Relative to $CaSnO_3$. [b] G.G. Long, J.G. Stevens, R.J. Tullbane and L.H. Bowen, J. Am. Chem. Soc., 92 (1970) 4230. [c] T.B. Brill, G.E. Parris, G.G. Long and L.H. Bowen, Inorg. Chem., 12 (1973) 1888.

TABLE A3

Data for diaryltellurium and complexes
$P_c = -\mathrm{QCC}_c/(15.7\ \mathrm{mm\ s^{-1}})$
$S_c = -[\mathrm{IS}_c/(\mathrm{mm\ s^{-1}}) - 0.45 P_c]/2.7$
Error limits: IS, ±0.08 mm s^{-1}; QCC±0.2 mm s^{-1}

	Ref.	IS[a]	QCC	IS_c	QCC_c	P_c	S_c	$S_c + P_c$
		(mm s^{-1})						
$L = Te(C_6H_4OEt\text{-}p)_2$	18	0.14	10.4					
$W(CO)_3(NCMe)L$	18	0.21	8.46	0.07	−3.88	0.25	0.02	0.27
$Mo(CO)_5L$	18	0.08	8.71	−0.06	−3.38	0.22	0.06	0.28
$Cr(CO)_5L$	18	0.21	8.06	0.07	−4.68	0.29	0.02	0.31
$W(CO)_5L$	18	0.22	8.02	0.08	−4.76	0.30	0.02	0.32
$PdCl_2L_2$	18	0.31	7.61	0.17	−5.58	0.36	0.00	0.36
$Fe(CO)_4L$	18	0.24	7.44	0.10	−5.92	0.38	0.03	0.41
$PdBr_2L_2$	18	0.29	6.78	0.15	−7.24	0.46	0.02	0.48
$PtCl_2L_2$	18	0.35	6.63	0.21	−7.54	0.48	0.00	0.48
$PtCl_2L_2$	18	0.12	6.61	−0.02	−7.58	0.48	0.09	0.57
$HgBr_2L_2$	19	0.37	6.0	0.23	−8.80	0.56	0.01	0.57
HgI_2L_2	19	0.28	6.25	0.14	−8.30	0.53	0.04	0.57
$HgCl_2L_2$	19	0.32	5.96	0.18	−8.88	0.57	0.03	0.60
$[L\cdot CH_3]I$	17	0.15	5.8	0.01	−9.2	0.59	0.09	0.68

[a] Relative to I/Cu.

TABLE A4

Data for iodo-complexes

$P_c = -\mathrm{QCC}_c/(70.3\ \mathrm{mm\ s^{-1}})$

$S_c = -[\mathrm{IS}_c/(\mathrm{mm\ s^{-1}}) - 1.5P_c]/9.0$

Error limits: IS, ±0.05 mm s^{-1}; QCC, ±0.2 mm s^{-1}

P_c	Ref.	IS[a]	QCC	IS_c	QCC_c	P_c	S_c	$S_c + P_c$
		(mm s^{-1})						
I^-	12[b]	−0.54	0					
trans $PtI(CH_3)(PMe_2Ph)_2$	5	−0.44	−23.8	0.10	−23.8	0.32	0.04	0.36
trans $PtI(H)(PEt_3)_2$	4	−0.47	−24.2	0.07	−24.2	0.34	0.05	0.39
trans $PtI(H)(PPh_3)_2$	4	−0.43	−24.7	0.11	−24.7	0.35	0.05	0.40
trans $PtI(CF_3)(PMe_2Ph)_2$	5	−0.41	−27.8	0.13	−27.8	0.36	0.05	0.41
$PdI_2[Ph_2Sb(CH_2)_3SbPh_2]$	4	−0.35	−26.8	0.19	−26.8	0.38	0.05	0.43
$PtI_2[o\text{-}C_6H_4(PPh_2)_2]$	4	−0.06	−30.2	0.48	−30.2	0.43	0.02	0.45
cis $PtI_2(C_5H_5N)_2$	4	−0.31	−28.8	0.23	−28.8	0.41	0.05	0.46
cis $PtI_2(NH_3)_2$	4	−0.22	−29.1	0.32	−29.1	0.42	0.04	0.46
$PtI_2[Ph_2P(CH_2)_2PPh_2]$	4	−0.27	−30.1	0.27	−30.1	0.43	0.04	0.47
$PdI_2[o\text{-}C_6H_4(SbPh_2)(AsPh_2)]$	4	−0.32	−29.3	0.22	−29.3	0.42	0.05	0.47
cis $PtI_2(PEt_3)_2$	4	−0.20	−30.8	0.34	−30.8	0.44	0.04	0.48
trans $PtI_2(NH_3)_2$	4	−0.35	−30.5	0.19	−30.5	0.43	0.05	0.48
trans$[PtI(CNEt)(PMe_2Ph)_2]PF_6$	5	−0.30	−31.9	0.24	−31.9	0.43	0.05	0.48
trans$[PtI\{PPh(OMe)_2\}(PMe_2Ph)_2]PF_6$	5	−0.29	−32.3	0.25	−32.3	0.43	0.05	0.48
$PdI_2[o\text{-}C_6H_4(AsPh_2)_2]$	4	−0.28	−30.4	0.26	−30.4	0.43	0.05	0.48
trans$[PtI(NCC_6H_4OMe)(PMe_2Ph)_2]PF_6$	5	−0.33	−32.6	0.21	−32.6	0.44	0.05	0.49

$PtI_2[Ph_2As(CH_2)_2AsPh_2]$	4	−0.22	−31.6	0.32	−31.6	0.45	0.04	0.49
$PtI_2[o\text{-}C_6H_4(SbPh_2)(AsPh_2)]$	4	−0.18	−31.7	0.36	−31.7	0.45	0.04	0.49
cis $PtI_2(PMe_2Ph)_2$	4	−0.26	−32.0	0.28	−32.0	0.45	0.05	0.50
trans $PtI_2(C_5H_5N)_2$	4	−0.24	−31.8	0.30	−31.8	0.45	0.05	0.50
$PtI_2[Ph_2P(CH_2)_3PPh_2]$	4	−0.29	−31.8	0.25	−31.8	0.45	0.05	0.50
cis $PtI_2(PMePh_2)_2$	4	−0.29	−32.4	0.25	−32.4	0.46	0.05	0.51
cis $PtI_2(PEtPh_2)_2$	4	−0.26	−32.4	0.28	−32.4	0.46	0.05	0.51
cis $PtI_2(PEt_2Ph)_2$	4	−0.27	−32.3	0.27	−32.3	0.46	0.05	0.51
trans $PtI_2(SEt_2)_2$	4	−0.25	−32.7	0.29	−32.7	0.46	0.05	0.51
trans $PtI_2(\beta$-picoline$)_2$	4	−0.31	−32.6	0.23	−32.6	0.46	0.05	0.51
trans$[PtI(AsPh_3)(PMe_2Ph)_2]PF_6$	5	−0.25	−34.5	0.29	−34.5	0.46	0.05	0.51
trans$[PtI(PPh_3)(PMe_2Ph)_2]PF_6$	5	−0.21	−35.3	0.33	−35.3	0.47	0.04	0.51
$HgI_2\cdot$dioxan	6	0.18	−36.2	0.72	−36.2	0.51	0.01	0.52
cis $PtI_2(PPh_3)_2$	4	−0.27	−33.7	0.27	−33.7	0.48	0.05	0.53
cis $PtI_2(\beta$-picoline$)_2$	4	−0.32	−32.8	0.22	−32.8	0.47	0.06	0.53
$PtI_2(C_{10}H_{12})$	4	−0.08	−35.0	0.46	−35.0	0.50	0.04	0.54
trans $PtI_2(SMe_2)_2$	4	−0.24	−35.2	0.30	−35.2	0.50	0.05	0.55
cis $PtI_2[NH_2(C_8H_{17})]_2$	4	−0.21	−36.4	0.33	−36.4	0.52	0.05	0.57
trans $PtI_2(PBu_3)_2$	4	−0.29	−35.7	0.25	−35.7	0.51	0.06	0.57
trans $PtI_2(PMe_2Ph)_2$	5	−0.30	−36.0	0.24	−36.0	0.51	0.06	0.57
cis $PtI_2(AsPh_3)_2$	4	−0.26	−36.5	0.28	−36.5	0.52	0.06	0.58
trans $PtI_2(PEt_3)_2$	4	−0.33	−35.9	0.21	−35.9	0.51	0.07	0.58
cis $PtI_2(SbPh_3)_2$	4	−0.25	−37.4	0.29	−37.4	0.53	0.26	0.59
cis $Fe(CO)_4I_2$	7,8	0.13	−42.2	0.67	−42.2	0.60	0.03	0.63

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[a] Relative to ZnTe. [b] B.S. Ehrlich and M. Kaplan, J. Chem. Phys., 54 (1971) 612.