Studies in Mossbauer Spectroscopy. Part 13.[1] Iodine-129 Spectra of Some Palladium(II) and Platinum(II) Iodo-complexes

By **Roger J. Dickinson** and **R. V. (Dick) Parish**,* Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD
Barrie W. Dale, Nuclear Physics Division, A.E.R.E. Harwell, Oxon OX11 0RA

Iodine-129 Mössbauer spectra are reported for the complexes *cis*-$[PtI_2L_2]$, *trans*-$[PtI_2L_2]$, *trans*-$[PtH(I)L_2]$, $[MI_2(L{-}L)]$, $[MI_2(L{-}L)_2]$, and $A_2[Pt_2I_6]$ [M = Pd or Pt; L, L–L = tertiary phosphine, arsine, or stibine uni- or bi-dentate ligands; A = NEt_4, $C_5H_5NCH_3$, or $P(CH_2Ph)Ph_3$]. Data for the four-co-ordinate complexes are discussed in terms of the *trans* and *cis* influences of the neutral ligands. The Mössbauer-indicated *cis* influence is of comparable magnitude but opposite direction to the *trans* influence, but neither is directly related to the conventional *cis* and *trans* influences. For $[MI_2(L{-}L)_2]$ the spectra indicate weak but significant interaction of the iodide with the metal atom. The spectra of the $[Pt_2I_6]^{2-}$ anions are consistent with bridged structures.

MOSSBAUER spectroscopy has been widely used to examine the effects of ligands on the central metal atom of a co-ordination complex, and extensive data are available for several metals. The potential of the technique for giving complementary information about the effects of co-ordination on the ligand has been relatively neglected. Ligands containing tin ($SnCl_3^-$) [2,3] or antimony (SbR_3) [4] have been investigated, for which the Mössbauer parameters show marked differences in the acceptor properties of different metals, but are relatively insensitive to changes in the ligation of a single metal. This lack of sensitivity is presumably due to the ' buffering ' effect of the other groups bound to the tin or antimony atom. A better candidate for this type of study is the iodide ion, which forms a wide variety of complexes and has the advantage of being one-co-ordinate; thus, the electron density in the metal–iodide bond can be investigated directly. We now present the results of such a study of palladium(II) and platinum(II) iodo-complexes. Two iodine isotopes are available, ^{127}I and ^{129}I, but the former has a large linewidth and gives very ill resolved spectra. The superior resolution of ^{129}I spectra far outweighs the inconvenience of handling this radioactive isotope. We have given brief reports of some of this work [5,6] and similar data were later reported by Bancroft and Butler.[7]

EXPERIMENTAL

Iodo-complexes containing ^{129}I were obtained by metathesis from the corresponding chloro-complexes. The chloro-complexes were prepared and characterised by standard methods, and metathesis was carried out by mixing cold ethanol or acetone solutions of the complexes with aqueous solutions containing a stoicheiometric amount of iodide-129, which usually gave quantitative exchange. It was assumed that the stereochemistry was unaffected by this process.

Iodine-129 was obtained from Union Carbide Corp., Oak Ridge, Tennessee as iodide ion in basic sulphite solution. This was acidified with dilute (<2 mol dm^{-3}) nitric acid and treated with lead(II) acetate solution until no further yellow precipitate was obtained. The resulting lead(II) iodide was isolated by centrifuging, and recrystallised from water to remove traces of lead(II) sulphate. The appropriate amount of PbI_2 was warmed with sodium carbonate solution, when quantitative precipitation of lead(II) carbonate occurred. The resulting solution was centrifuged and neutralised with dilute sulphuric acid.

Mössbauer spectra were obtained at P.C.M.U., Harwell, with source ($^{66}Zn^{129}Te$) and absorber immersed in liquid helium. The absorbers were finely ground and mulled with Apiezon grease. In some cases the samples decomposed when stored as mulls, and data were obtained on freshly prepared mulls whenever possible.

The spectra were fitted as sums of 12 Lorentzian lines with intensities constrained in the ratios corresponding to a randomly oriented powder. The line positions were obtained by full diagonalisation of the Hamiltonian matrix.[4] This process differs from that used previously,[5,6] and all data have been reprocessed using the above, rigorous treatment. In four cases, *cis*-$[PtI_2(PPh_3)_2]$, $[PtI_2(C_{10}H_{12})]$, *trans*-$[PtH(I)(PEt_3)_2]$, and $[PdI_2(pdma)_2]$[pdma = *o*-$C_6H_4(AsMe_2)_2$], fits were made with the thickness-integral approach of Shenoy and Friedt [8] using a numerical-integration technique [9] or the Cranshaw method.[4,10] Except for the last compound, the goodness-of-fit parameter, χ^2, was significantly reduced, but the parameter values were effectively identical with those obtained by the sum-of-Lorentzians method; the differences were considerably less than the standard deviations of the fitting procedures which, in turn, are less than the experimental errors. The complex $[PdI_2(pdma)_2]$ has a small quadrupole coupling constant (*ca.* -8 mm s^{-1}) and the spectrum is poorly resolved. In this case, use of the thickness-integral program gave a 5% reduction in the coupling constant, but χ^2 did not change significantly. Values of the coupling constants have been converted into those relative to ^{127}I by use of the relationship: $32.58\ e^2qQ^{129}/\text{mm s}^{-1} = e^2qQ^{127}h^{-1}/\text{MHz}$.

Analysis of Data.—The quadrupole coupling constant (q.c.c. = e^2qQ) and the asymmetry paramter (η) are measures of the electron distribution about the iodine nucleus

$$U_p = -\,e^2qQ^{129}/70.33\ \text{mm s}^{-1} = -\,e^2qQ^{127}/2\,295\ \text{MHz} = -N_z + \tfrac{1}{2}(N_x + N_y) \quad (1)$$

$$\eta = -3(N_z - N_x)/2U_p \quad (2)$$

$$h_p = 6 - (N_x + N_y + N_z) = h_x + h_y + h_z \quad (3)$$

and, hence, of the interaction of the iodide ligand with neighbouring atoms. If it is assumed that the electric-field gradient (e.f.g.) arises solely from the *p*-electron imbalance, U_p, and that π bonding is negligible, the usual Townes–Dailey treatment yields the relationships (1)—(3) where

-70.33 mm s^{-1} and $-2\,293$ MHz are the e^2qQ values for atomic ^{129}I and ^{127}I, $N_{x,y,z}$ are the populations of the $p_{x,y,z}$ orbitals, and h_p is the number of electron ' holes ' in the p shell. In our previous analysis of some of the present data[5,6] we incorrectly took $h_p = U_p$, which implies that $N_x + N_y = 4$ and, hence, that $N_x = N_y = 2$. This can only be the case when $\eta = 0$, whereas most of the complexes showed non-zero values. In order to obtain values for the three populations $N_{x,y,z}$ from only two experimental parameters, some constraint is necessary and we follow Bancroft's suggestion of arbitrarily setting N_x to 2.00.[7] This allows the calculation of h_p from which h_s is obtained using relationship (4).[11]

TABLE 1

Iodine-129 Mössbauer parameters and derived data for complexes of unidentate ligands

Complex	δ_{ZnTe} [a,b] mm s^{-1}	e^2qQ^{129} [b] mm s^{-1}	e^2qQ^{127}/h GHz	η [b]	Γ [b] mm s^{-1}	χ^2 [c] d.f.	U_p	h_y [d]	h_z	h_p	h_s
cis-[PtI$_2$(SbPh$_3$)$_2$]	−0.25(2)	−37.4(2)	−1.22	0.18(2)	1.15(2)	1.03	0.53	0.06	0.56	0.62	0.07
cis-[PtI$_2$(AsPh$_3$)$_2$]	−0.26(1)	−36.5(0.1)	−1.19	0.24(1)	1.00(2)	0.94	0.52	0.08	0.56	0.64	0.07
cis-[PtI$_2$(PPh$_3$)$_2$]	−0.27(1)	−33.7(1)	−1.10	0.26(1)	1.08(1)	1.37	0.48	0.08	0.52	0.60	0.07
	−0.27(1)	−33.7(0.4)	−1.10	0.26(1)	1.02(2)	1.17					
cis-[PtI$_2$(PMePh$_2$)$_2$]	−0.29(1)	−32.4(1)	−1.05	0.18(1)	0.99(1)	1.29	0.46	0.05	0.48	0.53	0.06
cis-[PtI$_2$(PMe$_2$Ph)$_2$]	−0.26(1)	−32.0(1)	−1.04	0.24(1)	1.20(2)	3.52	0.45	0.07	0.48	0.55	0.06
cis-[PtI$_2$(PEtPh$_2$)$_2$]	−0.26(2)	−32.4(2)	−1.06	0.20(2)	0.97(2)	1.10	0.46	0.06	0.49	0.55	0.06
cis-[PtI$_2$(PEt$_2$Ph)$_2$]	−0.27(1)	−32.3(2)	−1.05	0.20(2)	1.36(2)	7.06	0.46	0.06	0.49	0.55	0.06
cis-[PtI$_2$(PEt$_3$)$_2$]	−0.20(1)	−30.8(1)	−1.00	0.20(1)	1.24(1)	2.41	0.44	0.06	0.47	0.53	0.05
cis-[PtI$_2$\{NH$_2$(C$_8$H$_{17}$)\}$_2$] [f]	−0.21(1)	−36.4(1)	−1.19	0.23(1)	1.07(2)	1.88	0.52	0.08	0.56	0.64	0.07
cis-[PtI$_2$(β-pic)$_2$] [g]	−0.32(1)	−32.8(1.6)	−1.07	0.20(1)	1.39(2)	2.22	0.47	0.09	0.52	0.61	0.08
cis-[PtI$_2$(py)$_2$]	−0.31(1)	−28.8(1)	−0.946	0.12(1)	1.43(2)	2.01	0.41	0.03	0.42	0.45	0.05
cis-[PtI$_2$(NH$_3$)$_2$]	−0.22(1)	−29.1(1)	−0.955	0.14(1)	1.08(1)	1.09	0.41	0.04	0.43	0.47	0.04
trans-[PtI$_2$(PEt$_3$)$_2$]	−0.33(4)	−35.9(5)	−1.17	0.24(4)	1.07(5)	0.98	0.51	0.08	0.55	0.63	0.08
trans-[PtI$_2$(PBu$_3$)$_2$]	−0.29(1)	−35.7(1)	−1.16	0.20(1)	1.00(1)	1.20	0.51	0.07	0.54	0.61	0.07
trans-[PtI$_2$(PMe$_2$Ph)$_2$] [h]	−0.30	−36.0	−1.17	0.18	1.04		0.51	0.06	0.54	0.60	0.07
trans-[PtI$_2$(SEt$_2$)$_2$]	−0.25(1)	−32.7(1)	−1.06	0.12(1)	1.01(1)	1.80	0.50	0.04	0.52	0.56	0.06
trans-[PtI$_2$(SMe$_2$)$_2$]	−0.24(1)	−35.2(1)	−1.15	0.12(2)	1.22(2)	4.42	0.46	0.04	0.48	0.52	0.05
trans-[PtI$_2$(β-pic)$_2$]	−0.31(1)	−32.6(1)	−1.06	0.08(2)	1.27(1)	1.35	0.46	0.02	0.47	0.49	0.05
trans-[PtI$_2$(py)$_2$]	−0.24(1)	−31.8(1.6)	−1.04	0 [i]	1.12(2)	5.45	0.45	0.00	0.45	0.45	0.04
trans-[PtI$_2$(NH$_3$)$_2$]	−0.35(2)	−30.5(2)	−0.994	0 [i]	1.51(3)	5.12	0.43	0.00	0.43	0.43	0.05
trans-[PtH(I)(PPh$_3$)$_2$]	−0.43(1)	−24.7(1)	−0.804	0.34(1)	1.01(1)	1.28	0.35	0.08	0.39	0.47	0.06
trans-[PtH(I)(PEt$_3$)$_2$]	−0.47(1)	−24.2(1)	- 0.788	0.18(2)	1.12(1)	2.36	0.34	0.04	0.36	0.40	0.06
	−0.47(1)	−24.2(1)	−0.788	0.20(1)	1.09(0.2)	2.18					

[a] Relative to ZnTe at 4.2 K. [b] Figures in parentheses are the standard deviations of the fitting procedure. [c] d.f. = Degrees of freedom. [d] Assuming $h_x = 0.00$. [e] Parameters from thickness–integral fit. [f] C$_8$H$_{17}$ = n-Octyl. [g] β-pic = β-picoline. [h] Ref. 7. [i] η Constrained to zero. Unconstrained fits gave $\eta < 0$.

$$\delta_{\text{ZnTe}}/\text{mm s}^{-1} = -9.2\,h_s + 1.5\,h_p - 0.54 \qquad (4)$$

For a free iodide ion, $h_p = h_x = h_y = h_z = h_s = 0$. The non-zero values observed reflect the interaction of the iodide with the metal atom and the neighbouring non-bonded atoms. In most cases the largest interaction will be the formation of the metal–iodine co-ordinate bond and h_z, the largest component of h_p, should represent the extent of donation $\text{I}^- \longrightarrow \text{M}$. Similarly, h_s should represent primarily the effect of donation of iodine 5s electrons.

RESULTS AND DISCUSSION

In the four-co-ordinate platinum(II) complexes the Pt–I bonds are subject to the *cis* and *trans* influences of the other ligands. The *trans* influence has been studied by a variety of techniques. Much less is known about the *cis* influence, but it is thought to be relatively small and has been reported as varying in the same or the opposite direction to the *trans* influence.[12] The *trans* influence is here defined in the usual way,[13] as the extent to which a ligand weakens the metal–ligand bond *trans* to itself in the equilibrium ground-state configuration of the complex. It seems reasonable to seek an initial interpretation of the Mössbauer data in these terms, since the strength of the Pt–I bonds should be reflected in the h_z values for the iodide ligand. This assumes that a strong bond implies a high degree of donation from the iodide and hence a large value for h_z. An increase in the *trans* influence of the other ligands should thus be manifested by a decrease in h_z. A correlation has been reported between ^{35}Cl n.q.r. frequencies (proportional to q.c.c. values) in chloroplatinum(II) complexes and the Pt–Cl bond length, showing that h_p decreases as the bond length increases.[14]

Complexes of Unidentate Ligands.—(*i*) *The* trans *influence*. The Mossbauer data and derived parameters for complexes of unidentate ligands are given in Table 1. The lowest h_z values, 0.36 and 0.39, are found for *trans*-[PtH(I)L$_2$] (L = PEt$_3$ or PPh$_3$), and a similar low value (0.37) is reported for *trans*-[Pt(CH$_3$)I(PMe$_2$Ph)$_2$],[7] consistent with the known high *trans* influences of hydride and methyl ligands.[12] The values for *trans*-[PtI$_2$L$_2$] (L = PEt$_3$, PBu$_3$, or PMe$_2$Ph) are high and, where values for both isomers of a complex are available, h_z is usually larger for the *trans* form. Both these observations suggest that iodide has the lowest *trans* influence of all the ligands considered. A similar observation about the *trans* influence of chloride ion has been made from ^{35}Cl n.q.r. data,[15] although the range of h_z values is much less (Table 2). Taken with the value for *trans*-[Pt(CF$_3$)I(PMe$_2$Ph)$_2$],[7] the *trans* influence series for anionic ligands is H$^-$ ~ CH$_3^-$ > CF$_3^-$ > I$^-$.

Similar *trans* influence series can be constructed for neutral ligands, using the data for *cis*-[PtI$_2$L$_2$]. The series are PEt$_3$ $\gtrsim$ PMe$_2$Ph ~ PMePh$_2$ $\gtrsim$ PEt$_2$Ph ~ PEtPh$_2$ > PPh$_3$ > AsPh$_3$ ~ SbPh$_3$ and py $\gtrsim$ NH$_3$ > β-picoline > NHR$_2$ (py = pyridine, β-picoline = 3-methyl-pyridine). Individually these series are comparable to *trans* influence series derived from other data,[12] and parallel the basicities of the ligands. When the two series are amalgamated, however, many discrepancies appear: py $\gtrsim$ NH_3 > PEt_3 $\gtrsim$ PMe_2Ph $\sim$ $PMePh_2$ $\gtrsim$ PEt_2Ph $\sim$ $PEtPh_2$ > β-picoline $\sim$ PPh_3 > NHR_2 $\sim$ $AsPh_3$ $\sim$ $SbPh_3$. In particular, NH_3 and py appear to have much more substantial *trans* influences than are usually found. The larger spread of h_z values for the N-donor ligands than for P, As, and Sb donors may reflect the greater covalency of the Pt–I bond when harder ligands are present,[12] although the h_p and h_s values do not support this interpretation. From ^{35}Cl n.q.r. data [15] the series is py $\sim$ $NHMe_2$ $\sim$ PBu_3 $\sim$ PEt_2Ph $\gtrsim$ PBu_2Ph > bipy (2,2′-bipyridyl) > NCEt. The range of h_z values in this series is less than for the iodo-complexes; this presumable reflects the greater covalency of Pt–I than Pt–Cl bonds. No η values are available from the n.q.r. data, and the series is that of the h_p (= U_p) values. However, as Table 1 shows, h_p and h_z run very largely in parallel.

TABLE 2

Chlorine-35 n.q.r. data for chloroplatinum(II) complexes [15]

Complex	ν/MHz *	h_p
cis-$[PtCl_2(NCEt)_2]$	21.19	0.39
cis-$[PtCl_2(bipy)]$	18.98	0.35
cis-$[PtCl_2(PBu_2Ph)_2]$	18.33	0.33
cis-$[PtCl_2(PEt_2Ph)_2]$	17.91	0.32
cis-$[PtCl_2(PBu_3)_2]$	17.84	0.32
cis-$[PtCl_2(py)_2]$	17.70	0.32
cis-$[PtCl_2(NHMe_2)_2]$	17.21	0.32
trans-$[PtCl_2(PBu_2Ph)_2]$	21.48	0.39
trans-$[PtCl_2(PBu_3)_2]$	21.02	0.38
trans-$[PtCl_2(PEt_3)_2]$	20.99	0.38
trans-$[PtCl_2(py)_2]$	19.62	0.36
trans-$[PtCl_2(NHMe_2)_2]$	18.16	0.33
trans-$[PtCl_2(NH_3)_2]$	17.30	0.32

* Average ^{35}Cl n.q.r. frequency = $\frac{1}{2}e^2qQ$. e^2qQ_{atom} for ^{35}Cl is 109.7 MHz.

We have previously pointed out [5] that in *cis*-$[PtI_2L_2]$ the iodide ligands are subject not only to the *trans* influence of L but also to its *cis* influence. This may in part account for the discrepancies with the conventional *trans* influence series (see below). In an attempt to eliminate the *cis* influence, Bancroft and Butler [7] examined the series of compounds *trans*-$[PtI(L)(PMe_2Ph)_2][PF_6]$, for which the h_z values give the *trans* influence series CNEt $\gtrsim$ $P(OMe)_3$ $\gtrsim$ CNC_6H_4OMe-*p* $\gtrsim$ $PPh(OMe)_2$ > $AsPh_3$ > PPh_3. (This series is slightly different from that given by Bancroft, as we have used h_z as the criterion rather than U_p.) The positions of PPh_3 and $AsPh_3$ are the reverse of those found from *cis*-$[PtI_2L_2]$, which may reflect the crudity of the Townes–Dailey treatment or the differences in the *cis* influences in the two sets of compounds.

(*ii*) *The* cis *influence*. The *cis* influence can be directly and uniquely studied using the data for *trans*-$[PtI_2L_2]$, which give the series NH_3 > py > β-picoline $\gtrsim$ SMe_2 > SEt_2 > PBu_3 > PEt_3. The two hydride complexes, *trans*-$[PtH(I)L_2]$, also give the *cis* influence PEt_3 > PPh_3. A similar series is found [14,15] for ^{35}Cl: NH_3 $\gtrsim$ Cl^- $\sim$ $NHMe_2$ > py > PEt_3 $\sim$ PBu_3 $\gtrsim$ PBu_2Ph $\sim$ PPr_3 > $H_2C{=}CHCH_3$; the range of values is again less than for ^{129}I. In both series the range of $h_z(h_p)$ values is considerably greater than in the *trans* influence series. Thus, the *cis* influence is an important phenomenon and is at least comparable to or, possibly, even greater than the *trans* influence, in contrast to earlier reports.[12] With the limited range of ligands studied, the order of decreasing *cis* influence is N-donor > S-donor > P-donor, which is the reverse of the conventional *trans* influence series.

Previous studies with a variety of techniques suggest that the *cis* influence is often very small, and it is usually neglected. Where it can be detected, it may run parallel to or opposite to the *trans* influence.[12] However, in one bond-length study significant *cis* influences have been found, operating in both directions. In the complexes *cis*-$[PtCl_2(L)(PEt_3)]$ the *cis* influence of L on the Pt–P bond length is considerable and is similar to the *trans* influence of L on the Pt–Cl bond. Surprisingly, for the second Pt–Cl bond the *cis* influence of L is *in the opposite direction*, and somewhat smaller in magnitude.[16] There are indications that sensitivity to *trans* and *cis* influences may depend on the ligand studied,[12] but these results suggest that there may also be a change of sign. In some cases, steric effects are known to contribute to the *cis* influence,[17] but in this instance the effects seem to be purely electronic. If *cis* and *trans* influences in platinum–halogen bonds do indeed work in opposite directions, the discrepancies in the h_z-derived series for *cis*-$[PtX_2L_2]$ are less disturbing.

(*iii*) *Correlations with theory*. Theoretical studies by Zumdahl and Drago [18] and Perkins and co-workers [19] suggest that in platinum chloro- and iodo-complexes the two influences should be comparable in magnitude, as found here, but should operate in the same direction, in conflict with our findings. Shustorovich's calculations,[20] however, show that the *cis* influence should be the smaller and may be similar or opposite in sign to the *trans* influence, depending on the relative importance of metal *d* and *s* orbitals in the bonding. The calculated series were based on the total electron densities in the Pt–Cl or –I bonds, which should be related to bond strength.[18,19] Most of the experimental techniques involve parameters which are sensitive to bond strength or electron density in the whole metal–ligand bond. The Mössbauer and n.q.r. data are unique in that they derive from the e.f.g. at the particular nucleus under investigation, in this case that of the donor atom of the ligand. Since the e.f.g. has an inverse cubic dependence on distance, it gives a very polarised view of the metal–ligand bond, being heavily weighted towards the ligand and very lightly towards the metal. If this is taken into account, theory and observation are in agreement. Figure 1 shows the value of h_z calculated from the orbital occupancies [19] for *trans*-$[PtI_2L_2]$ (L = NH_3, SH_2, or PH_3) and *trans*-$[PtH(I)(PH_3)_2]$ plotted against the 'experimental' values for L = NH_3, SEt_2, or PEt_3; although the values differ, the trend is well reproduced.

It is thus apparent that the e.f.g.-derived data are not measures of the conventional *cis* and *trans* influences, but are indicators of the charge distribution on the iodide (chloride) ligand. As an index of the polarising effects of co-ordination, this information is actually more valuable than the *cis*- or *trans*-influence data, since in many instances it is the effect of co-ordination, and the effects of other ligands on a particular ligand, which control the chemistry of the system. This is particularly true, for instance, in homogeneous catalysis, where the polarisation (activation) of the substrate by co-ordination allows low-energy pathways to desirable reactions, but the activity of a given catalyst system is often very dependent on the nature of the other ligands bound to the metal.

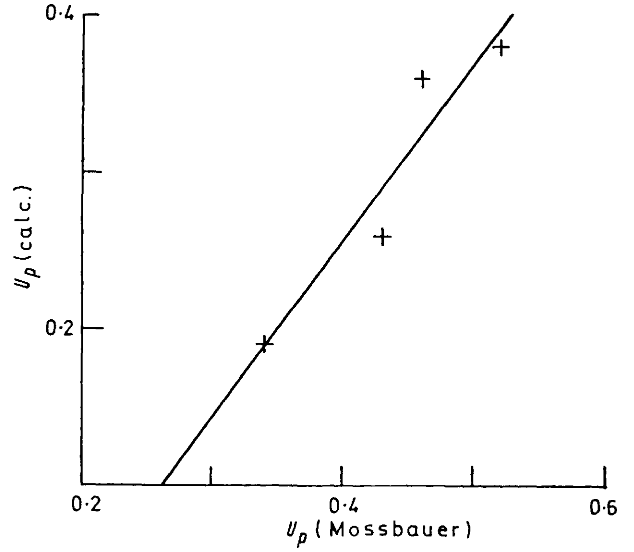

FIGURE 1 Plot of calculated *vs*. Mössbauer-derived U_p values

(*iv*) h_y *Values*. In the majority of cases the asymmetry parameter has a small but finite value, showing that the e.f.g. is not axially symmetric about the Pt–I bond. Several factors could contribute to this asymmetry. First, the geometry of the complexes places two other ligands and the iodide ion in a plane, giving a possible electrostatic interaction ($q_{\text{lat.}}$). Secondly, the non-bonding electrons of the platinum atom may play a part. The d_{xy} and d_{xz} orbitals would give negative contributions to the e.f.g., either *via* $q_{\text{lat.}}$ or by Pt–I π bonding, but these contributions would be equal unless significant p_z–d_{xz} mixing occurred. The d_{z^2} orbital, however, would produce a non-axial contribution. A third possibility is suggested by Perkins' calculations[19] which indicate a significant interaction between the in-plane *p*-orbital of the iodide and empty orbitals on adjacent ligands. This interaction is negligible for NH_3 but quite significant for PH_3 and SH_2, which have empty 3*d* orbitals available. The h_y values derived from our data are rather small, but are roughly consistent with the calculations, being in the range 0.06 for complexes of phosphines, 0.04 for thioethers, and 0.00—0.04 for the N-donors.

Mono(chelate) Complexes.—Data for several palladium(II) and platinum(II) complexes of bidentate ligands, $[MI_2(L–L)]$, are shown in Table 3. The h_z values show that in the palladium complexes less charge is removed from the iodide (h_z = 0.42—0.45) than in the platinum complexes (0.43—0.53). This trend is consistent with the softer nature of the heavier metal, and has also been found in ^{121}Sb Mossbauer studies of stibine complexes.[4] In the one case where direct comparison is possible, $[MI_2(pdma)]$, the h_z values differ by 0.05.

TABLE 3

Iodine-129 Mössbauer parameters and derived data for complexes of bidentate ligands

Complex	δ_{ZnTe} / mm s^{-1}	e^2qQ^{129} / mm s^{-1}	e^2qQ^{127}/h / GHz	η	Γ / mm s^{-1}	χ^2/d.f.	U_p	h_y	h_z	h_p	h_s
$[PtI_2(dppe)]$	−0.27(1)	−30.1(1)	−0.981	0.18(1)	1.06(1)	1.27	0.43	0.05	0.46	0.51	0.05
$[PtI_2(dppp)]$	−0.29(1)	−31.8(1)	−1.03	0.19(2)	1.01(2)	0.93	0.45	0.06	0.48	0.54	0.06
$[PtI_2(pdpp)]$	−0.06(4)	−30.2(5)	−0.984	0.30(4)	1.21(8)	1.60	0.43	0.09	0.48	0.57	0.03
$[PtI_2(dpae)]$	−0.22(3)	−31.6(4)	−1.03	0.27(3)	0.98(4)	1.05	0.45	0.07	0.49	0.56	0.05
$[PtI_2(pmsa)]$	−0.18(3)	−31.7(3)	−1.04	0.22(3)	1.13(4)	0.89	0.45	0.07	0.49	0.56	0.05
$[PtI_2(C_{10}H_{12})]$	−0.08(1)	−35.1(1)	−1.14	0.19(1)	1.29(1)	3.34	0.50	0.06	0.53	0.61	0.05
[a]	−0.08(1)	−35.0(1)	−1.14	0.19(1)	1.21(2)	3.02					
$[PdI_2(dpsp)]$ [b]	−0.35(3)	−26.8(4)	−0.873	0.31(4)	1.27(5)	0.93	0.38	0.08	0.42	0.50	0.06
$[PdI_2(pmsa)]$	−0.32(4)	−29.3(5)	−0.955	0.12(7)	1.20(6)	1.16	0.42	0.03	0.44	0.47	0.03
$[PdI_2(pdpa)]$ [c]	−0.28(2)	−30.4(2)	−0.990	0.09(4)	1.00(5)	*b*	0.43	0.03	0.45	0.48	0.06

[a] Parameters from thickness–integral fit. [b] dpsp = $Ph_2Sb(CH_2)_3SbPh_2$. [c] From composite spectrum with $[PdI_2(pdpa)_2]$ (see text).

TABLE 4

Iodine-129 Mossbauer parameters and derived data for bis(bidentate-ligand) complexes

Complex	δ_{ZnTe} / mm s^{-1}	e^2qQ^{129} / mm s^{-1}	e^2qQ^{127}/h / MHz	η	Γ / mm s^{-1}	χ^2/d.f.	U_p	h_y	h_z	h_p	h_s
$[PtI_2(pdma)_2]$	−0.28(1)	−11.9(1)	−387	0.35(2)	1.07(1)	1.48	0.17	0.04	0.19	0.23	0.009
$[PdI_2(pdma)_2]$	−0.32(1)	−8.58(6)	−279	0.41(2)	1.04(1)	1.02	0.12	0.04	0.14	0.18	0.005
[a]	−0.32(1)	−3.21(5)	−267	0.37(2)	1.00(2)	1.07					
[b]	−0.40(1)	−5.58(5)	−181	0.54(3)	1.11(5)	1.20	0.08	0.03	0.08	0.11	0.003
$[PdI_2(pdpa)_2]$	−0.36(4)	−13.8(5)	−449	0.17(12)	0.86(2)	*c*	0.20	0.02	0.21	0.23	0.018
$[PdI_2(pdpp)_2]$	−0.31(1)	−12.7(1)	−413	0.30(2)	1.02(1)	1.45	0.18	0.04	0.22	0.26	0.018

[a] Parameters from thickness–integral fit. [b] Sample obtained from ethanolic solution. [c] Composite spectrum containing also $[PdI_2(pdpa)]$ and I^-; χ^2/d.f. = 1.41.

For the platinum complexes, the order of increasing h_z is dppe < pdpp ~ dppp $\lesssim$ ppaps ~ dpae < $C_{10}H_{12}$

[dppe = $Ph_2P(CH_2)_2PPh_2$, pdpp = o-$C_6H_4(PPh_2)_2$, dppp = $Ph_2P(CH_2)_3PPh_2$, ppaps = o-$C_6H_4(AsPh_2)(SbPh_2)$, and dpae = $Ph_2As(CH_2)_2AsPh_2$]. This series is comparable to that found above for unidentate ligands, in that the iodide is able to donate more charge in complexes of arsines or stibines than in those of phosphines. With the diene ligand even greater donation is possible, which is consistent with the relatively poor σ-donor characteristics of alkenes. The chelates seem to give slightly lower h_z values than corresponding unidentate ligands with similar substituents. For instance, h_z is considerably lower for ppaps than for $SbPh_3$ or $AsPh_3$, and that for dppe is less than for $PEtPh_2$ and $PMePh_2$. This trend presumably indicates a change in hybridisation at platinum which, in turn, affects the Pt–I bonds and the extent of donation from iodide to platinum.

Bis(chelate) Complexes.—Four complexes each containing two bidentate ligands, $[MI_2(L\text{–}L)_2]$ (M = Pd or Pt), were examined (Table 4). These showed a tendency to lose a chelate ligand and revert to $[MI_2(L\text{–}L)]$, particularly when kept as mulls. In the case of $[PdI_2(pdpa)_2]$, a composite spectrum was obtained which was analysed as the superposition of three spectra: one with a large negative q.c.c., corresponding to the mono(chelate) complexes, presumably $[PdI_2(pdpa)]$ [pdpa = o-$C_6H_4(AsPh_2)_2$]; one with a smaller negative q.c.c., comparable to the other bis(chelate) complexes, presumably $[PdI_2(pdpa)_2]$; and a single peak suggesting a trace of ionic iodide impurity. The spectra of $[MI_2(L\text{–}L)_2]$ show considerably smaller quadrupole splitting than $[MI_2(L\text{–}L)]$ and are much less well resolved. For $[PdI_2(pdma)_2]$, use of the thickness-integral fitting procedure gave a q.c.c. values some 5% less than the sum-of-Lorentzians fit. A similar difference has been found for ^{121}Sb spectra.[4,21] The q.c.c. values indicate that the iodide ions are not free but interact with neighbouring atoms. *X*-Ray data for $[MI_2(pdma)_2]$ show square-planar MAs_4 units with iodide ions above and below the plane at distances suggesting weak bonds (340 and 350 pm for M = Pd or Pt respectively).[22] The other complexes presumably have similar structures. The h_z values are consistent with the formation of weak M–I bonds, resulting in the loss of *ca.* 0.2 electron from the iodide ions. However, for the pdma complexes the h_z values are not consistent with the bond lengths, but suggest greater interaction with platinum than with palladium. Interactions with other atoms are undoubtedly significant, as indicated by the relatively large η values; such interactions are shown by the *X*-ray data.[22] A second sample of $[PdI_2(pdma)_2]$, obtained from ethanolic solution, gave a much smaller q.c.c.; it is possible that this product was solvated, giving greater ionic character to the iodide.

Complexes of $[Pt_2I_6]^{2-}$.—When a large cation (*e.g.* $C_5H_5NMe^+$) was added to a solution of $[PtCl_4]^{2-}$ containing excess of iodide ion a black precipitate was obtained analysing as $[C_5H_5NMe][Pt_2I_6]$. Similar precipitates were obtained with NEt_4^+ and $P(CH_2Ph)Ph_3^+$ as cations. The spectra of these materials are shown in Figure 2. We have been unable to obtain any satisfactory computer fits, but visual inspection shows that in each case the spectra are composites of two or three sub-spectra. The shape of the low-velocity side of the spectra indicates one sub-spectrum with a negative q.c.c. of magnitude similar to those of the other directly bonded Pt–I species reported above. The high-velocity side, with peaks at 8—9 mm s^{-1}, suggests the presence of one or, more probably, two components with positive q.c.c. of somewhat smaller size. These components presumably derive from bridging iodides, for which the e.f.g. would almost certainly be negative and the asymmetry parameter would probably be substantial. These trends would be similar to those observed for crystalline and solvated HgI_2, which contain bridging and terminal iodide respectively: e^2qQ = 25.9 and −34.3 mm s^{-1}; η = 0.54 and <0.06.[23]

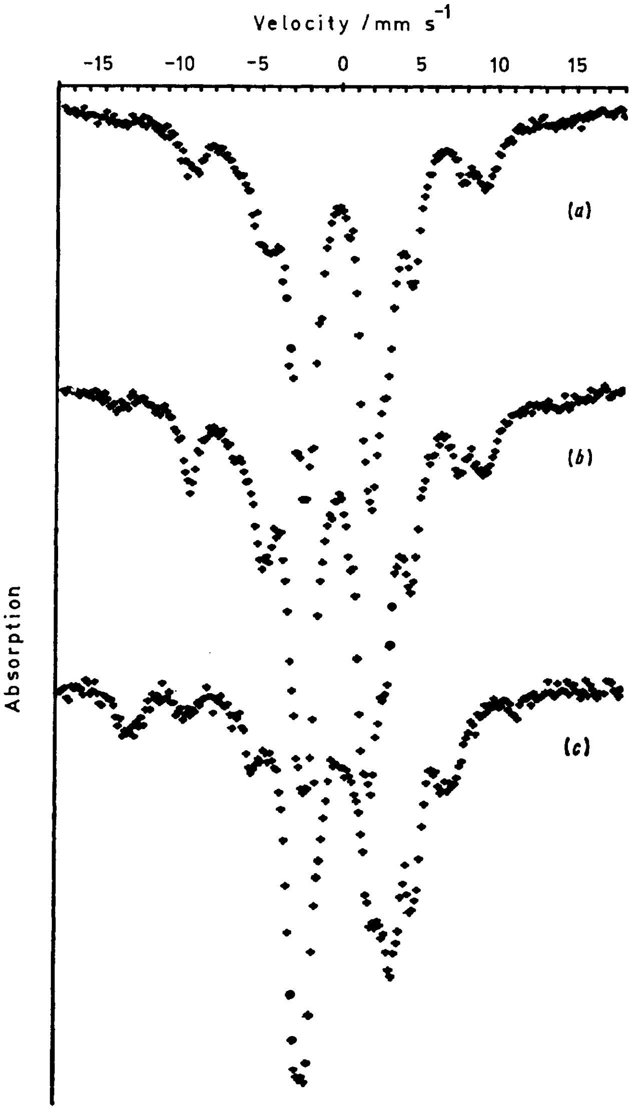

FIGURE 2 Iodine-129 Mössbauer spectra for $[Pt_2I_6]^{2-}$ salts. The cations are: (*a*) $[NEt_4]^+$, (*b*) $[P(CH_2Ph)Ph_3]^+$, and (*c*) $[C_5H_5NCH_3]^+$

Thus, the $[Pt_2I_6]^{2-}$ spectra are consistent with the bridged structure expected for this ion, but the overlapping of peaks in the central region is too severe to allow analysis.

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