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Cis- and *Trans-*Influences in Platinum(II) Iodide Complexes

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Cis- *and* trans-*influences in a number of square-planar platinum(II) complexes have been studied by a CNDO–MO method. The series considered were* $Pt(L)I_3^-$, trans-$Pt(L)_2I_2$ *and* cis-$Pt(L)_2I_2$, *where ligand L was varied to include* PH_3, C_2H_4, CO, H_2S, NH_3, H_2O, H^-, SiH_3^-, CN^-, CH_3^-, I^-, Cl^-, OH^-, *and* NO_2^-. *Comparison of the results between these series shows that the* cis-*influence is similar in magnitude to the* trans-*influence, although the two ligand sequences are not parallel. The variation in the iodine orbital populations within the* cis-*ligand series is in reasonable agreement with* ^{129}I *Mössbauer data.*

Introduction

Although the *trans*-effect series has been established for some time, it is only in recent years that the directive nature of the electronic forces involved has been extensively studied.[1,2] Sophisticated experimental and theoretical techniques have evaluated the relative importance of the *trans*-influence and correlated most of the experimental data pertaining to the *trans*-orientative forces operating in square-planar platinum(II) complexes.[3–6] However, current understanding of the corresponding *cis*-influence remains somewhat limited. This latter electronic manifestation is thought to be relatively small and has been reported to depend on the ligands in the same or in the opposite sense to the *trans*-influence.[3] Previous theoretical analysis suggests that the two influences should show similar dependence on the ligands,[5] while recent Mössbauer spectroscopic data[7] propose the opposite trend.

The aim of the present work, therefore, is to provide a more accurate description of the *cis*-influence, to compare it with that of the analogous *trans*-influence, and to examine the compound effect of both influences in complexes of the type *cis*-$Pt(L)_2X_2$. For this purpose we have implemented the molecular orbital formalism,[8] utilising a modified CNDO computational framework,[9,10] to study a variety of mono- and di-substituted derivatives of PtI_4^{2-}. The input parameters for all the atoms except iodine have been successfully used in previous calculations.[6] The iodine one-centre two-electron repulsion integrals were equated to 12.5 eV,[11] while the diagonal elements of the core Hamiltonian matrix were obtained from the corresponding valence orbital ionisation potentials. The bond lengths were extracted from references 5, 12, and 13.

Since the *trans*- and *cis*-influences of a ligand are defined in terms of their ability to weaken bonds, a quantitative measure of bond strength is desirable. It has been shown that the character of a bond is best described by a bond index defined[14] in terms of density matrix elements, *P*, as

$$B_{AB} = \sum_{\lambda\varepsilon A} \sum_{\sigma\varepsilon B} P_{\lambda\sigma}^2$$

where λ and σ are atomic orbitals on atoms A and B, respectively. Bond indices evaluated in this manner are compatible with chemical reasoning, *e.g.*, in ethylene the carbon–carbon bond index is 2.0, indicating the presence of a double bond.[15] In the present work, it is convenient to examine individual contributions to the bond index in order to determine the rôle of each atomic orbital in the bonding scheme. It is, therefore, useful to define a partial bond index in which the summation extends over only one orbital:

$$B_{\lambda B}' = \sum_{\sigma\varepsilon B} P_{\lambda\sigma}^2$$

In this way, the contribution of the orbital to the total interatomic bonding may be reliably assessed. It is possible to obtain a large amount of information on bonding and electronic distributions employing only atomic orbital populations and the two bond indices defined above. A large number of platinum complexes of the types $Pt(L)I_3^-$, *cis*- and *trans*-$Pt(L)_2I_2$ have been analysed in this manner. These complexes were selected in view of the current interest in, and availability of, platinum–iodide complexes.[7] The ligand L was systematically varied to include PH_3, C_2H_4, CO, H_2S, NH_3, H_2O, H^-, SiH_3^-, CN^-, CH_3^-, I^-, Cl^-, OH^-, and

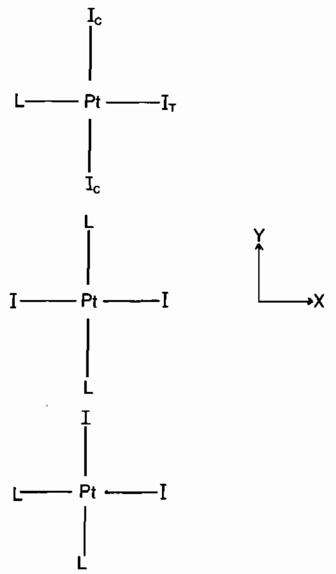

Figure 1. Geometries of $Pt(L)I_3^-$, *cis*-$Pt(L)_2L_2$ and *trans*-$Pt(L)_2I_2$.

NO_2^-. The series *trans*-$Pt(L)_2I_2$ displays primarily the *cis*-influence of L on the Pt–I bonds, whereas in the series $Pt(L)I_3^-$ both *cis*- and *trans*-influences may be examined in the same molecule. In the series *cis*-$Pt(L)_2I_2$, both influences operate and their combined effect may be determined. The coordinate systems are defined in Figure 1, and the results of the calculations are presented in Tables I–III.

Results and Discussion

The Trans-influence

In the complexes $Pt(L)I_3^-$ the $Pt–I_T$ bond is, of course, affected both by the *trans*-influence of L and by the *cis*-influence of the other two iodide ligands. It seems reasonable, however, to assume that the variations in the *cis*-influence of I_C will be small relative to the change in *trans*-influence induced by varying L, and the $Pt–I_T$ bond index is taken as a measure of the *trans*-influence of L.

When comparing the bond indices, it is essential that the overall charge on the complex remain unaltered, since this modifies the electronic distributions. For this reason the complexes containing the neutral and uni-negatively charged ligands have been considered separately.

It should be noted that the *trans*-influence series is not required to be the same as the *trans*-effect series, since *trans*-bond weakening may not control the ability of a ligand to labilise the position *trans* to itself. A comparison of the two series therefore proves interesting. The experimentally observed *trans*-effect series is[2] $C_2H_4 > CO > CN > PR_3 > SR_2 > H^- > CH_3^- > NO_2^- > I^- > Cl^- > NH_3 > OH^- > H_2O$. The calculated *trans*-influence series, based on *trans*-bond weakening in $Pt(L)I_3^-$, are

$$PH_3 > C_2H_4 > CO > H_2S > NH_3 > H_2O$$

and

$$H^- > SiH_3^- > CN^- > CH_3^- > I^- > Cl^- > OH^- > NO_2^-.$$

The discrepancies between the two series are greater when L is a π-bonding ligand, *e.g.*, CN^-, NO_2^-. This suggests that the controlling factor in ligand substitution reactions of the type

$$Pt(L)I_3 + X^- \rightarrow \textit{trans-}Pt(L)(X)I_2 + I^-$$

is stabilisation of the five-coordinate transition state rather than bond-weakening in the reactant. This is in agreement with calculations on the reaction coordinate of ligand substitutions in platinum–chlorine complexes containing π-bonding ligands.[6] For σ-bonding ligands, a much improved correlation between *trans*-influence and *trans*-effect is evident. This indicates that bond-weakening in the reactant plays a decisive rôle in determining the substitution patterns.

It has been suggested that both the *trans*-effect and the *trans*-influence operate *via* platinum p_σ orbitals.[16] However, the present data, our previous calculations for chloro–platinum complexes, and the more approximate calculations of earlier workers,[5] show that the contributions to the $Pt–I_T(Cl_T)$ bond of platinum 6*s* and $6p_x$ orbitals are almost independent of L, and the variation in bond order is caused principally by the changing participation of the $5d_{x^2-y^2}$ orbital.

The Cis-influence

The *cis*-influence may be studied both in $Pt(L)I_3^-$ (Table I) and in *trans*-$Pt(L)_2I_2$ (Table II). On the basis of total $Pt–I_C$ bond indices, the *cis*-influence series found are:

$$Pt(L)I_3^-: PH_3 > H_2S > C_2H_4 > NH_3 > H_2O > CO$$

and

$$SiH_3^- > CH_3^- > OH^- > I^- > CN^- > H^- > Cl^- > NO_2^-$$

$$\textit{trans-}Pt(L)_2I_2: PH_3 > H_2S > C_2H_4 > NH_3 > CO > H_2O$$

and

$$SiH_3^- > CH_3^- > I^- > H^- > OH^- > Cl^- > CN^- > NO_2^-$$

Although there are minor variations, these series are substantially the same. As might be expected, the bond index varies more widely in the second series than the first, reflecting the combined effect of two ligands. In both cases the contribution of all the platinum orbitals varies but that of the 6*s* orbital plays the dominant rôle. It is of interest to record that the contribution of

TABLE I. Electronic Distributions in $Pt(L)I_3^-$ Complexes.

	Atom Charges			Orbital Populations I_T					Bond Indices		
L	Pt	I_T	I_C	s	p_x	p_y	p_z	d	Pt–I_T	Pt–I_C	I_T–I_C
PH_3	+0.015	−0.355	−0.365	1.685	1.614	1.942	1.918	0.196	0.818	0.701	0.369
C_2H_4	+0.087	−0.357	−0.451	1.683	1.608	1.939	1.919	0.207	0.856	0.742	0.392
CO	+0.078	−0.336	−0.398	1.683	1.558	1.943	1.924	0.209	0.882	0.784	0.382
H_2S	+0.027	−0.320	−0.391	1.690	1.594	1.935	1.915	0.205	0.876	0.739	0.389
NH_3	+0.005	−0.335	−0.455	1.686	1.570	1.942	1.927	0.209	0.918	0.755	0.384
H_2O	+0.013	−0.304	−0.448	1.689	1.525	1.944	1.931	0.215	0.956	0.767	0.391
H^-	−0.068	−0.592	−0.545	1.713	1.821	1.939	1.918	0.201	0.572	0.701	0.366
SiH_3^-	−0.106	−0.512	−0.448	1.711	1.746	1.944	1.917	0.194	0.608	0.633	0.354
CN^-	−0.011	−0.539	−0.526	1.705	1.764	1.941	1.922	0.208	0.658	0.701	0.361
CH_3^-	−0.011	−0.526	−0.549	1.712	1.733	1.945	1.929	0.209	0.696	0.673	0.358
I^-	−0.041	−0.489	−0.489	1.727	1.697	1.944	1.941	0.180	0.699	0.699	0.324
Cl^-	+0.049	−0.499	−0.515	1.709	1.702	1.946	1.929	0.212	0.734	0.703	0.361
OH^-	+0.063	−0.516	−0.553	1.713	1.718	1.944	1.929	0.213	0.737	0.686	0.355
NO_2^-	+0.065	−0.473	−0.513	1.698	1.690	1.943	1.927	0.214	0.782	0.727	0.364

	Contributions to Pt–I_T Bonds						
L	Pt(s)–I_T	Pt(p_x)–I_T	Pt($d_{x^2-y^2}$)–I_T	I_T(s)–Pt	I_T(p_x)–Pt	I_T(p_y)–Pt	I_T(p_z)–Pt
PH_3	0.212	0.160	0.299	0.296	0.384	0.051	0.063
C_2H_4	0.236	0.168	0.305	0.318	0.396	0.057	0.063
CO	0.218	0.169	0.313	0.315	0.401	0.063	0.077
H_2S	0.211	0.156	0.356	0.302	0.434	0.051	0.062
NH_3	0.219	0.161	0.370	0.319	0.453	0.054	0.065
H_2O	0.224	0.156	0.413	0.318	0.498	0.052	0.061
H^-	0.134	0.149	0.132	0.292	0.273	0.043	0.060
SiH_3^-	0.170	0.145	0.163	0.233	0.246	0.044	0.061
CN^-	0.173	0.151	0.172	0.279	0.231	0.054	0.068
CH_3^-	0.189	0.155	0.202	0.273	0.289	0.049	0.060
I^-	0.171	0.140	0.249	0.268	0.299	0.043	0.053
Cl^-	0.184	0.152	0.249	0.278	0.324	0.047	0.058
OH^-	0.181	0.157	0.229	0.276	0.322	0.051	0.062
NO_2^-	0.195	0.148	0.272	0.305	0.332	0.052	0.065

	Contributions to Pt–I_C Bonds						
L	Pt(s)–I_C	Pt(p_y)–I_C	Pt($d_{x^2-y^2}$)–I_C	I_C(s)–Pt	I_C(p_x)–Pt	I_C(p_y)–Pt	I_C(p_z)–Pt
PH_3	0.167	0.147	0.256	0.258	0.043	0.316	0.058
C_2H_4	0.166	0.171	0.263	0.265	0.053	0.335	0.067
CO	0.201	0.161	0.253	0.295	0.063	0.323	0.076
H_2S	0.189	0.155	0.247	0.279	0.056	0.312	0.066
NH_3	0.194	0.159	0.246	0.288	0.060	0.309	0.073
H_2O	0.205	0.156	0.245	0.296	0.068	0.303	0.073
H^-	0.194	0.137	0.234	0.292	0.043	0.273	0.060
SiH_3^-	0.158	0.127	0.228	0.252	0.037	0.266	0.051
CN^-	0.201	0.146	0.214	0.288	0.049	0.273	0.064
CH_3^-	0.186	0.147	0.208	0.274	0.047	0.266	0.061
I^-	0.171	0.140	0.249	0.268	0.043	0.299	0.053
Cl^-	0.193	0.146	0.224	0.279	0.053	0.283	0.062
OH^-	0.212	0.147	0.181	0.290	0.058	0.246	0.067
NO_2^-	0.204	0.153	0.223	0.291	0.056	0.286	0.069

TABLE II. Electronic Distributions in *trans*-$Pt(L)_2I_2$ Complexes.

	Atom Charges and Bond Indices			Orbital Populations I			
L	Pt	I	Pt–I	*s*	p_x	p_y	p_z
PH_3	+0.109	−0.246	0.729	1.681	1.577	1.914	1.900
C_2H_4	+0.186	−0.398	0.843	1.785	1.568	1.946	1.938
CO	+0.234	−0.288	0.914	1.731	1.579	1.941	1.928
H_2S	+0.177	−0.290	0.828	1.702	1.624	1.923	1.909
NH_3	+0.191	−0.412	0.884	1.751	1.679	1.938	1.937
H_2O	+0.284	−0.404	0.931	1.739	1.704	1.941	1.932
H^-	−0.049	−0.609	0.708	1.769	1.775	1.981	1.963
SiH_3^-	−0.136	−0.408	0.599	1.684	1.689	1.934	1.911
CN^-	+0.052	−0.561	0.736	1.761	1.740	1.965	1.956
CH_3^-	+0.054	−0.607	0.684	1.781	1.756	1.966	1.961
I^-	−0.041	−0.499	0.699	1.727	1.697	1.944	1.941
Cl^-	+0.153	−0.545	0.729	1.751	1.741	1.949	1.950
OH^-	+0.176	−0.609	0.710	1.764	1.820	1.963	1.955
NO_2^-	+0.186	−0.545	0.788	1.756	1.750	1.959	1.949

	Contributions to Pt–I Bonds						
L	Pt(*s*)–I	(p_x)–I	Pt($d_{x^2-y^2}$)–I	I(*s*)–Pt	I(p_x)–Pt	I(p_y)–Pt	I(p_z)–Pt
PH_3	0.159	0.166	0.274	0.255	0.348	0.042	0.062
C_2H_4	0.152	0.224	0.306	0.269	0.416	0.062	0.084
CO	0.227	0.191	0.267	0.341	0.351	0.086	0.114
H_2S	0.205	0.185	0.263	0.301	0.355	0.066	0.084
NH_3	0.223	0.200	0.244	0.329	0.347	0.083	0.110
H_2O	0.252	0.199	0.235	0.352	0.346	0.098	0.119
H^-	0.212	0.140	0.223	0.324	0.253	0.029	0.065
SiH_3^-	0.147	0.120	0.218	0.245	0.246	0.033	0.049
CN^-	0.231	0.159	0.192	0.323	0.261	0.052	0.074
CH_3^-	0.204	0.161	0.180	0.297	0.249	0.049	0.069
I^-	0.171	0.140	0.249	0.268	0.299	0.043	0.053
Cl^-	0.220	0.159	0.195	0.304	0.272	0.059	0.069
OH^-	0.263	0.160	0.119	0.333	0.215	0.063	0.079
NO_2^-	0.247	0.177	0.182	0.334	0.275	0.069	0.091

TABLE III. Electronic Distributions in *cis*-$Pt(L)_2I_2$ Complexes.

	Atom Charges and Bond Indices				Orbital Populations I			
L	Pt	I	Pt–I	I–L	*s*	p_x	p_y	p_z
PH_3	+0.071	−0.235	0.826	0.380	1.673	1.556	1.921	1.902
C_2H_4	+0.191	−0.300	0.933	0.430	1.715	1.540	1.937	1.927
CO	+0.214	−0.219	1.032	0.408	1.693	1.529	1.927	1.915
H_2S	+0.117	−0.218	0.940	0.411	1.689	1.524	1.926	1.915
NH_3	+0.097	−0.276	1.020	0.400	1.705	1.552	1.935	1.934
H_2O	+0.127	−0.238	1.071	0.413	1.706	1.526	1.931	1.937
H^-	−0.126	−0.656	0.587	0.379	1.754	1.847	1.957	1.939
SiH_3^-	−0.161	−0.473	0.562	0.347	1.699	1.741	1.937	1.907
CN^-	+0.033	−0.573	0.695	0.363	1.734	1.777	1.950	1.937
CH_3^-	+0.042	−0.579	0.698	0.356	1.748	1.756	1.954	1.946
I^-	−0.041	−0.499	0.699	0.324	1.727	1.697	1.944	1.941
Cl^-	+0.147	−0.522	0.757	0.359	1.732	1.719	1.946	1.941
OH^-	+0.182	−0.562	0.749	0.356	1.742	1.770	1.949	1.942
NO_2^-	+0.186	−0.491	0.833	0.361	1.720	1.716	1.947	1.936

TABLE III. (Cont.)

	Contributions to Pt–I Bonds						
	Pt(s)–I	Pt(p_x)–I	Pt($d_{x^2-y^2}$)–I	I(s)–Pt	I(p_x)–Pt	I(p_y)–Pt	I(p_z)–Pt
PH_3	0.204	0.176	0.298	0.291	0.395	0.051	0.066
C_2H_4	0.230	0.214	0.326	0.329	0.440	0.069	0.076
CO	0.268	0.202	0.324	0.362	0.447	0.089	0.108
H_2S	0.235	0.179	0.349	0.322	0.448	0.068	0.076
NH_3	0.263	0.193	0.368	0.355	0.482	0.074	0.086
H_2O	0.284	0.185	0.404	0.359	0.522	0.083	0.081
H^-	0.145	0.158	0.126	0.282	0.141	0.053	0.077
SiH_3^-	0.158	0.185	0.149	0.226	0.219	0.038	0.057
CN^-	0.204	0.165	0.151	0.310	0.219	0.060	0.078
CH_3^-	0.211	0.167	0.170	0.291	0.268	0.052	0.066
I^-	0.171	0.140	0.249	0.268	0.299	0.043	0.053
Cl^-	0.212	0.164	0.223	0.297	0.312	0.057	0.065
OH^-	0.236	0.166	0.171	0.307	0.282	0.065	0.072
NO_2^-	0.243	0.171	0.236	0.341	0.318	0.067	0.082

the Pt $5d_{x^2-y^2}$ orbital varies in opposite directions in the two series.

These *cis*-influence series are clearly very different from the aforementioned *trans*-influence series, although omission of the strongly π-bonding ligands (CO, C_2H_4, CN^-, NO_2^-) considerably reduces the discrepancies. It is significant that high *cis*-influences are obtained when the ligand has formally unoccupied low-energy d orbitals such as those of PH_3, H_2S and SiH_3^-. These orbitals facilitate the formation of strong Pt–ligand bond with subsequent weakening of the *cis* Pt–I bond. In addition, further direct interaction with the iodine orbitals intensifies the electron withdrawal from the Pt–I bonds. Inspection of the density matrices of complexes containing these ligands shows that the d-orbital involvement is of primary importance to L–I interactions. The ligand d-orbital populations and relevant bond indices are given in Table IV. The importance of this d-orbital participation is better understood when compared with the L–I bond indices of 0.094, 0.069 and 0.116 found when L is NH_3, H_2O and CH_3^-, respectively. In each case the Ld_{xy} orbital contains the greatest electron density and the Ld_{xy}–I partial bond index makes a significant contribution to the total bonding. Clearly, the directional properties of the Ld_{xy} orbital enhances this ubiquitous L–I interaction. This is further substantiated by the lower *cis*-influence found for π-bonding ligands such as CO, CN^-, and NO_2^-, which do not possess low-energy d orbitals. It is expected that this ligand–halide contribution will be less significant when we replace the iodines by smaller halogen atoms. The Pt(6s) interactions will therefore assume a more dominant rôle in determining the ligand sequence.

Although this availability of low-energy d orbitals augments the *cis*-influence of a ligand, it does not detract from the observed high *trans*-effect of such ligands. This is a result of the ligand d_{yz} orbital accepting additional electron density in the transition state, thereby lowering the activation energy for substitution at the *trans*-position.[6, 17, 18] Although the metal $d_{x^2-y^2}$ orbital appears to be more effective in transmitting *trans*-influences than *cis*-influences, the interaction of the iodine atom with the metal s orbital is comparable with its interaction with the metal $d_{x^2-y^2}$ orbital.

Cis and Trans-Influences in Cis-Pt(L)$_2$I$_2$

In complexes of the type *cis*-$Pt(L)_2I_2$, the Pt–I bond is subjected to a combination of *cis*- and *trans*-influences of the ligand and these results are expected to verify the trends found in both $Pt(L)I_3$ and *trans*-$Pt(L)_2I_2$. The results for this series of complexes are presented in Table III. The ligand series obtained are

$$PH_3 > C_2H_4 > H_2S > NH_3 > CO > H_2O$$

and

$$SiH_3^- > H^- > CN^- > CH_3^- > I^- > OH^- > Cl^- > NO_2^-.$$

TABLE IV. Electronic Distributions in Ligands with Low-energy d Orbitals.

L	$d_{x^2-y^2}$	d_{xz}	d_{z^2}	d_{yz}	d_{xy}	L(d_{xy})–I	L($d_{x^2-y^2}$)–I	L–I
PH_3	0.068	0.053	0.047	0.056	0.162	0.105	0.047	0.398
H_2S	0.041	0.022	0.026	0.096	0.129	0.090	0.030	0.288
SiH_3^-	0.059	0.045	0.041	0.042	0.120	0.083	0.039	0.369

These ligand sequences are readily related to the results of the two previous series of complexes. For example, the high positions of PH_3 and SiH_3^- are a consequence of both the high *trans-* and *cis-*influences exhibited by these ligands. The positioning of H_2S above CO in the series is due to the higher *cis-*influence of the former. Analogous reasoning may be used to rationalise the positions in the series containing the uni-negatively charged ligands. These results demonstrate the importance of the *cis-*influence in these complexes.

The reasoning outlined above may be extended to more complicated systems and, in order to exemplify this, a few complexes of the type *trans*-$Pt(L)_2XI$ were studied. The results are shown in Figure 2. Comparison of *trans*-$Pt(PH_3)_2(CH_3)I$, (A) with *trans*-$Pt(NH_3)_2(CH_3)I$, (B), or *trans*-$Pt(PH_3)_2(H)I$, (C) with *trans*-$Pt(NH_3)_2(H)I$, (D), evinces that the higher *cis-*influence of PH_3 with respect to NH_3 weakens both the Pt–I and Pt–C bonds. Similarly, comparison of (A) with (C) or (B) with (D) demonstrates the higher *trans-*influence of H^-. Thus, the overall bonding patterns in any square-planar platinum(II) complex may be rationalised in terms of *cis-* and *trans-*influences.

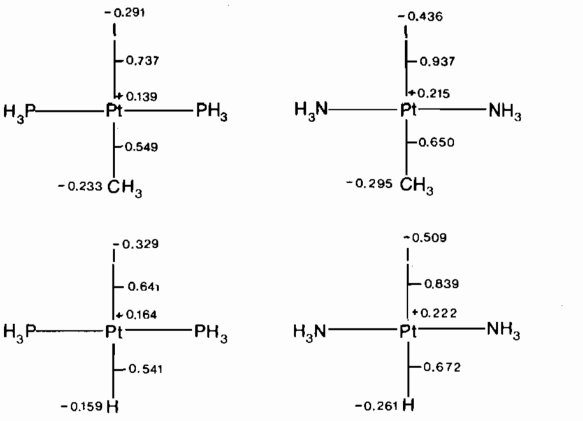

Figure 2. Charges and bond indices in *trans*-$Pt(L)_2XI$ complexes.

Comparison with Experiment

An appraisal of the physical validity of these results may be acquired by comparison with ^{129}I Mössbauer data recently obtained for complexes of the type, *cis-* and *trans*-$Pt(L)_2I_2$, and *trans*-$Pt(L)_2HI$.[7] The quadrupole coupling constants derived for these species may be rationalised in terms of the extent of donation from the lone pair of the formally uninegative iodine ligand to the platinum since, as in the interpretation of N.Q.R. data,[19,20] the degree of electron donation parallels the magnitude of the coupling constant. The quadrupole coupling constants and isomer shifts for six complexes, representative of the aforementioned series are presented in Table V.

The observation that the smallest negative values of the quadrupole coupling constant are found for two hydrido complexes suggests a correlation based on the high *trans-*influence of the hydrido ligand.[7] This can be confirmed by inspection of the electronic structure of complexes of type $Pt(L)I_3^-$ in Table I where the largest I_T population occurs when the ligand is the hydride ion. In the series *cis-* and *trans*-$Pt(L)_2I_2$ the most negative coupling constant is obtained when a P-donor is the ligand while the smallest values occur when $L = NH_3$. These results can be explained by reference to the charge on iodine in *cis-* and *trans*-$Pt(L)_2I_2$ from $L = NH_3$ and $L = PH_3$ (Tables II and III). It can be seen that in both series the larger negative charge occurs when $L = NH_3$. It has been suggested that the greater accumulation of charge on iodine will mean the presence of a weaker Pt–I bond and hence will indicate a stronger directive influence. The results in Tables II and III reveal that this is not necessarily true. The weakest Pt–I bond in the two series occurs when $L = PH_3$ but the corresponding iodine population is not the largest. This unexpected trend arises from the presence of non-bonded L–I and I–I interactions directed along the edges of the square-planar complex.

The *p*-electron imbalance, U_p, is defined as $U_p = h_x - {}^1/_2(h_y + h_z)$ where h_x, h_y, and h_z are the number of 'electron-holes' in the *p*-orbitals (note the Pt–I axis has been taken as the *x* axis). The quadrupole coupling constant, e^2qQ, is related to U_p in the Townes–Dailey approximation[19] by

$$U_p = e^2qQ/e^2qQ(\text{atom}) = e^2qQ/(-70.33\ \text{mm s}^{-1})$$

TABLE V. The Quadrupole Coupling Constants, Isomer Shifts and Orbital Populations for Iodine.

	$e^2qQ(^{129}I)/(\text{mm s}^{-1})$	$\delta_{ZnTe}/(\text{mm s}^{-1})$	h_s	$\hbar_s{}^c$	U_p	$U_p{}^c$
trans-$Pt(PH_3)_2HI$	-23.9^a	-0.46^a	0.32	0.05^a	0.19	0.34^a
trans-$Pt(PH_3)_2I_2$	-36.3^a	-0.35^a	0.32	0.06^a	0.33	0.52^a
trans-$Pt(SH_2)_2I_2$	-32.3^b	-0.25^b	0.30	0.04^b	0.29	0.46^b
trans-$Pt(NH_3)_2I_2$	−30.5	−0.32	0.25	0.05	0.26	0.43
cis-$Pt(PH_3)_2I_2$	-30.2^a	-0.21^a	0.33	0.03^a	0.36	0.43^a
cis-$Pt(NH_3)_2I_2$	−28.0	−0.16	0.30	0.02	0.38	0.40

[a] $L = Et_3P$. [b] $L = Et_2S$. [c] Ref. 7.

Although computational limitations precluded the acquisition of theoretical results pertaining to the bulkier ligands, the experimental trends are well reproduced, especially when the differences down the series are computed. Hence, it appears that a reasonable estimate of the *p*-electron imbalance, U_p for iodine atoms, can be obtained from the Townes–Dailey relation.

The calculated and previously reported[7] h_s values (Table V) show a significant discrepancy. The latter were obtained from the empirical relationship

$$h_s = (-\delta_{ZnTe}/(mm\ s^{-1}) + 1.5\ h_p - 0.54)/9.1$$

This equation was suggested by Bukshpan, Goldstein, and Sonnino[20] as a modification of one derived by Pasternak and Sonnino.[21] In obtaining their expression the latter authors assumed the distribution of electrons between 5*s* and 5*p* orbitals of iodine in IO_3^-, IO_4^- and IO_6^{5-} to be given exactly by the limiting tetrahedral and octahedral hybrid forms.

$$\psi_t = \frac{1}{2}\psi_s + \frac{\sqrt{3}}{2}\psi_p$$

$$\psi_o = \frac{1}{\sqrt{6}}\psi_s + \frac{1}{\sqrt{2}}\psi_p + \frac{1}{\sqrt{3}}\psi_d$$

This is a drastic assumption which is most unlikely to accord with reality: even in the 'ideal' case of diamond, for example, the valence electrons are not equally distributed between the 2*s* and 2*p* orbitals.[22] Hence, we believe that the h_s values calculated in the present work are more reliable and we suggest the modified empirical equation

$$h_s = (-\delta_{ZnTe}/(mm\ s^{-1}) + 1.5h_p + 1.84)/9.1$$

The calculations reported here have shown that for a series of ligands, the *cis*- and *trans*-influences are similar in magnitude and, although the ligand sequences are not identical, they are in the same direction. For the *trans*-influence series, the weakening of the *trans*-bond is caused by the differing participation of the Pt $5d_{x^2-y^2}$ orbital, while both the rôle of the Pt 6*s* orbital and the ligand–iodine interaction are important in the *cis*-influence series. The ^{129}I Mössbauer data for *cis*- and *trans*-$Pt(L)_2I_2$ complexes can be adequately explained by reference to the calculations of the *cis*- and *trans*-influence series in the complexes.

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