cis-Influence in Platinum(II) Complexes Demonstrated by ^{129}I Mössbauer Spectroscopy

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Summary ^{129}I Mössbauer spectra of *trans*-L_2PtI_2 show that the neutral ligands exert a range of *cis*-influences in opposition to their *trans*-influence.

trans-INFLUENCE effects are well documented and many techniques have been used to study this phenomenon.[1] Much less is known about the *cis*-influence, but it is thought to be relatively small and is reported to vary in the same or the opposite direction to the *trans*-influence.[1] We now report ^{129}I-Mössbauer data for the complexes *trans*-L_2PtI_2 which demonstrate a significant *cis*-influence in opposition to the *trans*-influence.

Spectra were obtained with source ($^{66}Zn^{129}Te$, $t_{\frac{1}{2}} = 70$ min) and absorbers (*ca.* 90% enriched in ^{129}I) at 4·2 K. The eight-line spectra were computer fitted using the isomer shift (δ), the quadrupole coupling constant (e^2qQ), the square of the asymmetry parameter (η^2), the overall intensity (using the ratios expected for a random powder), and the half-width (equal for all lines) as variables. The results are shown in the Table together with derived values for h_p and h_s.[2,3]

TABLE. ^{129}I Mössbauer data for *trans*-L_2PtI_2 at 4·2 K[a]

L	δ_{ZnTe} /(mm s^{-1})	e^2qQ^{129} /(mm s^{-1})	e^2qQ^{127}/h[b] /MHz	η	Γ/ (mm s^{-1})	χ^2/degrees of freedom	h_p	h_s
Et_3P	$-0·35(2)$	$-36·3(2)$	-1183	0·21(2)	0·89(5)	191/233	0·52	0·06
Me_2S	$-0·24(1)$	$-34·7(1)$	-1131	0·13(1)	1·13(1)	625/233[c]	0·49	0·05
Et_2S	$-0·25(1)$	$-32·3(1)$	-1052	0·12(1)	1·00(2)	283/242	0·46	0·04
β-Picoline ..	$-0·30(1)$	$-32·3(1)$	-1052	0·07(4)	1·24(3)	224/242	0·46	0·05
Pyridine ..	$-0·23(1)$	$-31·5(1)$	-1026	d	1·11(2)	888/243[c]	0·45	0·04
NH_3	$-0·32(1)$	$-30·5(1)$	-994	d	1·67(3)	754/226[c]	0·43	0·05

[a] Numbers in parentheses are uncertainties in the last figure. [b] Calculated from[2] $32·58\ e^2qQ^{129}/(\text{mm s}^{-1}) = (e^2qQ^{127}/h)/\text{MHz}$. [c] Large χ^2 due to intensity-constraint. [d] Computer fitting gave $\eta^2 < 0$. Data shown are for η constrained to zero.

The isomer shifts and h_s-values show no systematic trends and are probably equal within the experimental error. The quadrupole coupling constant values show well defined, systematic variations, clearly indicating the operation of a *cis*-influence. Similar trends have been seen in n.q.r. data for related chloro-complexes,[4] but these show much less sensitivity to change in the neutral ligand [*e.g.* the difference in h_p between $(py)_2MX_2$ and $(R_3P)_2MX_2$ is 0·02 for Pd–Cl and Pt–Cl but 0·07 for Pt–I]. This difference is presumably related to the more covalent character of the metal–iodine bond. The n.q.r. results were originally interpreted in terms of long-range electrostatic effects.[4] However, in view of the inverse cubic dependence of *eq* on distance, the major part of the electric field gradient must arise in the valence-shell of the halogen atom. Thus, the e^2qQ-values and h_p reflect the charge donated from iodide to platinum and the strength of the Pt–I bond. The order of bond strength is therefore L = N-donor < S-donor < P-donor, *i.e.* the *cis*-influence operates in the opposite direction to the *trans*-influence.

Most theoretical treatments of the *trans*-influence suggest that it must operate through metal *p*-orbitals,[1] which cannot account for a *cis*-influence. M.O. calculations by Zumdahl and Drago[5] suggest that the *cis*- and *trans*-influences should run parallel, which is contrary to our observation. A satisfactory explanation may be found in Syrkin's theory of the *trans*-effect,[6] in which *d*–*s* hybridisation is used to show that a ligand which forms a strong bond to platinum would strengthen the bonds in the *cis*-positions. This is clearly compatible with our data.

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