Letter

Ligand-field parameters for square-planar platinum(II) compounds

In a recent paper Bridgeman and Gerloch[1] reinvestigated the ligand-field analyses of square-planar $[PtCl_3L]^-$ complexes and stated that 'earlier analyses are shown to be incorrect'. Past disagreements about the interpretation of spectra of square-planar platinum complexes were based on the differing assignments of the spectra.[2–6] However, the above authors use the spectra of Zink and co-workers[7–9] and (with one exception) their assignments. In this letter it is shown that the origin of the differences is the use of an unusual ligand-field model containing parameters that are different from ours, and the results of the reinvestigation are commented upon.

The first important issue to be settled is the accuracy of the calculations. Our model is adapted from that of Francke and Moncuit.[6] Their method of 6s–5d orbital mixing is employed (but with $a = b = a_0 = 0$), and two parameters are added to distinguish between in- and out-of-plane π interactions. When the parameters reported by Francke and Moncuit[6] for $[PtCl_3(NH_3)]^-$ are used their reported transition energies can be calculated exactly. Under these conditions (the mixing model of Vanquickenborne and Ceulemans[5] $\sigma_{sd} = \sigma$) and when the in- and out-of-plane π parameters are set equal, our calculated transition energies agree with those of Vanquickenborne and Ceulemans[5] for $[PtCl_4]^{2-}$. Thus, for the numerical comparison calculations cited by Bridgeman and Gerloch to test the 'veracity' of their calculation, our calculation gives the literature results.

The model of Bridgeman and Gerloch is different. They use a σ parameter defined as the arithmetic mean of the ligand-field parameters of the unique ligand and the *trans*-chloride ligand, a σ parameter for the *cis*-chloride ligand, and π parameters for the *cis*- and *trans*-chloride ligands. They also use a σ parameter (but no π parameter) for the 'void'. Their inability to reproduce our results lies in the different model that they use.

The interpretations of the ligand-field parameters in Bridgeman and Gerloch's model are very different from ours. They report π parameters for chloride in $[PtCl_3(NH_3)]^-$ which are twice as large for *cis* than for *trans* ligands. The difference between them, 2500 cm^{-1}, is four times larger than the 600 cm^{-1} difference between chloride and bromide ligands.[5] Furthermore, they calculate *cis*-chloride π values of 2750 cm^{-1} for the PEt_3 complex and 3800–4200 cm^{-1} for the $AsPh_3$ complex. Their interpretation that changing the ligand from PPh_3 to $AsPh_3$ results in large changes (>10^3 cm^{-1}) in the chloride parameters but 'virtually indistinguishable' changes in the unique ligand parameters is questionable. Their most unusual interpretation is that of a σ-acceptor ability of the void (defined by them to be the 'co-ordination void normal to the co-ordination plane') that is large and variable (ranging from −6250 to −7300 cm^{-1}). This unique concept suffers from at least two inconsistencies: it does not recognize a corresponding π contribution from the void, and it selectively identifies voids. (How many voids exist in a monocapped octahedron?) Mathematically, their parameter changes the energy of the d_{z^2} orbital in a manner similar to that of 6s–5d mixing,[5,6] but the concept of the absence of a ligand providing a ligand field lacks meaning.

As pointed out by Zink and co-workers,[7–9] there are more angular-overlap-model parameters than observables, and exact fits to the spectra cannot be made. We restrict the number of variables by making the approximations that the parameters for the chloride ligand are transferable between similar compounds. (For the compounds discussed here the σ parameter for the chloride ligand was fixed at 11 800 cm^{-1} and both the in- and out-of-plane π parameters restricted to 2850 ± 150 cm^{-1}.) Given this assumption, we obtain the trends in σ-donor ability $PEt_3 > NMe_3 > PPh_3 > AsPh_3$, and in π-acceptor ability $AsPh_3 \geqslant PPh_3 > PEt_3 > NMe_3$. We[7] and others[5] do not make the assumption that the π interaction parameter for amine ligands is zero because there is no *a priori* reason to exclude any π contribution from amines.[5,7] We base our assignment of the spectrum of the NMe_3 complex on the temperature dependence of the intensity; the assignment cannot be made based on the ligand-field calculation. Our previous work, based on a model where the chloride parameters are transferable between compounds, provides a meaningful interpretation of the ligand field.

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Bridgeman and Gerloch reply. Three issues are raised by Zink's letter: (*a*) the 'accuracy' of the calculations, (*b*) the nature of co-ordination void parameters, and (*c*) ligand-field π paramaterization for amines. We address these in order.

(*a*) For $[PtCl_4]^{2-}$, Vanquickenborne and Ceulemans[5] write the energy of the d_{z^2} orbital as $E(d_{z^2}) = \sigma^{Cl} - \sigma^{sd}$ or, in terms of more generally used notation, $E(d_{z^2}) = e_\sigma(Cl) - e_{sd}$. They recommend the simplification $e_\sigma(Cl) \approx e_{sd}$, corresponding to Francke and Moncuit's[6] and Chang and Zink's[7] taking $a_0 = 0$, so that $E(d_{z^2}) = 0$. Within the notation of the cellular ligand-field (CLF) model, employing a void cell above and below the co-ordination plane, $E(d_{z^2}) = e_\sigma(Cl) + 2e_\sigma(void)$, and $e_{sd} = -2e_\sigma(void)$. For $PtCl_3X$ species, $E(d_{z^2}) = \frac{1}{4}[3e_\sigma(Cl) + e_\sigma(X)] + 2e_\sigma(void)$ so, if it is assumed that $E(d_{z^2}) = 0$, $e_{sd} = \frac{1}{4}[3e_\sigma(Cl) + e_\sigma(X)]$; that is, e_{sd} is taken as the weighted mean of $e_\sigma(Cl)$ and $e_\sigma(X)$ when $a_0 = 0$.

However, the e_{sd} value quoted by Chang and Zink[7] at the foot of their Table II is the simple average, $\frac{1}{2}[e_\sigma(Cl) + e_\sigma(X)]$. Their set of angular overlap model (AOM) values do not reproduce the transition energies quoted in their table. Our assertion[1] that their calculations were incorrect was based upon this fact (and exactly similar ones in other related papers[8,9]). As they have been able to reproduce earlier results,[5] and replacement of their quoted e_{sd} values by the weighted mean above yields the transition energies of their[7] Table II, it appears that they correctly used the weighted mean, but provided an incorrect caption for their table. The origin of the differences between the models of Zink and co-workers and ourselves is therefore nothing to do with different parameterization schemes.

(*b*) Zink proposes that the CLF parameterization scheme with $e_\sigma(void)$ is without meaning. The basis of the parameterization has been described many times,[10–14] and in particular detail.[15] The neglect of $e_\pi(void)$ in the CLF scheme is paralleled by the neglect of e_{dp} within the AOM. Smith[16] was the first to introduce e_{sd} and e_{dp} parameters. The e_{dp} were later neglected because (*i*) $E(4_p) - E(3d)$ is expected to be rather greater than $E(4s) - E(3d)$, and (*ii*) ligand-field analyses without e_{dp} parameters were found to be empirically satisfactory.

In the CLF model, $e_\lambda(void)$ parameters relate to real potentials (see, for example, ch. 11 of ref. 10 or section IVb of ref. 15) rather than fictitious ligands. The $e_\pi(void)$ parameters are neglected because (*i*) the p–d energy separation is larger than the s–d (as in the AOM), and (*ii*) the spatial proximity of the metal p functions in the void region to the aspherical potential there is far less close than that of the metal s function.

(*c*) Far more important than these is the question of a possible π ligand-field strength for amines. In both CLF and AOM models, e_π parameters are expected to be negligible in the absence of ligand π functionality and empirical e_π values for amines generally reflect[17] that. In analyses for mixed ligations, one must not ignore the following two issues.

First, the consequences of holohedral symmetry[18] render the ligand-field strengths of diametrically sited ligands totally inseparable within a single-parity basis. This applies with equal rigour to the AOM and CLF schemes. That is why our analyses[1] employ the means $\frac{1}{2}[e_\sigma(\mathrm{Cl}) + e_\sigma(\mathrm{N}\ )]$ and $\frac{1}{2}[e_\pi(\mathrm{Cl}) + e_\pi(\mathrm{N})]$ for the amines and *trans*-Cl ligations. We assume that $e_\pi(\mathrm{N}) = 0$ and so interpret $\frac{1}{2}[e_\pi(\mathrm{Cl}) + e_\pi(\mathrm{N})]$ as $\frac{1}{2}e_\pi(\mathrm{Cl})$ but that has no effect whatsoever on the fitting process.

Secondly and crucially, there is every reason, from chemical bonding considerations, to expect that $e_\pi(\mathrm{Cl})$ for a chloride *trans* to an amine (or other X ligand) differs significantly from $e_\pi(\mathrm{Cl})$ for a chloride *trans* to another chloride. The well known and accepted *trans* influence is based upon that idea. It is therefore wholly undesirable to set $e_\pi(\mathrm{Cl})$ for *trans*- and *cis*-chloride ligations equal and *we* did not do so.[1] Our analysis of $[\mathrm{PtCl_3(NMe_3)}]^-$ led to a value for e_π(*trans*-Cl) approximately twice as large as that for e_π(*cis*-Cl). The calculations and approximations of Chang and Zink[7] led to a value for $e_\pi(\mathrm{NMe_3})$ almost twice as large as that for $e_\pi(\mathrm{Cl})$ in their analysis and for $e_\pi(\mathrm{NH_3})$ in the calculations of Vanquickenborne and Ceulemans[5] on $[\mathrm{PtCl_3(NH_3)}]^-$. Such a value does not accord with chemical bonding expectations.

Overall we did not wish to fix the value of e_σ(void) either and so attempted an overparameterized model.[1] We were very careful to detail the inevitable correlations between the various optimum parameter values that followed. Qualitative indications of the *trans* influence emerged from the careful analyses. We believe the neglect of e_π(void) and of e_π(amine) is a reasonable and widely used procedure that is preferable to transferring ligand-field parameters between *trans* and *cis* sites in these complexes.

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