Angular Overlap Treatment of d–s and d–p Mixing in Chlorocuprates(II)

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Received August 23, 1976

The electronic spectrum of square coplanar $CuCl_4^{2-}$ cannot be explained by conventional angular overlap or crystal field treatments. The possibility that this may arise from neglect of $3d_{z^2}$–$4s$ mixing is discussed. We propose an extension of the angular overlap method which includes the effects of d–s and d–p mixing, and show that the d–d spectra of several chlorocuprates(II) can be satisfactorily fitted to four freely-chosen parameters. The theory explains the apparently anomalous spectrum of square coplanar $CuCl_4^{2-}$, and gives a satisfactory account of the effects of distant ligands in tetragonal octahedral $CuCl_6$ chromophores. A difficulty in explaining the d–d spectrum of molecular $CuCl_2$ may be resolved, and the parameters used to fit the spectra of known chlorocuprates(II) give a more reasonable value for the parameter Δ_t for tetrahedral $CuCl_4^{2-}$.

Introduction

The angular overlap model [1] provides a simple empirical method of computing the relative energies of d-orbitals in non-cubic complexes, and has been applied with some success to the d–d spectra of copper(II) complexes [2]. Chlorocuprates(II) have provided a useful test for the angular overlap model [3, 4] since they provide a remarkable range of coordination geometries. The crystal field model has also been extensively used in the discussion of the d–d spectra of chlorocuprates (II) [7–12]. Success has been claimed for both models, but some problems remain. Both models tend to place the d_{z^2} orbital too high in energy in tetragonal octahedral $CuCl_6$ chromophores; the crystal field model is particularly unsatisfactory in this respect. Both models predict that a regularly tetrahedral $CuCl_4^{2-}$ ion should have a splitting parameter Δ_t of around 5–6 kK, which seems excessive compared with the values of around 3 kK found for other MCl_4^{2-}. A recent crystal structure [13] has established the existence of square coplanar $CuCl_4^{2-}$ in $(C_6H_5CH_2CH_2NMeH_2)_2CuCl_4$. Neither the angular overlap nor the crystal field model can explain the d–d spectrum of this system using parameters consistent with the spectra of other chlorocuprates (II). Bands are observed [13, 14] at

12.5, 14.3 and 16.9 kK; with the parameters required to fit the spectra of other chlorocuprates(II), either model would predict the $^2B_{1g} \rightarrow\ ^2E_g$ transition to occur at about 14 kK, with the $^2B_{1g} \rightarrow\ ^2B_{2g}$ and $^2B_{1g} \rightarrow\ ^2A_{1g}$ transitions lying fairly close together at about 11 kK. The single crystal polarized spectrum of $(C_6H_5CH_2CH_2NMeH_2)_2CuCl_4$ has failed to provide a definite assignment of the bands [14]. However, there is now some evidence [15] for the energy sequence $^2B_{1g} <\ ^2B_{2g} <\ ^2E_g <\ ^2A_{1g}$, corresponding to the one-electron sequence $d_{z^2} < d_{xz,yz} < d_{xy} < d_{x^2-y^2}$. This is consistent with the relative intensities of the bands, and with the energy sequence is found [16] for square coplanar $PdCl_4^{2-}$ and $PtCl_4^{2-}$. The chief difficulty in accounting for these energies arises from the very high energy of the $^2A_{1g}$ state. We suggest that this may be accounted for in terms of mixing between $3d_{z^2}$ and $4s$ in D_{4h} symmetry; this would result in stabilization of the d_{z^2} orbital and lead to a high energy for the $^2B_{1g} \rightarrow\ ^2A_{1g}$ transition. We now outline a theoretical approach which will enable us to allow for d–s and d–p mixing within the angular overlap model.

Theory

Mixing between two metal orbitals ϕ_1 and ϕ_2 in a complex may arise if one or more ligand group orbitals can overlap with both metal orbitals. The extension of the angular overlap model to such a situation is fairly straightforward [17]. The interaction can be described by the determinant:

$$\begin{vmatrix} H_{11} - E & H_{12} \\ H_{21} & H_{22} - E \end{vmatrix} = 0$$

The off-diagonal element should be approximately proportional to $\Sigma_i\ G_{1i}G_{2i}$, where G_{ni} is the group overlap integral between ϕ_n and the ligand group orbital ψ_i. The energy correction to the lower-energy orbital ϕ_n is approximately equal to $H_{12}^2/(H_{11} - H_{22})$, assuming that the off-diagonal element is small compared with $(H_{11} - H_{22})$. Thus in the case of an nd-orbital mixing with the $(n + 1)s$-orbital, the energy correction to the d-orbital can be expressed as:

$(\Sigma_i k_{si} k_{di})^2 e_{ds}$

where k_{si} and k_{di} are the group overlap integral coefficients appropriate to the s- and d-orbitals respectively, and e_{ds} is a parameter analogous to the usual e_σ and e_π. A similar expression may be derived for d–p mixing. Thus we can express the relative energies of the d-orbitals in terms of four parameters: e_σ, e_π, e_{ds} and e_{dp}. With the abundance of spectroscopic and structural data for chlorocuprates(II), we hope to be able to find a consistent set of values for these. We shall take e_σ and e_π to vary with the internuclear distance in accordance with the square of the appropriate diatomic overlap integrals $S_{d\sigma}$ and $S_{d\pi}$; however, in this paper we abandon the previous assumption that the ratio e_π/e_σ can be deduced from the ratio $[S(3p_\pi, 3d_\pi)/S(3p_\sigma, 3d_\sigma)]^2$. After all, the metal $3d$-orbitals overlap with the ligand $3s$-orbitals as well and this interaction is likely to affect e_σ. We might therefore expect the ratio e_π/e_σ to be rather lower than in previous calculations. If the overlap integrals $S(3s_\sigma, 3d_\sigma)$ vary with the internuclear distance in approximately the same way as the corresponding integrals for $3p$-orbitals, we shall come to little harm in using the latter to gauge the variation of e_σ with the metal–ligand distance. The parameters e_{ds} and e_{dp} are assumed to be proportional to the products of the appropriate overlap integrals, and will depend accordingly on the internuclear distance. We would expect e_{ds} to be considerably greater than e_{dp}. In all the calculations which follow, the required overlap integrals were calculated from the functions of Richardson et al. [18] for the metal, and of Clementi [19] for chlorine. These integrals have been previously published in the form of plots against internuclear distance [20]. Group overlap integral coefficients were determined by the method of Kettle [21].

Results and Discussion

Square Coplanar $CuCl_4^{2-}$

Here we only have to contend with mixing between d_{z^2} and s; the totally-symmetric a_{1g} group orbital overlaps with both $3d_{z^2}$ and $4s$, and the product of the group overlap integral coefficients is -2. The d–d transition energies are predicted to be:

$$E(^2B_{1g} \rightarrow ^2B_{2g}) = 3e_\sigma - 4e_\pi$$

$$E(^2B_{1g} \rightarrow ^2E_g) = 3e_\sigma - 2e_\pi$$

$$E(^2B_{1g} \rightarrow ^2A_{1g}) = 2e_\sigma + 4e_{ds}$$

With $e_\sigma = 5.37$ kK, $e_\pi = 0.90$ kK and $e_{ds} = 1.54$ kK, we obtain the observed d–d transition energies of 12.5, 14.3 and 16.9 kK, assuming the energy sequence $^2B_{1g} < ^2B_{2g} < ^2E_g < ^2A_{1g}$. These values seem reasonable, with the ratio e_π/e_σ much lower

than that used in our previous papers; this is as we would expect if both the chlorine $3s$ and $3p$ orbitals contribute to e_σ. We take these values to be appropriate to the mean internuclear distance of 2.265 Å found [13] in $(C_6H_5CH_2CH_2NMeH_2)_2 CuCl_4$.

Distorted Tetrahedral $CuCl_4^{2-}$

Here we assume D_{2d} symmetry, where d_{z^2} mixes with s and (d_{xz}, d_{yz}) and d_{xy} mix with (p_x, p_y) and p_z respectively. We consider separately the effects of σ- and π-overlaps on the d–p mixing. The d–d transition energies are predicted to be:

$$E(^2B_2 \rightarrow ^2E) = 3e_\sigma(\sin^4\theta - 1/2 \sin^2 2\theta) + e_\pi (\sin^2 2\theta - 2\cos^2 2\theta - \cos^2\theta)$$

$$E(^2B_2 \rightarrow ^2B_1) = 3e_\sigma (\sin^4\theta) + e_\pi (\sin^2 2\theta - 4\sin^2\theta) - 12e_{dp\sigma} (\sin^4\theta \cos^2\theta) - 16e_{dp\pi} (\sin^4\theta \cos^2\theta)$$

$$E(^2B_2 \rightarrow ^2A_1) = 3e_\sigma (\sin^4\theta) - 4e_\sigma (\cos^2\theta - 1/2 \sin^2\theta)^2 - e_\pi(2 \sin^2 2\theta) + 16e_{ds} (\cos^2\theta - 1/2 \sin^2\theta)^2 - 12e_{dp\sigma} (\sin^4\theta \cos^2\theta) - 16e_{dp\pi} (\sin^4\theta \cos^2\theta)$$

In these expressions, θ is the angle between a Cu–Cl vector and the z-axis.

Note that since the effects of d–p mixing on d_{xy} and on $d_{xz,yz}$ are exactly the same, no term in e_{dp} arises in the expression for the $^2B_2 \rightarrow ^2E$ transition energy. Since we have no empirical way of separately determining $e_{dp\sigma}$ and $e_{dp\pi}$, we assume that their relative magnitudes are determined by the appropriate overlap integral products.

We shall consider specifically Cs_2CuCl_4, whose electronic spectrum has been definitely assigned [22] and whose crystal structure has been determined to a high degree of refinement [23]. θ is found to be 64.6°, and the mean Cu–Cl bond length is 2.230 Å. At this distance, e_σ, e_π and e_{ds} are found by overlap integral calculations to be respectively 5.78, 1.01 and 1.70 kK. Experimentally [22], the energies of the ^2E, $^2B_1$ and $^2A_1$ states relative to $^2B_2$ are found to be 5.55, 7.90 and 9.05 kK. With the above values of e_σ, e_π and e_{ds}, and with $e_{dp\sigma} = 0.75$ kK, these transition energies are found to be 5.95, 7.63 and 9.31 kK, in reasonable agreement with experiment. The value of $e_{dp\sigma}$ was obtained simply by finding the value which led to the best fit to the experimental results; the ratio $e_{dp\pi}/e_{dp\sigma}$ was calculated from the overlap integrals to be 0.082. The magnitude of $e_{dp\sigma}$ seems reasonable; we expect it to be rather lower than e_{ds}. A good test of the significance of this value of e_{dp} is to calculate the splitting parameter Δ_t for a regularly tetrahedral $CuCl_4^{2-}$ ion ($\theta = 54.7°$), since this will be

considerably affected by d–p mixing. Assuming a Cu–Cl distance of 2.23 Å, we obtain $\Delta_t = 4.43$ kK. Most other MCl_4^{2-} ions have Δ_t in the range 3.0–3.5 kK; our predicted value for $CuCl_4^{2-}$ seems more reasonable than the values of around 6 kK which are predicted by the usual crystal field and angular overlap models.

Trigonal Bipyramidal CuCl₅³⁻

Here, the d-orbital splitting is believed to follow the sequence $d_{z^2}(a_1') > d_{xy, x^2-y^2}(e') > d_{xz,yz}(e'')$. Our model gives the d–d transition energies as:

$$E(^2A_1' \rightarrow {}^2E') = 2e_\sigma(a) - (3/8)e_\sigma(e) - (3/2)e_\pi(e)$$
$$- 4e_{ds}(a) - (9/4)e_{ds}(e)$$
$$+ 6[e_{ds}(a)e_{ds}(e)]^{1/2} + (27/16)e_{dp\sigma}$$
$$+ (9/4)e_{dp\pi}$$

$$E(^2A_1' \rightarrow {}^2E'') = 2e_\sigma(a) + (3/4)e_\sigma(e) - 2e_\pi(a)$$
$$- (3/2)e_\pi(e) - 4e_{ds}(a) - (9/4)e_{ds}(e)$$
$$+ 6[e_{ds}(a)e_{ds}(e)]^{1/2}$$

The postscripts (a) and (e) refer to axial and equatorial ligands respectively. Note the term $[e_{ds}(a) e_{ds}(e)]^{1/2}$ in the expressions; this arises from the proportionality of the off-diagonal element in the mixing determinant to $[2S_d(a)S_s(a) - (3/2)S_d(e)S_s(e)]$; obviously the products of the group overlap integrals for equatorial and axial overlaps must be of opposite sign, since the d_{z^2} orbital has negative amplitude in the equatorial plane but positive amplitude along the z-axis.

The axial and equatorial Cu–Cl distances are taken to be 2.30 and 2.39 Å respectively [24]. We thus obtain $e_\sigma(a) = 4.97$ kK, $e_\sigma(e) = 4.03$ kK, $e_\pi(a) = 0.79$ kK, $e_\pi(e) = 0.55$ kK, $e_{ds}(a) = 1.38$ kK, $e_{ds}(e) = 0.99$ kK, $e_{dp\sigma} = 0.54$ kK and $e_{dp\pi} = 0.022$ kK. Substituting these into the expressions for the d–d transition energies, we obtain $E(^2A_1' \rightarrow {}^2E') = 7.78$ kK and $E(^2A_1' \rightarrow {}^2E'') = 9.77$ kK. Experimentally [25], these are observed at about 8.7 kK and 10.8 kK respectively, so that our calculated energies are about 10% too small, although the relative energies of the two bands are essentially correct.

Tetragonal Octahedral CuCl₆ Chromophores

Compounds containing tetragonal octahedral $CuCl_6$ chromophores usually have equatorial Cu–Cl distances of about 2.30 Å, with longer axial Cu–Cl distances of 2.8–3.2 Å. Here only d–s mixing has to be considered, and the off-diagonal element is proportional to $2[S_d(e)S_s(e) - S_d(a)S_s(a)]$, where the postscripts (a) and (e) refer respectively to axial and equatorial overlaps. Obviously this term vanishes in the limit of O_h symmetry. Thus the d–d transition energies can be expressed as:

$$E(^2B_{1g} \rightarrow {}^2B_{2g}) = 3e_\sigma(e) - 4e_\pi(e)$$
$$E(^2B_{1g} \rightarrow {}^2E_g) = 3e_\sigma(e) - 2e_\pi(e) - 2e_\pi(a)$$
$$E(^2B_{1g} \rightarrow {}^2A_{1g}) = 2e_\sigma(e) - 2e_\sigma(a) + 4e_{ds}(e) + 4e_{ds}(a)$$
$$- 8[e_{ds}(a)e_{ds}(e)]^{1/2}$$

Assuming equatorial bond lengths of 2.30 Å with the axial ligands at 2.90 Å, we obtain $e_\sigma(e) = 4.97$ kK, $e_\sigma(a) = 0.94$ kK, $e_\pi(e) = 0.79$ kK, $e_\pi(a) = 0.066$ kK, $e_{ds}(e) = 1.38$ kK and $e_{ds}(a) = 0.078$ kK. These lead to the energies 11.27, 11.75 and 13.20 kK for the $^2A_{1g}$, $^2B_{2g}$ and ^2E_g states respectively. These may be compared with the transitions observed [10] in $(CH_3NH_3)_2CuCl_4$ at 10.8, 12.2 and 13.3 kK. Compared with square coplanar $CuCl_4^{2-}$, the $^2B_{1g} \rightarrow {}^2A_{1g}$ transition has fallen in energy by over 5 kK; the largest single contribution to this is the d–s mixing term, which is reduced by about half as a consequence of the axial ligands. As we have already noted, a major defect in previous crystal field and angular overlap treatments has been their inability to place correctly the energy of the $^2A_{1g}$ state. This problem is solved by the introduction of the d–s mixing term.

Molecular CuCl₂

The assignment of the d–d spectrum of $CuCl_2$ (g) has aroused some controversy. Bands have been observed [12] at 9.0 kK and 19.0 kK, but the latter seems too intense to be assigned to a d–d transition. Simple ligand field arguments lead to the energy sequence $d_{z^2}(\sigma) > d_{xz,yz}(\pi) > d_{xy, x^2-y^2}(\delta)$. DeKock and Gruen [12] assign the 9 kK band to the $^2\Sigma \rightarrow {}^2\Delta$ transition, with the $^2\Sigma \rightarrow {}^2\Pi$ transition lying undetected below 4 kK. The present author [6] has suggested, on the basis of angular overlap calculations, that the 9 kK band is actually the $^2\Sigma \rightarrow {}^2\Pi$ transition, with the $^2\Sigma \rightarrow {}^2\Delta$ transition lying at about 16 kK where it is masked by the intense charge transfer band at 19 kK, though Lever and Hollebone [26] prefer the assignment of Dekock and Gruen [12]. However, the introduction of d–s mixing could lead to transition energies consistent with the latter assignment. The d–d transition energies are found to be:

$$E(^2\Sigma \rightarrow {}^2\Pi) = 2e_\sigma - 2e_\pi - 4e_{ds}$$
$$E(^2\Sigma \rightarrow {}^2\Delta) = 2e_\sigma - 4e_{ds}$$

Assuming a Cu–Cl distance of 2.00 Å, we obtain $e_\sigma = 8.60$ kK and $e_\pi = 2.46$ kK. Ignoring for the moment the e_{ds} term, we would predict d–d transitions at 12.28 kK and 17.20 kK. If $4e_{ds}$ were equal to about 9 kK, we would predict d–d transitions at 8.2 and 3.3 kK, consistent with experimental observation. Our calculations suggest that $4e_{ds}$ should actually be about 12 kK, which seems too high. This error may arise from the assumptions made in gauging the variation of the parameters with the internuclear distance. We are presently working on the possibility

of partitioning e_σ and e_{ds} into components arising from ligand s- and p-orbitals; this should help to improve the calculations. We are reluctant to introduce additional parameters into the model, but the wealth of structural variety in chlorocuprates(II), together with an increasing amount of spectroscopic data, should provide sufficient experimental data to which these can be fitted.

Acknowledgment

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