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Angular Overlap Treatment of the Variation of the Intensities and Energies of the d–d Transitions of the $CuCl_4^{2-}$ Ion on Distortion from a Planar toward a Tetrahedral Geometry: Interpretation of the Electronic Spectra of Bis(*N*-benzylpiperazinium) Tetrachlorocuprate(II) Bis(hydrochloride) and *N*-(2-Ammonioethyl)morpholinium Tetrachlorocuprate(II)

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The single-crystal d–d spectra of the title complexes are reported and the transition energies of the pseudotetrahedral $CuCl_4^{2-}$ ions that the complexes contain are compared with those of other compounds having varying degrees of distortion by using the angular overlap model. Significant mixing between the metal 4s and $3d_{z^2}$ orbitals occurs toward the square-planar limit of this series, though little mixing between the metal $3d_{xz,yz}$ and 4p orbitals takes place even in those complexes with large pseudotetrahedral distortions. The long axial interactions in bis(*N*-benzylpiperazinium) tetrachlorocuprate(II) bis(hydrochloride) (Cu–Cl = 337 and 385 pm) apparently have little influence either upon the d-orbital energies directly or upon the d–s mixing. The angular overlap model is used to derived expressions for the way in which the intensities of the Laporte-allowed transitions in the $CuCl_4^{2-}$ ion vary as a function of distortion from a planar to a tetrahedral geometry. The intensities calculated from these expressions are consistent with those observed for the *N*-(2-ammonioethyl)morpholinium salt of $CuCl_4^{2-}$ and Cs_2CuCl_4, though the model significantly underestimates the intensities of those transitions of planar $CuCl_4^{2-}$ that are induced by coupling with the vibration which carries this complex toward a tetrahedral geometry.

Introduction

Because chlorocuprates are comparatively simple and exhibit a wide range of stereochemistries, they have frequently been used to test theoretical models of the bonding in metal complexes.[1,2] In addition, they have been the subject of numerous spectroscopic investigations,[2,3] and the $CuCl_4^{2-}$ ion has recently acted as a simple model of the active site in copper "blue" proteins.[4,5]

Compounds of the general formula $(cation)_2CuCl_4$ show a particularly rich stereochemistry. In some of these, 4-coordinate $CuCl_4^{2-}$ ions with flattened tetrahedral geometries are present, though the degree of flattening is highly variable, being strongly influenced by the nature of the countercation.[2] In several cases, the *trans*-ClCuCl angle opens to 180°, leading to a centrosymmetric planar geometry. In the green form of the compound *N*-(2-ammonioethyl)morpholinium tetrachlorocuprate(II), [(Naem)$CuCl_4$], both planar and pseudotetrahedral $CuCl_4^{2-}$ ions are present, the latter having a moderate distortion away from planarity (*trans*-ClCuCl angles of 146°).[6] When the organic cations are relatively small, the planar $CuCl_4^{2-}$ units are often linked by the formation of long axial bonds to neighboring groups, giving rise to the 4+2 coordination geometry so common in copper(II) chemistry.[2] The complex bis(*N*-benzylpiperazinium) tetrachlorocuprate(II) bis(hydrochloride), [$(NbzpipzH_2Cl)_2CuCl_4$], provides a structural link between the limiting types of chlorocuprate, as it contains $CuCl_4^{2-}$ ions that have only a slight distortion away from planarity toward a tetrahedral geometry (the *trans*-ClCuCl angles are both ~166°) with each metal ion being linked to a neighboring complex via a very long axial bond (337 pm).[7]

The spectral properties of chlorocuprates provide a useful means of probing not only their stereochemistry but also the ease with which this can be changed. In this context we have recently studied the EPR and electronic spectra of the $CuCl_4^{2-}$ ion, both in pure copper(II) compounds[3bcd,8] and as a "guest" in various zinc(II) host lattices.[9] The electronic spectrum of planar $CuCl_4^{2-}$ has proved especially interesting. Analysis of the vibrational fine structure observed at low temperature[3cd] and the shifts in band maxima as a function of temperature[3d,10] have allowed the geometry of the excited states to be determined, while the temperature dependence of the band intensities has provided estimates of the energies of the intensity-inducing vibrational modes.[3c,d] The out-of-plane bending vibration of β_{2u} symmetry, which carries the complex from a planar toward a tetrahedral geometry, was consistently found to be very low in energy, and this has an important influence on the spectra.[3c,d] Another unusual feature of planar $CuCl_4^{2-}$ concerns the transition $^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2 - y^2)$, which occurs ~6000 cm^{-1} higher in energy than is predicted by simple bonding models. This has been rationalized in terms of the depression of the d_{z^2} orbital by configuration interaction with the metal 4s orbital,[1f,3c,11,12] and it has been suggested that this should diminish as the ligand coordination geometry approaches cubic symmetry, either by an angular distortion toward a tetrahedral arrangement[11a] or by the approach of axial ligands to give an octahedral stereochemistry.[11b]

The unusual structural features of $(NbzpipzH_2Cl)_2CuCl_4$ and (Naem)$CuCl_4$, involving extremely weak axial coordination in the former case and relatively small distortions of the $CuCl_4^{2-}$ ions away from planarity, mean that they are ideally suited to investigate the above conclusion. We report here the single-crystal electronic spectra of these complexes and compare them with the spectra of other chlorocuprates. The variation of the transition

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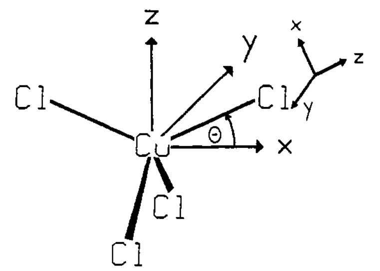

Figure 1. Idealized geometry of the pseudotetrahedral $CuCl_4^{2-}$ ion, showing the metal- and ligand-based coordinate systems.

energies as a function of the distortion from planarity is interpreted quantitatively by using the angular overlap model (AOM)[13] of the bonding in metal complexes. This model also forms the basis of a treatment of the changes in band intensity that occur as the $CuCl_4^{2-}$ ion distorts from a planar toward a tetrahedral geometry.

Experimental Section

Large, green crystals of $(NbzpipzH_2Cl)_2CuCl_4$ were prepared by the method of Antolini et al.[7] and had a satisfactory analysis (Anal. Calcd: C, 41.7; H, 5.7; N, 8.9. Found: C, 41.1; H, 5.7; N, 8.9.) Electronic spectra of the prominent (100) crystal face were measured on several samples by using a Cary 17 spectrophotometer at 18 and 290 K with polarized light parallel to each of the extinction directions using a technique described previously.[3c,14] The crystal morphology was deduced by measuring the interfacial angles of the crystals on a stereoscopic polarizing microscope and checked by analyzing the anisotropy of the crystal EPR spectrum. Large crystals of the green form of $(Naem)CuCl_4$ were grown as described by Battaglia et al.[6] and had a satisfactory analysis (Anal. Calcd: C, 21.3; H, 4.8; N, 8.3. Found: C, 21.6; H, 4.8; N, 8.3.) The compound was found to change to the yellow crystal modification[6] in a matter of a few days, so freshly prepared crystals were used for the spectral measurements. Spectra of the $(10\bar{1})$ crystal face, obtained by cleaving a large crystal, were recorded as for the $(NbzpipzH_2Cl)_2CuCl_4$ complex. The samples were cooled by using a Cryodyne Model 21 refrigerator, and the crystal thicknesses used to convert the measured absorption values into molar extinction units were measured by using a graduated microscope eyepiece.

Results and Discussion

The stereochemistry of the chromophore in $(NbzpipzH_2Cl)_2CuCl_4$, illustrated schematically in Figure 1, deviates from a centrosymmetric, planar geometry by virtue of several low-symmetry perturbations. Most important is the slight distortion toward a tetrahedral geometry. The two *trans*-ClCuCl angles are equal within experimental error (166.6 and 166.3°), so that the effective symmetry is lowered from D_{4h} to D_{2d}. Weak axial coordination occurs to the chloride ions of neighboring complexes, though the extreme length of these "bonds", 337 and 385 pm, means that it is hard to say whether they will have any detectable effects on the properties of the copper(II) ion. The asymmetry of the axial coordination lowers the effective symmetry to C_{2v}. Finally, one Cu–Cl bond, that along y in the present coordinate system, is slightly longer than the other three (233 pm, compared with 224 ± 1 pm), lowering the symmetry to C_s, and the true crystallographic site symmetry is no higher than C_1.[7]

Typical spectra measured at 18 and 290 K with the electric vector parallel to the b and c crystal axes are shown in Figure 2. In marked contrast to the spectrum of the planar $CuCl_4^{2-}$ ion,[3d] which shows a dramatic increase in intensity when the temperature is raised from 10 to 290 K, the spectrum of $(NbzpipzH_2Cl)_2CuCl_4$ shows little change beyond a broadening of the bands. This is consistent with the noncentrosymmetric nature of the chromophore in the latter complex and implies that the bulk of the intensity is derived from a static rather than a vibronic intensity mechanism.[15] If the x axis is defined as parallel to the vector connecting the two Cl^- ions with similar bond lengths, as indicated in Figure 1, the y axis as the cross-product of x and the vector bisecting that connecting these two Cl^- ions and z as the cross-product of x and y give the squares of the molecular projections when the electric vector is parallel to the b and c crystal axes, averaged over the two molecules in the monoclinic unit cell, indicated below: b, $0.000x^2 + 0.566y^2 + 0.434z^2$; c, $0.001x^2 + 0.433y^2 + 0.566z^2$. It may be seen that there is comparatively little difference between the molecular projections for the two polarization directions. Selection rules based on an effective point group of D_{2d} or C_{2v} symmetry would therefore imply that the spectrum should show little polarization, in marked contrast to experimental observation (Figure 2). It thus appears that as far as the band intensities are concerned, the effective point group is lower than this, which means that the band polarizations cannot be used to assign the spectrum. However, the fact that the peak positions fall smoothly between those observed for the planar and more distorted $CuCl_4^{2-}$ ions discussed below for $(Naem)CuCl_4$ leaves little doubt that the three bands, centered at ~11 500, 13 150, and 15 200 cm^{-1}, may be assigned to transitions from the d_{xy}, $d_{xz,yz}$, and d_{z^2} orbitals to the half-filled $d_{x^2-y^2}$ orbital, respectively.

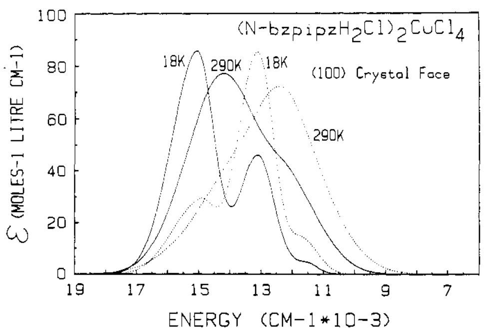

Figure 2. Spectrum at 18 and 290 K of a crystal of $(NbzpipzH_2Cl)_2CuCl_4$ with the electric vector parallel to the c (full line) and b (dashed line) crystal axes.

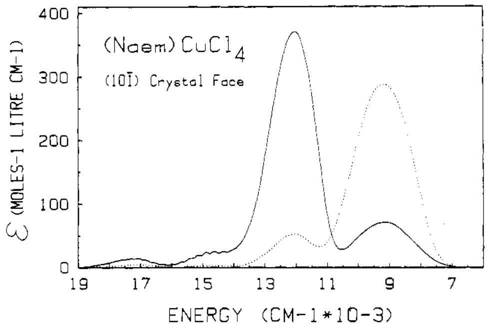

Figure 3. Spectrum of a crystal of the green form of $(Naem)CuCl_4$ with the electric vector parallel to the [010] (dashed line) and [101] (full line) directions, measured at 10 K.

The bands in $(NbzpipzH_2Cl)_2CuCl_4$ show a significant shift to lower energy as the temperature is raised (Figure 2), and this may be indicative of a more highly distorted pseudotetrahedral equilibrium nuclear geometry in the excited electronic states, as has recently been inferred from shifts of this kind observed for planar $CuCl_4^{2-}$.[10] However, it is also possible that the distortion angle is effectively temperature dependent. This would correspond to the vibration carrying the complex from a near-planar geometry toward tetrahedral geometry being of low energy and highly anharmonic. A mechanism of this kind has recently been proposed by Bacci[16] to explain the temperature-dependent EPR parameters of various pseudotetrahedral copper(II) complexes.

The green modification of $(Naem)CuCl_4$ has one planar and one pseudotetrahedral $CuCl_4^{2-}$ ion in the asymmetric unit,[6] and the low-temperature spectrum of the compound shows that the absorptions of these two species are quite well separated (Figure 3). The planar complex gives rise to the higher energy, com-

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paratively weak absorptions centered at ~17 000 and 14 500 cm^{-1}. These bands show extensive vibrational fine structure, which will be discussed elsewhere.[17] The bond distances in the pseudotetrahedral $CuCl_4^{2-}$ ion are very similar (226.6 and 226.9 pm), with the *trans*-ClCuCl angles being crystallographically equivalent. The ion thus has a geometry very close to the idealized D_{2d} point group expected for a four-coordinate Cu(II) complex distorted by Jahn–Teller coupling. If a coordinate system is defined as in Figure 1, the molecular projections when the electric vector of polarized light is parallel to the [010] and [101] crystal axes are

$$[010]\text{:}\quad 0.494x^2 + 0.506y^2 + 0.000z^2$$

$$[101]\text{:}\quad 0.022x^2 + 0.021y^2 + 0.957z^2$$

In the D_{2d} point group (with nonconventional axes defined as in Figure 1) the transition $(z^2) \leftarrow (x^2 - y^2)$ is allowed in *z* polarization, while $(xz,yz) \leftarrow (x^2 - y^2)$ is allowed in *xy* polarization, so that the intense bands centered at 12 050 and 9300 cm^{-1} (Figure 3) may be assigned to these transitions, respectively. The weak shoulder at ~9000 cm^{-1} in *xy* polarization is then due to the symmetry-forbidden $(xy) \leftarrow (x^2 - y^2)$ transition.

Comparison with Other Chlorocuprates. Band Energies. Several previous studies have noted that as the $CuCl_4^{2-}$ ion distorts from a planar geometry toward a tetrahedral geometry the electronic spectrum undergoes a red shift, and empirical expressions have been derived relating the shift in overall band maximum to the change in the dihedral angle between the planes formed by the copper and cis chloride ions[18] or the *trans*-ClCuCl angle.[19] The AOM provides a particularly convenient method of quantifying more fully the change in transition energies as a function of geometry,[13] as, provided that the bond lengths do not alter significantly, the transition energies of any complex of general D_{2d} symmetry are given by simple equations[11] involving just the distortion angle α ($\alpha = 90° - \theta$, Figure 1):

$$E(z^2) = 3e_\sigma \sin^4 \alpha - 4e_\sigma(\cos^2 \alpha - \tfrac{1}{2} \sin^2 \alpha)^2 - 2e_\pi \sin^2 2\alpha + 16e_{ds}(\cos^2 \alpha - \tfrac{1}{2} \sin^2 \alpha)^2 - 13.3e_{dp}(\sin^4 \alpha \cos^2 \alpha)$$

$$E(xy) = 3e_\sigma \sin^4 \alpha + e_\pi(\sin^2 2\alpha - 4 \sin^2 \alpha) - 13.3e_{dp}(\sin^4 \alpha \cos^2 \alpha)$$

$$E(xz,yz) = 3e_\sigma(\sin^4 \alpha - \tfrac{1}{2} \sin^2 2\alpha) + e_\pi(\sin^2 2\alpha - 2 \cos^2 2\alpha - 2 \cos^2 \alpha) \quad (1)$$

Here, *E* represents the energy of the excited state involving the d orbital in parentheses; note that the coordinate system has the *x* and *y* axes coincident with the bond directions in the limiting complex of D_{4h} symmetry. The parameters e_σ and e_π represent the σ- and π-bonding effects of the chloride ligands, while e_{ds} takes into account the depression of the d_{z^2} orbital due to configuration interaction with the metal 4s orbital. Following Smith,[11a] the factor e_{dp} has been included to represent possible effects of the admixture of metal p orbitals.

The room-temperature transition energies $E(z^2) = 15\,500$ cm^{-1}, $E(xz,yz) = 13\,200$ cm^{-1}, and $E(xy)$, = 11 500 cm^{-1} observed for planar $CuCl_4^{2-}$ suggest the values $e_\sigma = 5030$ cm^{-1}, $e_\pi = 900$ cm^{-1}, and $e_{ds} = 1320$ cm^{-1}. Assuming e_{dp} is negligible, eq 1 then implies the variation in transition energies as a function of θ given by the solid lines in Figure 4. Here, the effects of spin–orbit coupling have been included by using a value of 580 cm^{-1} for the effective value of the coupling constant.[20] Optimum agreement (the dotted line) is obtained by a small value of $e_{dp} = 160$ cm^{-1}. Included on the figure are the transition energies reported in the literature for four-coordinate tetrachlorocuprates of known crystal structure.

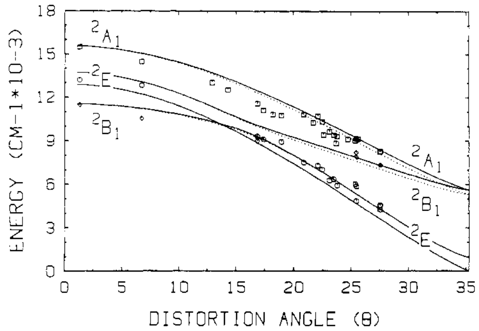

Figure 4. Plot of the energies observed for transitions to the d_{z^2} (squares), $d_{xz,yz}$ (circles) and d_{xy} (diamonds) excited states of compounds containing $CuCl_4^{2-}$ ions as a function of the distortion from a planar geometry toward a tetrahedral geometry. The distortion angle θ is illustrated in Figure 1, and the references to the 22 data sets included on the plot, in order of increasing distortion angle, are as follows: 1, ref 3d and 45; 2, ref 7; 3, ref 18 and 46; 4, ref 36; 5, ref 6; 6, ref 44; 7, ref 18 and 47; 8, ref 18; 9, ref 19b; 10, ref 36; 11, ref 19a and 48; 12, ref 37; 13, ref 38 and 49; 14, ref 6; 15, ref 36; 16, ref 39; 17, ref 40 and 50; 18, ref 41; 19, ref 42 and 51; 20, ref 9; 21, ref 43; 22, ref 9). Curves calculated by using the angular overlap model are shown, both neglecting (full lines) and including (dashed lines) the effects of d–p mixing; see text for the method of calculation and the values of the parameters.

It may be noted that the Cu–Cl bond lengths in these are approximately constant.

The transition energies observed for $(NbzpipzH_2Cl)_2CuCl_4$ agree reasonably well with the calculated curves. This implies that the weak axial coordination in this compound (Cu–Cl bonds of 337 and 385 pm) has no discernible effect on the parameter e_{ds}, which is consistent with a recent analysis of the spectra of a range of chlorocuprates by Deeth and Gerloch.[21] Here, it was found that in $[Pt(NH_3)_4][CuCl_4]$, which contains centrosymmetric axial bonds 326 pm long, the parameter e_{ds} was not greatly reduced from the value deduced for the truly four-coordinate planar $CuCl_4^{2-}$ ion. This is in contrast to analogous complexes with axial bonds 304–278 pm long, in which the d_{z^2}, orbital energy progressively approaches that expected if the AOM is used in its simple form where the d_{z^2} - 4s interaction is neglected.

The fact that the parameter e_{ds} is so large implies a significant admixture of the 4s orbital into the predominantly d_{z^2} orbital in planar $CuCl_4^{2-}$ (a simple perturbation calculation[3c] suggests ~6% 4s participation, and this agrees with recent, more direct estimates based on the metal hyperfine parameters of tetragonally distorted copper(II) complexes with d_{z^2} ground states—~3% in CuF_6^{2-},[22] rising to a much larger value in the linear CuF_2 molecule).[23] In marked contrast to this, only a very small value of e_{dp} is required to obtain optimum agreement with experiment, this only affecting complexes with large pseudotetrahedral distortions. This may be seen from the dashed lines in Figure 4, which were calculated by using the value $e_{dp} = 160$ cm^{-1}. The very modest participation of the metal 4p orbitals in the ground-state wave functions that this implies (~0.2%) agrees with recent interpretations of the metal hyperfine parameters of the pseudotetrahedral $CuCl_4^{2-}$ ion.[9,24] This contrasts with earlier proposals that the 4p orbitals made a significant contribution to the ground-state wave function.[25]

Band Intensities. Several quantitative studies have been reported of the intensities of the d–d transitions of tetrahedral complexes in general[26,27] and of the $CuCl_4^{2-}$ ion when this has the distorted

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Table I. Symmetry-Adapted Basis Functions[a]

D_{2d} symmetry	metal orbitals	ligand functions	ligand label
a_1	d_{z^2}	$^1/_2(p_{z1} + p_{z2} + p_{z3} + p_{z4})$	ϕ_1
		$^1/_2(p_{x1} - p_{x2} + p_{x3} - p_{x4})$	ϕ_2
a_2		$^1/_2(p_{y1} + p_{y2} + p_{y3} + p_{y4})$	ϕ_3
b_1	d_{xy}	$^1/_2(p_{y1} - p_{y2} + p_{y3} - p_{y4})$	ϕ_4
b_2	$d_{x^2-y^2}$	$^1/_2(p_{z1} - p_{z2} + p_{z3} - p_{z4})$	ϕ_5
		$^1/_2(p_{x1} + p_{x2} + p_{x3} + p_{x4})$	ϕ_6
e	d_{xz}, d_{yz}	$1/2^{1/2}(p_{z1} - p_{z3})$	ϕ_7
		$1/2^{1/2}(p_{x1} - p_{x3})$	ϕ_8
		$1/2^{1/2}(p_{y1} - p_{y3})$	ϕ_9
		$1/2^{1/2}(p_{z2} - p_{z4})$	ϕ_{10}
		$1/2^{1/2}(p_{x2} - p_{x4})$	ϕ_{11}
		$1/2^{1/2}(p_{y2} - p_{y4})$	ϕ_{12}

[a] The basis functions with p_z atomic orbitals are involved with σ bonding, those with p_x are π bonding parallel to the *z* molecular axis, and those with p_y are π bonding perpendicular to z.

tetrahedral geometry expected in the absence of lattice forces, as exemplified in Cs_2CuCl_4.[9,28] As the $CuCl_4^{2-}$ ion in (Naem)$CuCl_4$ has a symmetry similar to that in Cs_2CuCl_4, but a considerably smaller distortion from planarity (*trans*-ClCuCl angles of 146°, compared with ~128°), it is of interest to see whether the intensities of both complexes may be explained by using a single simple model and whether this can be extended to treat the intensity of the transitions in planar $CuCl_4^{2-}$, which are derived by coupling with the vibrational mode that carries the complex into a pseudotetrahedral geometry. As the change in energies of the transitions may be explained so successfully by using the AOM (see preceeding section), it was decided to see whether an approach based on this model could be used to treat the changes in band intensities.

Within the framework of the AOM[13] the energy shift of each d orbital in a complex involving just one ligand is given by

$$\Delta E = e_\lambda (F_{ML})^2 \qquad \lambda = \sigma, \pi \tag{2}$$

where e_λ represents the energy shift caused by one ligand and F_{ML} is an angular factor that takes into account the geometry of the complex. Following the Wolfsberg–Helmholz approximation[29]

$$e_\lambda \simeq H_{ML}{}^2/F_{ML}{}^2(H_{MM} - H_{LL}) \tag{3}$$

where H_{MM}, H_{LL}, and H_{ML} represent ligand field matrix elements of the metal and ligand orbitals. As shown in the Appendix, an analogous perturbation procedure may be used to obtain an expression for the coefficient C_λ, which describes the component of a ligand orbital ψ_L of λ symmetry in the predominantly d-orbital wave function

$$\psi \simeq (1 + (C_\lambda F_{ML})^2)^{-1/2}(\psi_M + C_\lambda F_{ML}\psi_L) \tag{4}$$

where

$$C_\lambda \simeq H_{ML}/F_{ML}(H_{MM} - H_{LL}) = [e_\lambda/(H_{MM} - H_{LL})]^{1/2} \tag{5}$$

The ground-state wave function of $CuCl_4^{2-}$ at distortions between square planar and tetrahedral is dominated by the $d_{x^2-y^2}$ function, and as expected from the simple predictions of group theory the only nonzero transitions are

$$\psi_{x^2-y^2} \xleftarrow{xy} \psi_{xz,yz}$$

$$\psi_{x^2-y^2} \xleftarrow{z} \psi_{z^2}$$

where the wave functions are labeled according to their dominant d component. These wave functions may be written as

$$\psi_{x^2-y^2} = a_1 d_{x^2-y^2} + b_5\phi_5 + b_6\phi_6$$
$$\psi_{xz} = a_2 d_{xz} + b_7\phi_7 + b_8\phi_8 + b_{12}\phi_{12}$$
$$\psi_{z^2} = a_3 d_{z^2} + b_1\phi_1 + b_2\phi_2 \tag{6}$$

Table II. Group Overlap Integrals[a]

$G(z^2,1) = (1 - 3\sin^2\theta)S_\sigma$
$G(z^2,2) = 3^{1/2}\sin 2\theta\, S_\pi$

$G(xy,4) = -2\cos\theta\, S_\pi$

$G(x^2 - y^2,5) = -3^{1/2}\cos^2\theta\, S_\sigma$
$G(x^2 - y^2,6) = -\sin 2\theta\, S_\pi$

$G(xz,7) = -(^3/_2)^{1/2}\sin 2\theta\, S_\sigma$
$G(xz,8) = 2^{1/2}\cos 2\theta\, S_\pi$
$G(xz,12) = -2^{1/2}\sin\theta\, S_\pi$

$G(yz,9) = -2^{1/2}\sin\theta\, S_\pi$
$G(yz,10) = -(^3/_2)^{1/2}\sin 2\theta\, S_\sigma$
$G(yz,11) = 2^{1/2}\cos 2\theta\, S_\pi$

[a] Note: (1) S_σ, S_π are σ and π diatomic overlap integrals. (2) θ is as defined in Figure 1. (3) In practice only seven of the above integrals are needed. (4) All other group overlap integrals are zero.

with the symmetry-adapted ligand molecular orbitals ϕ_i being given in Table I. Substituting the appropriate wavefunctions into eq A12 and expressing the dipole moment operator as outlined in the appendix yield the expressions

$$\langle\psi_{x^2-y^2}|\mathbf{z}|\psi_{z^2}\rangle = R\sin\theta[a_1b_1G(x^2 - y^2,5)/2 + a_1b_2G(x^2 - y^2,6)/2 + b_5a_3G(z^2,1)/2 + b_6a_3G(z^2,2)/2 + b_5b_1 + b_6b_2]$$

$$\langle\psi_{x^2-y^2}|\mathbf{x}|\psi_{xz}\rangle = (\tfrac{1}{2})^{1/2}R\cos\theta[a_1b_7G(x^2 - y^2,5)/2 + a_1b_8G(x^2 - y^2,6)/2 + b_5a_2G(xz,7)/2 + b_6a_2G(xz,8)/2 + b_5b_7 + b_6b_8] \tag{7}$$

Here *R* sin θ and *R* cos θ represent the projection of the bond vectors onto the electric vectors **z** and **x**, respectively, and the group overlap integrals *G*(M, L) are given in Table II. If *R* is in picometers, the oscillator strength is then given by[27]

$$f = (1.085 \times 10^{-9})\nu|\langle\psi_i|r|\psi_f\rangle|^2 \tag{8}$$

where ν is the energy of the transition in cm^{-1}.

The coefficients a_i and b_i may be estimated in terms of the parameters C_σ, C_π, and θ (see Appendix), so that it is now possible to calculate the band intensities of the $CuCl_4^{2-}$ ion as a function of angular distortion from planarity. From the use of eq 7 with the group overlap integrals in Table II, it was found that the total contribution from the metal–ligand terms is less than ~30% of the total intensity of both transitions over the whole range of θ. To a reasonable approximation the dipole moments are thus given by the expressions for ligand–ligand contributions only, which in terms of C_σ, C_π, and θ explicitly, are

$$\langle\psi_{x^2-y^2}|\mathbf{z}|\psi_{z^2}\rangle = -3^{1/2}R\sin\theta\, N_1N_2[C_\sigma{}^2\cos^2\theta\,(1 - 3\sin^2\theta) + C_\pi{}^2\sin^2 2\theta]$$

$$\langle\psi_{x^2-y^2}|\mathbf{x}|\psi_{xz}\rangle = R\cos\theta\, N_1N_3[3C_\sigma{}^2\cos^2\theta\sin 2\theta - C_\pi{}^2\sin 4\theta]/2 \tag{9}$$

where the normalization constants are given by

$$N_1 = [1 + 3C_\sigma{}^2\cos^4\theta + C_\pi{}^2\sin^2 2\theta]^{-1/2}$$

$$N_2 = [1 + C_\sigma{}^2(1 - 3\sin^2\theta)^2 + 3C_\pi{}^2\sin^2 2\theta]^{-1/2}$$

$$N_3 = [1 + 3C_\sigma{}^2(\sin^2 2\theta)/2 + 2C_\pi{}^2(\cos^2 2\theta + \sin^2\theta)]^{-1/2}$$

As with the analogous AOM energy parameters e_σ and e_π, it is unrealistic to attempt to calculate C_σ and C_π. Instead, these were varied to give optimum agreement with experiment, and the calculated intensity changes as a function of θ for the transitions in question are shown in Figure 5, together with the experimentally observed intensities for the $CuCl_4^{2-}$ ions in (Naem)$CuCl_4$ and Cs_2CuCl_4. The intensities observed for $(NbzpipzH_2Cl)_2CuCl_4$ have not been included in the plot as they are apparently strongly influenced by lower symmetry effects (see preceeding section). The intensities of Cs_2CuCl_4 were obtained by repeating the measurements of Ferguson[3a] using a large crystal of Cs_2ZnCl_4 doped with a small amount of Cu^{2+}, the concentration of the dopant being measured by atomic absorption spectroscopy. It is estimated that the uncertainties in the experimental values are ~±10% for (Naem)$CuCl_4$ and ~±20% for Cs_2CuCl_4. Optimal agreement is obtained by using the values $C_\sigma \simeq 0.39$ and $C_\pi \simeq 0.31$ in the full expressions (eq 7) (Figure 5, full curves). The intensities calculated by using these values in the approximate expressions (eq 9) are show by the dashed curves in Figure 5. This

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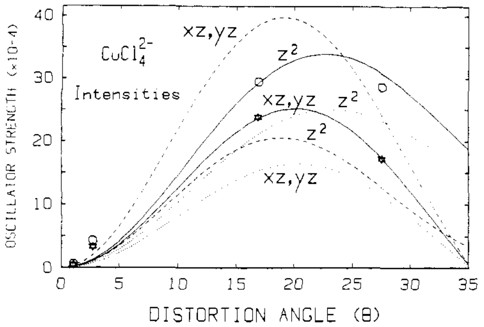

Figure 5. Variation as a function of the distortion angle θ of the oscillator strengths of the $(z^2) \leftarrow (x^2 - y^2)$ and $(xz,yz) \leftarrow (x^2 - y^2)$ transitions in z and xy polarizations, respectively, calculated by using the full expressions with optimum values of C_σ and C_π (—), with the values $C_\sigma = 0.37$ and $C_\sigma/C_\pi = 2.0$ (--), and with ligand-ligand contributions only (---). See text for the method of calculation. The experimentally observed intensities for (Naem)CuCl$_4$ ($\theta = 17°$) and Cs$_2$CuCl$_4$ ($\theta = 27.5°$) and also for planar CuCl$_4^{2-}$ were measured at 10 and 290 K. The latter data are from ref 3d, and here the distortion angle refers to the root-mean-square displacement along the intensity-inducing β_{2u} vibration; for the $(xz,yz) \leftarrow (x^2 - y^2)$ transition, just the component of the intensity due to coupling with the β_{2u} mode is included.

value of C_σ may be used to estimate the covalency of the ground-state wave function via eq 6 and the relationships given in the Appendix and implies that the unpaired electron spends ~68% of its time in the metal $d_{x^2-y^2}$ orbital in the planar CuCl$_4^{2-}$ ion, rising to ~73% when this ion has it prefered distorted tetrahedral geometry. These values agree well with recent calculations,[24] and the estimates of 65 ± 7% metal character obtained from the photoelectron spectrum of square-planar CuCl$_4^{2-}$ [30] and ~75% obtained from the ESR spectrum of the distorted ion.[9]

As expected, the calculations show that the intensity rises steeply from zero for the planar complex, obeying the quadratic dependence in θ required by the simple vibronic coupling model of intensity stealing up to a value of $\theta \simeq 3°$. Above this, the rate of intensification falls away, and in fact the present approach suggests that the transition intensities should maximize at $\theta \simeq 22°$ and actually decrease above this value. This is because the oscillator strength depends on the transition energy (eq 8). This drops substantially for the $d_{z^2} \xleftarrow{z} d_{x^2-y^2}$ transition as the complex approaches tetrahedral geometry, while for the $d_{xz,yz} \xleftarrow{xy} d_{x^2-y^2}$ transition the energy separation with the ground state actually falls to zero in the tetrahedral limit. The limited experimental data agree with this trend, as the intensities of Cs$_2$CuCl$_4$ are quite similar to those of (Naem)CuCl$_4$ despite the greater distortion from planarity in the former complex.

It can be seen that with the above choice of C_σ and C_π the intensity of the transition from the $d_{xz,yz}$ orbitals is significantly less than that from the d_{z^2} orbital for all values of θ. This is in agreement with the observed spectra of the CuCl$_4^{2-}$ ions in both (Naem)CuCl$_4$ and Cs$_2$CuCl$_4$ (Figure 5). However, it should be noted that the ratio C_σ:C_π of ~1.3, which gives optimum agreement with the experimentally observed intensities, is lower than might be expected. Just as the AOM energy parameters e_σ and e_π are expected to be approximately proportional to the square of the diatomic metal–ligand σ and π overlap integrals, so C_σ and C_π should depend on the overlap integrals themselves (eq 3 and 4). As the metal 3d – chlorine 3p σ and π overlaps are estimated[31] to be ~0.08 and ~0.04, respectively, this implies a ratio C_σ:C_π of ~2.0. The calculated intensities obtained for this ratio with $C_\sigma = 0.37$ are shown by the dotted lines in Figure 5, and these are in poor agreement with experiment. In particular, the transition to the ^{2}E(xz,yz) state is now calculated to be more intense than that to the ^{2}A$_1(z^2)$ state. Possibly, the low ratio of C_σ:C_π may simply reflect general inaccuracies in the estimation of the intensities. However, it may be noted that the dependence of the AOM parameters on the diatomic overlap integrals has been criticized as far as the energy parameters e_σ and e_π are concerned; for instance, it has been pointed out[13c] that the interaction with ligand s orbitals with add to e_σ while leaving e_π unaffected. One basic assumption of the AOM in its simple form that may be invalid is that the digonal matrix element H_{LL} is identical for the ligand orbitals of σ and π symmetry. While this will be true for an isolated chloride ion, the interaction with the metal 4s and 4p orbitals will lower the energy of the chlorine p orbital of σ symmetry with respect to those of π symmetry. This could well lead to the factor $(H_{MM} - H_{LL})$ in eq 5 being greater for the metal–ligand π-interaction than the corresponding σ-interaction and hence to an increase in C_π relative to C_σ.

The present results may be compared with those reported by Mason and co-workers[26c] in their interpretation of the "d–d" band intensities of tetrahedral complexes in terms of a ligand polarization model (LPM). The dominant source of the intensity in the present study is similar to that in the LPM, namely transitions between ligand-based orbitals. The LPM was used to investigate the temperature dependence of the band intensities of CoCl$_4^{2-}$. The observed decreases were related to the thermal population of excited levels of vibrations, which carry the complex away from its time-averaged tetrahedral geometry, and in particular the bending vibration considered in the present study. While behavior of this kind is to be expected for higher energy transitions, such as those treated by Mason et al.,[26c] the present study suggests that for low-energy transitions the band intensity of a tetrahedral complex may actually *increase* as the temperature is raised (Figure 5). This is because the oscillator strength depends not only on the dipole-moment integral but also on the transition energy (eq 5). This will be relatively temperature independent for the higher energy transitions, which are dominated by interelectron-repulsion effects. However, for the lowest energy transition, which has not yet been studied over a temperature range experimentally, the present calculations suggest that the frequency shift to higher energy as the effective ligand geometry shifts away from tetrahedral may well dominate the intensity mechanism, causing the intensity to increase with temperature. It will be interesting to see whether future studies of the spectrum of CoCl$_4^{2-}$ confirm this prediction.

One way of interpreting the intensities of the d–d transitions of centrosymmetric complexes is by considering the selection rules appropriate to the geometry of the complex when the ligands are displaced along each *ungerade* normal vibration.[14] This approach implies that the observed band intensities induced by coupling with a particular *u*-mode should correlate with those of complexes having static distortions of the corresponding symmetry, and the present study provides a chance to test this idea.

The intensity of the transition ^{2}B$_{1g}(x^2 - y^2) \leftarrow {}^2A_{1g}(z^2)$ in z polarization of the planar CuCl$_4^{2-}$ ion is derived solely by coupling with the mode of β_{2u} symmetry, which carries the complex into a pseudotetrahedral geometry. The temperature dependence of the band suggests an energy of ~60 cm^{-1} for the vibration, which implies a root-mean-square displacement of $\theta \simeq 1.1°$ at 10 K and an average rms displacement of $\theta \simeq 2.7°$ at 290 K. The band intensities measured at these two temperatures are shown in Figure 5. It may be seen that while the temperature dependence of these is mirrored correctly, the values calculated for the present model, optimized for the statically distorted complexes, significantly underestimated the intensity due to vibronic coupling. The transition ^{2}B$_{1g}(x^2 - y^2) \leftarrow {}^2E_g(xz,yz)$ of planar CuCl$_4^{2-}$ in xy polarization is allowed by vibrations of β_{2u} and α_{2u} symmetry, and the temperature dependence of the band suggests that ~40% of the intensity is due to coupling with the former mode at 10K,[3d] implying the intensity shown in Figure 5. While the calculations show the correct relative intensity of the ^{2}B$_{1g}(x^2 - y^2) \leftarrow {}^2E_g(xz,yz)$ transition compared with that to the ^{2}A$_{1g}(z^2)$ state, the absolute value is again significantly underestimated. It would thus seem that while the above method of interpreting the intensities of vibronically induced transitions shows promise, it does not produce estimates that are in close agreement with experiment at this stage of refinement. The reason for this is unclear, though it may be noted that the present model suggests that even in the centro-

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symmetric planar $CuCl_4^{2-}$ ion the intensity is derived from ligand → ligand transitions rather than being "stolen" from a higher energy charge-transfer state, as is assumed in the normal Herzberg–Teller model of vibronic coupling.[14,15] In fact, the *z*-polarized charge-transfer transitions in planar $CuCl_4^{2-}$ have a very low intensity, and it has been suggested[5] that this explains why the "d–d" transitions in this polarization are considerably weaker in intensity than those in *xy* polarization (Figure 2). The present model suggests that, for the ${}^2A_{1g}(z^2) \leftarrow {}^2B_{1g}(x^2-y^2)$ transition at least, the *z* intensity is due to integrals involving the ligand parts of the relevant molecular orbitals, rather than being due to coupling with the weak charge transfer states.

The widespread acceptance of the AOM as a method of parameterizing the d-orbital energies in metal complexes results from a number of advantages. The two most important are probably that complexes of different stereochemistry involving the same ligands can be related in a simple manner via the angular overlap matrix and that the bonding parameters e_σ and e_π can readily be related to "chemical common sense", e.g. the belief that π-bonding interactions are considerably weaker than σ interactions. The present treatment of band intensities has the potential to offer similar advantages, and we are currently investigating other types of complex, such as metal amines where π-bonding effects should be negligible, to probe these possibilities.

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Appendix

Derivation of the Wave Functions. We are concerned with the intensities of the "d–d" transitions of a $CuCl_4^{2-}$ center with D_{2d} symmetry as it distorts along a normal coordinate that carries it from a planar to a tetrahedral geometry. The distortion is measured in terms of the angle θ illustrated in Figure 1, and the metal and ligand coordinate systems used in the calculations are also shown in this figure; note that the molecular axes are not defined as in the standard D_{2d} point group. The relevant molecular orbitals may be written

$$\psi = \sum_i a_i\psi_i(\mathrm{M}) + \sum_j b_j\phi_j(\mathrm{L}) \qquad \text{(A1)}$$

where $\psi_i(\mathrm{M})$ and $\phi_j(\mathrm{L})$ are metal and ligand orbitals, respectively. In the present approach, only the metal 3d and chlorine 3p atomic orbitals are considered. It has been shown[27] that neglect of the metal s and p functions has little effect on the intensities. The 12 linear combinations of the ligand p orbitals involved in bond formation

$$\phi_i(\mathrm{L}) = \sum_j k_{ij}\mathrm{p}_j \qquad i, j = 1, ..., 12 \qquad \text{(A2)}$$

are shown in Table I, where, for example, $\mathrm{p}_j = \mathrm{p}_{x1}$ refers to the p_x orbital in the local axes on ligand 1. The coefficients of the wavefunctions in (A1) may be obtained by diagonalizing the 17 × 17 secular determinant of the basis functions

$$|H_{ij} - EG_{ij}| = 0 \qquad \text{(A3)}$$

Here, H_{ij} are the matrix elements of the ligand field operator and G_{ij} are group overlap integrals[32] which are a product of a geometric factor F_{ij} and a diatomic overlap integral S_{ij}:

$$G_{ij} = F_{ij}S_{ij} \qquad \text{(A4)}$$

All nonzero group overlap integrals are listed in terms of the angle θ in Table II. The metal d orbitals are orthonormal, and it is assumed that the ligand functions are orthogonal also; i.e., the ligand–ligand overlaps are negligible.

In the following discussion the interaction between one metal function and only one ligand function is considered. The ligand orbital may be made orthogonal to the metal orbital by[13b,33]

$$\chi(\mathrm{L}) = (1 - G_{\mathrm{ML}}{}^2)^{-1/2}[\phi(\mathrm{L}) - G_{\mathrm{ML}}\psi(\mathrm{M})] \qquad \text{(A5)}$$

so that $\langle\psi(\mathrm{M})|\chi(\mathrm{L})\rangle = 0$ in the 2 × 2 secular equation. The only off-diagonal element will now be $H_{\mathrm{M}\chi}$, and first-order perturbation theory gives the energy of the mainly d state raised by

$$\Delta E = (H_{\mathrm{M}\chi})^2/(H_{\mathrm{MM}} - H_{\chi\chi}) \qquad \text{(A6)}$$

on interaction with the ligand function, with the corresponding unnormalized wave function becoming

$$\Psi = \psi(\mathrm{M}) + [H_{\mathrm{M}\chi}/(H_{\mathrm{MM}} - H_{\chi\chi})]\chi(\mathrm{L}) \qquad \text{(A7)}$$

A basic assumption of Wolfsberg–Helmholz theory[29] is that G_{ML} is proportional to $H_{\mathrm{M}\chi}$[13] and in the AOM this proportionality is represented by an empirical parameter

$$\Delta E = e_\lambda(F_{\mathrm{ML}})^2 \quad \lambda = \sigma, \pi \qquad \text{(A8)}$$

The wave function corresponding to (A7) is then

$$\Psi = [1 + (c_\lambda F_{\mathrm{ML}})^2]^{-1/2}(\psi(\mathrm{M}) + c_\lambda F_{\mathrm{M}\chi}\chi(\mathrm{L}))$$

$$c_\lambda = [e_\lambda/(H_{\mathrm{MM}} - H_{\chi\chi})]^{1/2} \qquad \text{(A9)}$$

Substitution of (A5) into the above expression then results in a wave function that is in terms of the metal $\psi(\mathrm{M})$ and the ligand $\phi(\mathrm{L})$ basis functions.

The generalization to the participation of many ligand functions is straight forward, assuming the second of the AOM tenets,[13b] which is that the perturbation due to the ligands is additive:

$$\Psi = [1 + \sum_{\mathrm{L}}(c_\lambda F_{\mathrm{ML}})^2]^{-1/2}(\psi(\mathrm{M}) + \sum_{\mathrm{L}} c_\lambda F_{\mathrm{ML}}\chi(\mathrm{L})) \qquad \text{(A10)}$$

The orthogonal ligand functions $\chi(\mathrm{L})$ (and hence c_λ, via $\mathbf{H}_{\chi\chi}$) will then be dependent on the geometry of the complex from the group overlap integrals $\mathbf{G}_{\mathrm{ML}}$ in (A5). However, trial calculations show that for the small overlaps being considered ($S < 0.1$), this effect is only small. $\chi(\mathrm{L})$ can then be replaced by $\phi(\mathrm{L})$ in (A9) and (A10) and $\mathbf{H}_{\chi\chi}$ by $\mathbf{H}_{\mathrm{LL}}$ in the expression for c_λ.

Derivation of the Transition Moment Integrals. For the transition $\Psi_i \rightarrow \Psi_j$ the dipole moment integral is given by

$$\begin{aligned}\langle\Psi_i|r|\Psi_j\rangle &= \sum_{i,j} a_ib_j\langle\psi_i(\mathrm{M})|r|\phi_j(\mathrm{L})\rangle + \sum_{i,j} b_ia_j\langle\phi_i(\mathrm{L})|r|\psi_j(\mathrm{M})\rangle \\ &= \sum_{i,j} b_ib_j\langle\phi_i(\mathrm{L})|r|\phi_j(\mathrm{L})\rangle\end{aligned} \qquad \text{(A11)}$$

The first two terms involving metal-ligand integrals were the only ones considered in an early study by Ballhausen and Liehr,[26a] though later work[27,35] has shown that the last (ligand–ligand) term

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is the most important source of the intensity. This was the only term considered by Desjardins et al.[5], but in the present study, all three have been included. An approximate expression for the metal–ligand type integral is given by[34]

$$\langle\psi_i(\mathrm{M})|r_\mu|\phi_j(\mathrm{L})\rangle = \sum_n k_{jn} r_{n\mu}/2\langle\psi_i(\mathrm{M})|\mathrm{p}_n\rangle \quad (\mathrm{A12})$$

where $r_{nx} = \mathbf{R}\cos\theta_n\cos\alpha_n$, $r_{ny} = \mathbf{R}\cos\theta_n\sin\alpha_n$, $r_{nz} = \mathbf{R}\sin\theta_n$ are operators that rotate the *n*th p orbital of ligand $\phi_j(\mathrm{L})$. The angles θ_n, and α_n describe the position of the *n*th ligand; θ_n is the angle out of the *xy* plane and α_n is measured clockwise from the *x* axis in Figure 1. This then gives an expression of the form

$$\langle\psi_i(\mathrm{M})|r_\mu|\phi_j(\mathrm{L})\rangle = G(\psi_i,\phi_{j'})KR_\mu/2 \quad (\mathrm{A13})$$

where $R_x = R_y = |\mathbf{R}\cos\theta|$, $R_z = |\mathbf{R}\sin\theta|$ are the magnitudes of the bond length **R** in picometers, projected along the molecular axes. Note that $G(\psi_i,\phi_{j'})$ is not necessarily equal to $G(\psi_i,\phi_j)$ because of the sign changes produced by the operator $r_{n\mu}$. $K = 1/2^{1/2}$ if the transition involves an orbital of E symmetry, or K = 1 otherwise.

The ligand–ligand integrals generally involve three centers, but redefining the electronic dipolar operator onto ligand *n*, $r_\mu = r_{n\mu} + r'_\mu$ gives

$$\langle\phi_i(\mathrm{L})|r_\mu|\phi_j(\mathrm{L})\rangle = \sum_{n,m} k_{in}k_{jm}[r_{n\mu}\langle\mathrm{p}_n|\mathrm{p}_m\rangle + \langle\mathrm{p}_n|r'_\mu|\mathrm{p}_m\rangle] \quad (\mathrm{A14})$$

The second term in (A14) is now a two-centered integral, which is zero when evaluated by approximation A12, as it has been assumed that there is no ligand–ligand overlap. The form of the expression is then

$$\langle\phi_i(\mathrm{L})|r_\mu|\phi_j(\mathrm{L})\rangle = KR_\mu\langle\phi_i(\mathrm{L})|\phi_j(\mathrm{L})\rangle \quad (\mathrm{A15})$$

where the symbols have the same meaning as for (A13).

The required expressions for the dipole moments, given as eq 7 in the main text, may now be obtained by substituting the appropriate wave functions (see eq 6 of the main text) into (A11) and making use of (A13) and (A15) above.

Registry No. $(\mathrm{NbzpipzH_2Cl})_2\mathrm{CuCl_4}$, 81567-09-1; $(\mathrm{Naem})\mathrm{CuCl_4}$, 82621-22-5; $\mathrm{Cs_2CuCl_4}$, 13820-31-0; $\mathrm{CuCl_4}^{2-}$, 15489-36-8.

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Weak Field–Strong Field Correlation Diagrams in Transition-Metal Complexes

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Ab initio SCF calculations have been performed for two typical Co(III) complexes, viz. $\mathrm{CoF_6}^{3-}$ and $\mathrm{Co(CN)_6}^{3-}$, not only on their ground state and a selected set of excited states but also on the average of all ligand field states. The frozen orbitals of the latter calculation were used to set up a correlation diagram connecting the free Co(III) ion (weak field side) with all possible $\mathrm{t_{2g}}^m\mathrm{e_g}^n$ configuration averages for both complexes (strong field side). A comparison of these diagrams with the conventional ligand field picture shows very good qualitative agreement, for instance in characterizing $\mathrm{CoF_6}^{3-}$ as a high-spin complex and $\mathrm{Co(CN)_6}^{3-}$ as a low-spin complex. Conceptually, however, the interpretation of the diagrams and of the ligand field parameters 10*Dq*, *B*, and *C* is thoroughly modified by the subtle role of differential covalency and by the influence of shape modifications in the metal d orbitals.

I. Introduction

A key concept in ligand field theory is the Tanabe–Sugano correlation diagram[1] (or the related Orgel diagram[2]), connecting the d^N energy levels at the strong field limit and the weak field limit.[3] If $4 \leqslant N \leqslant 7$, the correlation diagram is characterized by a multiplicity change of the ground state, thereby giving rise to the existence of high-spin and low-spin complexes. The classification of a specific compound as high-spin or low-spin is supposed to depend on the relative values of 10*Dq* and *P*. The one-electron parameter 10*Dq* is a measure of the strength of the ligand field, whereas the spin-pairing parameter *P* describes the interelectronic d–d repulsion energy.

It is somewhat surprising that correlation diagrams have received so little attention from the ab initio point of view. Indeed, most of the Hartree–Fock calculations on transition-metal complexes have concentrated on other aspects, such as the reproduction of an individual ligand field spectrum, density shifts in the bonding region, bond distances, photoelectron spectra, substitution effects, etc. As a matter of fact, apart from an early study by Kalman and Richardson[4] (using very approximate wave functions) we are aware of only one communication on the subject, where Nieuwpoort[5] compares $\mathrm{FeF_6}^{4-,3-}$ and $\mathrm{Fe(CN)_6}^{4-,3-}$. Although the author does not discuss correlation diagrams explicitly, he offers an interesting comparison of some of the relevant ligand field energies.

It is the purpose of this paper to present a detailed analysis of the octahedral ligand field levels in the high-spin $\mathrm{CoF_6}^{3-}$ and in the low-spin $\mathrm{Co(CN)_6}^{3-}$ complexes. Moreover, the basic physical assumptions of ligand field theory will be critically examined in the light of the ab initio wave functions.

II. Method of Calculation

Roothaan's restricted Hartree–Fock scheme[6] for open shells (two Hamiltonian formalism) was used throughout in Sections IV and V. The Roothaan equations have been solved for each specific state, but also for the d^N configuration average. The orbitals of the configuration average were used to recalculate the energies of the individual states. More details on the calculational procedure and on the "frozen orbital calculations" are given in ref 7 and 8.

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