

Redirected Ligand-Field Analysis. 3. A Basis for Parameter Transferability and Noncylindrical π Bonding in Chlorocuprates[†]

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Ligand-field analyses of the electronic d-d spectra of six chlorocuprates are presented. Parameter values within the angular overlap model (AOM) have been determined for each of three different band assignments for each system. A detailed discussion provides a consistent rationale of parameter trends for favored assignment choices and establishes a new basis for parameter transferability in ligand-field analysis: the sum of all AOM parameter values in each molecule defines an empirical invariant throughout the series. At the same time arguments are presented that show how the ligand fields reflect the noncylindrical nature of the Cu-Cl bonding where this involves nonlinear Cu-Cl-Cu' bridging.

Introduction

In the first¹ of this series of papers, we reported ligand-field analyses for a group of copper(II) complexes with geometries approaching that of a tetragonally distorted octahedron. In the final paragraph we noted that the algebraic sums of the e parameters of the angular overlap model (AOM) were essentially equal throughout seven molecules whose coordination was dominated by amines and remarked that this might reflect the operation of the electroneutrality principle. In following up this observation here with a study of several geometrically similar chlorocuprates, we advance the proposition that the algebraic sum of all AOM e parameters in a complex—for both σ and π interactions—may serve as a general basis for parameter transferability in ligand-field analysis.

It is apparent from many studies,^{2,3} perhaps most graphically from that⁴ in part 2 of the present series, that individual AOM e parameters are not transferable from complex to complex, at least in terms simply of the metal and ligand concerned. This observation is central to our view^{2,3} that ligand-field parameters probe the valence-electron distribution within a given complex as it is rather than as it is suggested by putative bonding properties of the metal and ligand precursors. In general we cannot expect e parameters to be proportional to the squares of the corresponding metal-ligand overlap integrals of simple molecular orbital theory; however, approximate proportionality between such quantities may well occur "accidentally" and underlies contrary claims that have been made^{5,6} on occasion. On the other hand, the remarkable constancy of the sum of e_e values in the amines studied in part 1 might well monitor valence-electron drift onto the central metal. It is important, therefore, first to establish the empiricism of this "sum rule": only then might quantitative relationships with bond length variations, electronegativities, and other chemical concepts form a proper focus of future study.

The basis for our interest in these parameter sums does not rest on empiricism alone. We have argued recently^{2,3,7,8} that the AOM is to be regarded as a cellular decomposition of the ligand field, and, as such, its linear relationship with the conventional expansion in spherical harmonics has been set out in detail.^{2,9} The upshot of that connection is that the coefficients c_{kq} of the harmonics Y_q^k appearing in the global (molecular) multipole expansion of the ligand field are expressed as linear combinations of the many AOM e_λ parameters in the system ($\lambda = \sigma, \pi_x, \pi_y$), the precise forms of these combinations being determined by the detailed molecular geometry. At the same time, a contribution to the totally spherical component Y_0^0 of the ligand field is given,^{2,9} with total generality, by the sum of all locally diagonal ligand-field matrix elements, that is, by the sum of all AOM e_λ parameters in the system. Normally one regards this fact as incidental in ligand-field calculations, for interest properly centers on energy splittings. In any case, there is no question of that sum giving the spherical (average) energy shift undergone by the free metal d-orbital set upon complexation. Nevertheless, the sum does give

some measure of it, and we might reasonably hope to learn something of the whole thereby. Accordingly, we are led to enquire whether a connection between ligand-field parameters as such and the "central-field covalency" idea^{10,11} of the Nephelauxetic effect might then emerge. This must remain something for the future, but the idea is lent some support by the present exploration.

Comparison of the e_λ sums for the three chlorocuprates in part 1 certainly lends little credence to the notion of an empirical invariant. While the AOM values for the pentachlorocuprate ion are ill established, those for the tetrahedral ion in Cs_2CuCl_4 sum to a much greater number than those for the planar CuCl_4^{2-} entity. We are actively studying the planar/tetrahedral relationship in this connection and with respect to various metals. Meanwhile, we have restricted our choice of complex, here, to chlorocuprates with planar and tetragonally elongated octahedral geometries so as to maximize comparability with the series of copper(II) amines in part 1. Our selection has been determined by the joint needs for molecular structural information and d-d spectra characterized by more than two absorption maxima. The geometries of the six chlorocuprates we analyzed are collected in Figure 1 in order of increasing tetragonality, that being assessed in terms of the axial/mean-equatorial bond length ratio. All but the last of these six compounds involve some bridging chlorine ligands: some approximately linear, some with nearly right-angular bridges, some with essentially symmetrical bridging, others strongly asymmetric. It transpires that these complications actually help our understanding of the ligand fields in chlorocuprates, and the present study has therefore evolved into an examination both of a parameter transferability criterion and of the significance of bridging in chlorocuprates.

Procedures and Spectral Assignments

Electronic spectra for the six chlorocuprates have been reported from studies of mulls at 77 K for the *n*-propylammonium⁵ and tetraammineplatinum(II)¹² salts, from absorption spectroscopy of single crystals at 8 K using polarized light for the cesium,¹³ ethylammonium,⁵ and unbridged nmp¹⁴ salts, and at 77 K in

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Table I. AOM Parameter Values for Chlorocuprates (cm⁻¹)^a

assignt	params	chlorocuprate complex						
		Cs (A)		Me (B)	Et (C)	n-Pr (D)	Pt (E)	nmph (F)
1	$e_{\sigma}(\text{eq})$	5400	4500	4800	4737	4900	5167	6000
	$e_{\pi}(\text{eq})$	1500	1100 ^b	550	455	600	600	1400
	$e_{\sigma}(\text{ax})$	1250	375	-600	-828	-750	-283	350
	Σ	36100	23150	22400	20930	22900	24900	38300
2	$e_{\sigma}(\text{eq})$	5900	4500	5267	5157	5233	5900	7167
	$e_{\pi}(\text{eq})$	2300	1700 ^b	1250	1087	1100	1700	2250
	$e_{\sigma}(\text{ax})$	800	-600	-833	-1038	-917	-650	67
	Σ	43600	23600	29400	27230	27900	35900	46800
3	$e_{\sigma}(\text{eq})$	4000	3500	4533	4550	4433	5100	5300
	$e_{\pi}(\text{eq})$	900	700 ^b	700	630	500	1100	850
	$e_{\sigma}(\text{ax})$	-2400	-2800	-2117	-2100	-2317	-2050	-3200
	Σ	18400	11200	19500	19040	17100	25100	21600
	mean Cu-Cl (eq), Å	2.31		2.3	2.28	2.29	2.29	2.26
	Cu-Cl (ax), Å	2.78		2.9	2.98	3.04	3.26	

^a Those values for A were determined as "best-fit" sets by using the published crystallographic geometry¹⁷ and the CAMMAG system;¹⁶ those values for B-F were obtained by using the analytical expressions in eq 1. Spin-orbit coupling is not included. Parameters for favored assignments are shown in boldfaced type. ^b $e_{\pi\perp}$ values, when $e_{\pi\parallel} = 0$. Assignments are defined in Figure 2. $\Sigma \equiv \Sigma_i \text{ligands} (e_{\sigma} + e_{\pi\parallel} + e_{\pi\perp})_i$.

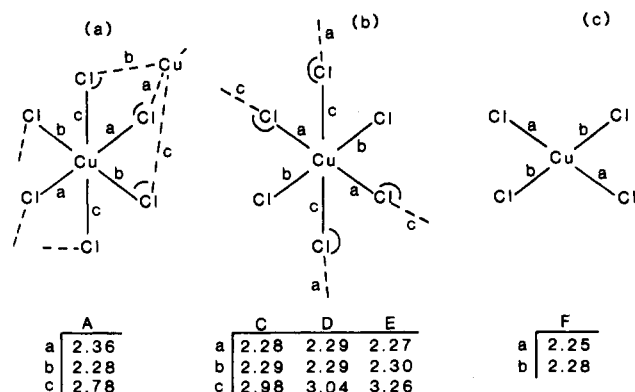


Figure 1. Coordination geometries and chlorine bridging for the following compounds: (a) CsCuCl₃ (A)¹⁷ for which the marked angles are all about 76°; (b) [NH₃R][CuCl₄] (R = Me, Et, and n-Pr for B, C,¹⁸ and D¹⁹) and [Pt(NH₃)₄][CuCl₄] (E),²⁰ where all marked angles are about 165°; (c) [C₆H₅(CH₂)₂NH₂CH₃⁺]₂[CuCl₄]₂⁻ (F)²¹. The mean bond lengths for the methylammonium salt (B), given in Table I, are estimated simply as averages of corresponding distances in the ethylammonium (C) and unsubstituted ammonium²² salts. The latter complex has not been included in the present ligand-field study as only two bands have been resolved in its absorption spectrum.

unpolarized light for the methylammonium¹⁵ complex. All spectra are characterized by three band maxima, and generally those obtained from measurements on single crystals are not especially better resolved than those from mulls. The middle band is occasionally the least well resolved, and the dependence of AOM parameter values upon the relative uncertainty in its position is discussed later.

Our ligand-field analyses, which are based entirely upon the reported spectral bands, begin within the framework of idealized D_{4h} molecular symmetry. The efficacy of this approach emerges throughout the analysis, which was adopted initially because of the close approach to this symmetry at least in terms of the various Cl-Cu-Cl bond angles. This is least accurate for the cesium complex, a point we shall refer to again. Within the present idealization, the d_{xz} and d_{yz} orbitals are degenerate (ignoring spin-orbit coupling) and so we are left exactly three d-d transitions to assign to three experimental absorption bands.

A further assumption carried throughout the study is that the chlorine ligands function as π donors toward the copper atom so

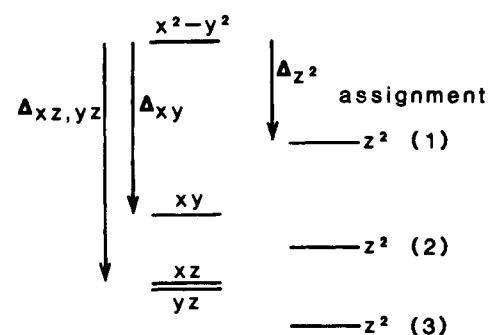


Figure 2. Definition of transition energies Δ and assignments 1, 2, and 3 considered in the ligand-field analyses.

that in these tetragonally elongated octahedral species we can be confident of the relative orbital energy ordering, $d_{x^2-y^2} > d_{xy} > d_{xz,yz}$. Fits to the experimental data have then been determined for each of the six chlorocuprates according to three different spectral band assignments (Figure 2): corresponding to the d_{z^2} orbital energy being placed (1) between $d_{x^2-y^2}$ and d_{xy} , (2) between d_{xy} and $d_{xz,yz}$, and (3) as the lowest of the set. Finally, we presume no bonding role for the distant axial chlorine ligands in any complex, thus restricting the variable set to the AOM parameters: $e_{\sigma}(\text{axial})$, $e_{\sigma}(\text{equatorial})$, $e_{\pi}(\text{equatorial})$. With the neglect of spin-orbit coupling, this approach allowed the use of the analytical relationships within the idealized D_{4h} environments

$$e_{\pi}(\text{eq}) = \frac{1}{2}(\Delta_{xz,yz} - \Delta_{xy}) \quad e_{\sigma}(\text{eq}) = \frac{1}{3}(\Delta_{xz,yz} + 2e_{\sigma}(\text{eq}))$$

$$e_{\sigma}(\text{ax}) = e_{\sigma}(\text{eq}) - \frac{1}{2}\Delta_{z^2} \quad (1)$$

Δ being defined in Figure 2.

The possibility of significant errors arising from the geometry idealization—as opposed to the question of equating the ligand fields of all equatorial ligands—was checked in the case of the cesium complex, whose angular geometry departs most—though only slightly—from the ideal D_{4h} symmetry, by using the non-analytical procedures of our usual computational package:^{2,16} here

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the actual crystallographic coordinates of all ligands are employed strictly in the AOM calculations. The differences among the three analyses corresponding to the various spectral assignments, arising from the idealized and crystallographic geometries, are $<150\text{ cm}^{-1}$ for e_g values and $<50\text{ cm}^{-1}$ for $e_x(\text{eq})$. Accordingly, the best-fit parameter values listed in Table I, which serve as a basis for our discussion, were obtained via the crystallographic geometry for CsCuCl_3 but via eq 1 for the other five complexes.

Discussion

The complexes in Table I are arranged in order of increasing tetragonality. Both bond lengths and spectroscopic data clearly define the group of salts B, C, and D—also labeled by their substituted ammonium cations—as possessing virtually identical chlorocuprate chromophores. Our discussion of the ligand-field parameter values given in the table is directed initially toward the selection of the most probable assignment—1, 2, or 3—in each case, given that each set of AOM parameters present, *prima facie*, an equally acceptable account of the observed spectra. As far as possible we pursue this investigation by a process of elimination on the balance of probabilities, reserving a direct and positive description of our final choice for a summary.

The nonbridged nmph complex F provides a benchmark and starting point, for its spectrum is the best resolved of this group of complexes and, more importantly, the most polarized. The polarization ratios have been interpreted¹⁴ independently in terms of assignment 3, and the large negative value of $e_g(\text{void})$ associated with this choice places the ligand-field characteristics of this complex firmly in line with the various planar and tetragonally elongated species described in part 1. The corresponding values for $e_g(\text{void})$ with assignment 1 or 2, let alone the associated $e_g(\text{eq})$ values, only serve to confirm assignment 3 as the appropriate spectral assignment for this system.

The platinum complex E must involve very little Cu—Cl interaction in the axial direction. It is on this basis especially that we again favor assignment 3, for in this near-planar coordinated species, the large negative value for $e_g(\text{ax})$ falls nicely into line with the corresponding values for the nmph complex F and with those determined¹ for other distant ligands in part 1. In any case the very small negative values for $e_g(\text{ax})$ yielded by assignments 1 and 2 both fail to place the ligand field of E between those of B—D and that of F—for any assignments—as would be expected from the tetragonality indicated by the bond lengths in the table. A final objection to assignment 2 would be founded upon the large $e_g(\text{eq})$ value: this would be unexpected (a) because the equatorial Cu—Cl bond length in E is longer than that in F and (b) because we might expect a larger $e_g(\text{eq})$ value to be offset by a larger, negative $e_g(\text{ax})$ value, as found for the complexes in part 1. This last point is strongly associated with the “sum rule”, of course, and we observe that while assignment 1 or 3 for E might accord with assignment 3 for F in this respect, the sum of AOM parameters in E, assignment 2, seems unacceptable. We note at this point that the position of the middle absorption band in the platinum complex is not especially well established, certainly less well established than all transition energies of F. If, for example, that band were estimated to lie only 200 cm^{-1} lower in energy, the parameter values in E, assignment 3, would be replaced by 4967, 1000, -2183 , and $23\,540\text{ cm}^{-1}$, respectively. Incidentally, this provides some gauge of the sensitivity of the values in the table—though this sensitivity varies as we note later—and diminishes the importance of the difference between the sums quoted in E, assignment 3, and F, assignment 3.

We shall consider the assignments for complexes B—D as a group. Our ultimate choice is for assignment 1, but we reach that conclusion only after several steps. Underlying our reasoning is an awareness that the middle absorption band, in particular, in these spectra is less well established than the rest. So we bear in mind—but no more than that, given that the data in Table I do represent “raw” data in this study—the possibility of, e.g., a $\pm 400\text{-cm}^{-1}$ shift in this band. The sensitivity of the computed

AOM parameter values to such changes varies and is typified by shifts of ± 1500 , ± 300 , and $\pm 3000\text{ cm}^{-1}$ in the values for the sums Σ of parameters for assignments 1, 2, and 3, respectively. Straightaway, therefore, we are led to disfavor assignment 2 on the grounds that $\Sigma \approx 28\,000\text{ cm}^{-1}$ falls too far from the likely value of $23\,000\text{ cm}^{-1}$ suggested by E and F (recall that the parameters for F are probably better established). The same prejudice is expressed by the marked algebraic increase in $e_g(\text{ax})$ values on changing from E and F to B—D not being accompanied by a commensurate decrease in $e_g(\text{eq})$ values. The trends in these values and in the sum Σ appear more satisfactory within the table as a whole if assignment 1 is used for the complexes B—D. In one respect, however, assignment 3 for these systems must be entertained as a serious possibility. Bearing in mind the sort of parameter shifts accompanying a small change in the estimate of the middle spectral band energy, the sums Σ associated with assignment 3 could be brought into line with those for E and F. Shifting $\Delta_{xz,yz}$ for the ethylammonium complex, for example, by $+500\text{ cm}^{-1}$ replaces the values in C assignment 3, by 4890, 885, -1760 , and $23\,120\text{ cm}^{-1}$, respectively. While such Σ and $e_g(\text{eq})$ values might be satisfactory, notwithstanding the “readjusted” nature of these data, the $e_g(\text{ax})$ values pose some problems. It was clear from the examination of “semicoordination” in part 1 that the relationship between $e_g(\text{ax})$ and the metal—ligand bond length is far from linear. Perhaps, therefore, we should accept the rather large negative values for these systems as suggested by the (modified) values of C, assignment 3. But, if so, we are led to consider Cu—Cl bond lengths of 2.98 \AA to be nearly out of the “region of bonding interaction” and to consider that, in effect, all the complexes B—F involve virtually planar coordinated copper atoms. Comparison with the $e_g(\text{ax})$ values determined for the various systems in part 1 suggests to us that such a view is too extreme and we regard values of ca. -1700 cm^{-1} as too negative for the present complexes. While we shall support this prejudice further shortly, at this stage a choice between assignments 1 and 3 for B—D is less clear-cut than the choice of assignment 3 for E.

The choice is helped ultimately by considerations of the ligand field in CsCuCl_3 . First, it is clear that no simple choice for the correct assignment in this complex is suggested by the AOM parameters in column A(i) of Table I. Assignment 2 seems unacceptable, not only with respect to the sum Σ but also from the large values of both $e_g(\text{eq})$ and $e_x(\text{eq})$ for Cu—Cl bonds, which are significantly longer on average than those in the nmph complex F. The same arguments apply, though with a little less force perhaps, with respect to assignment 1. If the “sum rule” has any validity—as we do believe, at least in the present series of complexes—assignment 1 is to be rejected out of hand. (Otherwise, the large $e_g(\text{eq})$ and $e_x(\text{eq})$ values—which are experimentally rather better established than those for the complexes B—E—must be ignored, presumably via some prejudice that generally disavows the efficacy of ligand-field models at this level of accuracy. To that we would direct the critic’s attention to our final view, seeking to interpret *all* of the AOM values throughout this series in a self-consistent and chemically consistent way.) However, having discarded assignments 1 and 2, we are not convinced by assignment 3 either, for the sum Σ , though nearer to $23\,000\text{ cm}^{-1}$ than those for assignments 1 and 2, is still rather low. We are then left in the position of observing a significant reduction in $e_g(\text{eq})$ going from E to A without this being accompanied by a comparable change in $e_g(\text{ax})$, especially strange in view of the significant decrease in axial Cu—Cl bond lengths. Given the overall tetragonality series, assignment 3 for complex A virtually demands that the spectra of all the complexes be assigned in this way and we still observe incompatible trends throughout the parameters in the bottom row of the table.

Rejection of all three blocks of parameter values for the cesium salt necessitates a reexamination of the basic approximations of our starting model. We have already noted that the small angular differences within the coordination spheres between A and the rest are essentially trivial; even so, the results in column A(i) of Table I derive from the true molecular geometry for closer com-

Table II. CsCuCl₃ Parameters for Assignment 1 with Noncylindrical Bonding (cm⁻¹)

$e_{\pi\perp}$ (both)	1100 ^a	1100	1300	1500
$e_{\pi\parallel}$ (asym)	0 ^a	0.2 $e_{\pi\perp}$	0.4 $e_{\pi\perp}$	$e_{\pi\perp}$
e_{σ} (eq)	4500 ^a	4625	4750	5000
e_{σ} (ax)	375 ^a	437	600	850
Σ	23150 ^a	24215	26440	30700
calcd $\Delta_{xz,yz}$ splitting	1035	877	853	463

^a Values are the same as in column A(ii) of Table I. $e_{\pi\parallel} = 0$ for the symmetric Cu-Cl-Cu' bridge.

parison with what follows. Perhaps the greater rhombicity—that is, larger difference between equatorial Cu-Cl bond lengths—in the cesium complex sets this aside from the rest. Accordingly, we have studied this possibility by setting e_{σ} and e_{π} values for the longer equatorial bonds at 0.9 times, and then at 0.8 times, freely ranging values for the shorter bonds. Parameter sets that optimize fits differed little from those in column A(i) of Table I. The sum Σ changed by <200 cm⁻¹ and e_{σ} (ax) by <50 cm⁻¹, while e_{σ} and e_{π} for the equatorial bonds took values whose means barely differed from those in Table I—the e_{σ} values varied by up to 600 cm⁻¹ above or below the means, and the e_{π} values varied by up to 200 cm⁻¹. In summary, reasonable recognition of the rhombicity in CsCuCl₃ failed utterly to provide an interpretation of the ligand field in line with that described for the other five complexes.

Consider then the nature of the bridging in these molecules. The structure of CsCuCl₃ characterizes a distortion of the hexagonal close-packed AMX₃ type, and the CuCl--Cu' bridges are right angular rather than linear as in the complexes B-E: actually about 76° instead of 165°. There arises the possibility, therefore, that the chlorine ligands in CsCuCl₃ may not act as "linear ligands". Noncylindrical chlorine π donation to the reference copper atom would result if the appropriate ligand π functions were unequally involved with other copper atoms. Regarding the chlorine atoms as bonding via pure p orbitals—for heuristic reasons—we observe in CsCuCl₃ that one p_{π} orbital is already "preempted" into σ bonding with another copper atom. The resulting π -donor function of this orbital with respect to the reference copper atom would be expected to be diminished on the grounds of both the lesser lateral spread of the engaged p orbital and the lower energy of what is now a σ (Cu') bonding orbital.

A first step in implementing these ideas within the AOM formalism was to define $e_{\pi\perp}$ and $e_{\pi\parallel}$ for the equatorial chlorine ligands in CsCuCl₃, corresponding to the involvement of the "free" and " σ -bridging" chlorine p orbitals, respectively: thus, $e_{\pi\perp}$ refers to Cu-Cl π bonding perpendicular to the corresponding Cu-Cl--Cu', plane. Setting $e_{\pi\parallel} = 0$, representing the extreme situation that the bridging chlorine p orbital cannot π bond to the reference copper atom at all, yields the best-fit parameter values shown in column A(ii) of Table I. It is immediately apparent how the dramatic changes in other AOM values are such as to suggest close comparison with the values quoted in Table I for the other five complexes. Less extreme noncylindricity for the bridging equatorial chlorine ligands in CsCuCl₃ is represented by the parameter values collected in Table II, shown for the case of assignment 1. These models were investigated on noting that the shorter Cu-Cl equatorial bond of 2.28 Å is associated with a long Cl--Cu' bridge—actually the axial bond of the second copper chromophore—while the longer equatorial one of 2.36 Å is involved in a symmetrical bridge. The models summarized in Table II are therefore characterized by taking $e_{\pi\parallel} = 0$ for the longer (2.36 Å) Cu-Cl bonds and $e_{\pi\parallel} = 0.0, 0.2, 0.4,$ and 1.0 times $e_{\pi\perp}$ for the shorter Cu-Cl bonds. The rhombicity introduced by this model yields the energy splittings of the $\Delta_{xz,yz}$ transitions given in Table II. Some evidence for such splitting obtains from the experimental spectrum.¹³ All this was in recognition that the cylindricity of the more weakly bridging chlorine atom might be less perturbed than that for the symmetrically bridging one.

With respect to the values in Tables I and II, we address the question of spectral assignment in CsCuCl₃, and indeed in the complexes B-D in consequence. Considering first the sums Σ ,

it is apparent that either assignment 1 or 2 for the cesium complex A would agree well with those for B-F. However, in view of the clear trends in tetragonality throughout the series, if assignment 2 is correct for A, we should choose assignment 3 for all the rest; conversely, assignment 1 for A would fall in line with either assignment 1 or 3 for B-D.

Consider, first, trends in the σ -bonding parameters throughout the series. Taking assignment 1 for A-D with assignment 3 for E and F, we observed a smooth trend in both e_{σ} values, reflecting the continuous variation in tetragonality. On the other hand, taking assignment 2 for A and assignment 3 for B-F, we have already noted the lack of change in e_{σ} (ax) for B-D; now we observe a large change in this parameter from the linearly bridged species to the cesium complex without a concomitant decrease in e_{σ} (eq). Turning then to the π -bonding values, we note first the approximate 2-fold decrease in the e_{π} value on changing from A to the group B-D. Insofar as AOM e parameters monitor electron drift, these values are actually not greatly different, as the value of 1100 cm⁻¹ for $e_{\pi\perp}$ in A(ii), assignment 1, is to be compared with one of ca. 550 cm⁻¹ for each of the $e_{\pi\parallel}$ and $e_{\pi\perp}$ parameters in B-D, assignment 1. It is as though the overall electron donation from the equatorial chlorine ligands toward the metal atom is effectively constant but is concentrated into one mode (\perp) where "right-angular" bridges are involved instead of being implemented cylindrically in the linear bridging geometries. Of course, the bond length variations between the Cu-Cl(eq) contacts in A-D and also the fact that twice as many bridges are involved in A as in B-D mean that the factor of 2 between $e_{\pi\perp}$ in A(ii) assignment 1, and e_{π} in B-D is doubly fortuitous. It is unlikely that we can estimate any of the AOM parameters more exactly than, e.g., ± 200 cm⁻¹ so that we are content to rationalize only qualitative trends here.²³

The increase in e_{π} from ca. 550 cm⁻¹ for B-D, assignment 1, to ca. 1100 cm⁻¹ for E assignment 3, is large enough to be significant, however, and we believe it reflects a change from a bridged species to an essentially planar mononuclear entity. Reference to the dimensions in Figure 1 shows that the axial Cu-Cl bond of the reference molecule is the bridging Cu-Cl--Cu' contact with the neighbors: the near noncoordination of the axial chlorine in E therefore implies the virtual loss of bridging between chromophores. Complexes E and F are thus closely similar, and we consider the e_{π} (eq) values in assignment 3 of E and F to be closely similar too, at least within experimental error. The fact that e_{π} (eq) for E and F are significantly larger than those for B-D is now taken to reveal the changing role of the chlorine whose local charge must reflect its involvement with one or two copper atoms, respectively. Finally, a similar argument disfavors the choice of assignment 2 for A as the larger value of 1700 cm⁻¹ for $e_{\pi\perp}$ —significantly larger than 1100 cm⁻¹—should be associated with a less bridging rather than a more bridging ligand, as seems indicated by the geometrical details given in Figure 1.

Summary

Our choices of assignments for the spectra of these six chlorocuprates have necessarily been made only after somewhat intricate comparisons. It is appropriate, therefore, to summarize the overall trends, as we believe them to be, without lengthy justification.

Consider the changes on traversing from the isolated planar complex F to the most octahedral system A. In F the metal atom achieves some optimal approach to electrical neutrality from four chlorine ligands, each donating negative charge cylindrically in response to their own exigency for near neutrality. The lack of axial coordination is reflected by the large negative values for e_{σ} (void), as discussed in part 1. In E we see the onset of axial bonding: e_{σ} (axial) is very sensitive in this region, and the small

(23) Recognition of the differing roles of bridging and nonbridging chlorine ligands logically demands a relaxation of the 4-fold symmetry in B-D implied by the average e_{σ} and e_{π} (eq) values in Table I. Calculations, like those described for A, yield closely similar AOM values on the average, but their grossly overparametrized nature fails to quantify the issue.

increase in electron donation along the axial direction relieves the equatorial ligands somewhat, this being attested by the small decrease in $e_{\sigma}(\text{eq})$ value and the equally small increase in equatorial Cu-Cl bond length. Within the block of complexes B-D, a significant bridging role for two of the equatorial chlorine ligands is indicated by the AOM parameters. The increased bridging is associated geometrically with a greater proximity of the (still distant) axial ligands so that we see a continuing trend in smaller values for $e_{\sigma}(\text{eq})$ and decreasingly negative ones for $e_{\sigma}(\text{ax})$. The bridging chlorine atoms are each engaged—predominantly via σ bonding—with two copper atoms and so will be less good donors—by both σ and π pathways—toward the reference copper atom. Some part of the decrease in the $e_{\sigma}(\text{eq})$ value on changing from E to B-D no doubt monitors this effect. The change in π bonding is more clearly monitored by the AOM parameters. Finally, on moving to A, the geometric nature of the bridges changes and we observe the noncylindricity of the equatorial Cu-Cl interactions. The overall donation of charge from these

ligands to the central metal has decreased a little—accompanied once again by an increased role for the axial ligands—as monitored by the smaller $e_{\sigma}(\text{eq})$ value (and marginally longer Cu-Cl bond) and by the fact that $(e_{\pi_{\parallel}} + e_{\pi_{\perp}})$ may be somewhat less here than for the complexes B-D.

Throughout these complex checks and balances—that accord with generally acquired chemical intuition—the sum Σ of AOM parameters remains sensibly constant. In the Discussion we tried to present arguments that were not overdependent on the notion of the “sum rule”, and to the extent that that was possible, therefore, the validity and utility of this transferability criterion is reasonably well demonstrated, at least, within the present series of chlorocuprate complexes. The concept is clearly one to be tested further in complexes involving other geometries, coordination numbers, and, of course, other metals and ligands.

Registry No. A, 18437-47-3; B, 16950-47-3; C, 55940-27-7; D, 55940-28-8; E, 95979-40-1; F, 51751-78-1; Cu, 7440-50-8; Cl, 7782-50-5.

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Correlation of Ligand Field Excited-State Energies with Ligand Field Strength in (Polypyridine)ruthenium(II) Complexes

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The temperature dependence of the emission intensities and lifetimes for several (polypyridine)ruthenium(II) complexes have been evaluated. For complexes that have weaker ligand fields than tris(bipyridine)ruthenium(II), a dramatic decrease in the emission intensity and lifetime occurs near 170 K. This behavior is ascribed to population of a ligand field state that lies only 2000 cm^{-1} above the lowest metal-to-ligand charge-transfer excited state. Above 250 K, a weak emission remains and an additional activated process can be observed in the vicinity of 260–330 K. This weak emission is assigned to emission from an impurity, most likely tris(bipyridine)ruthenium(II).

Introduction

Extensive studies on tris(bipyridine)ruthenium(II), $\text{Ru}(\text{bpy})_3^{2+}$, have led to the model shown in Figure 1.¹ The intense absorption in the visible region (450 nm) has been assigned as a metal-to-ligand charge-transfer (MLCT) transition.² The initially produced ¹MLCT rapidly undergoes intersystem crossing to the corresponding triplet state, ³MLCT, with unit efficiency.³ This ³MLCT state is reasonably long-lived ($\approx 0.6 \mu\text{s}$ in water at 298 K) and is thought to be deactivated by three processes: radiative decay, k_r , radiationless decay, k_{nr} , and thermal population of a higher lying excited state, $k_0 \exp(-\Delta E/RT)$. For the latter process, Van Houten and Watts were able to evaluate the energy difference between these two states (ΔE) as 3600 cm^{-1} in water.⁴ A low-yield photosubstitution occurs that is believed to result from population of this thermally accessible excited state.⁵ As a result, the higher excited state has been designated a ligand field (LF) excited state.

However, the energy of this presumed LF state did not seem to depend upon the ligand field strength in the expected manner. For example, the 4,5-diazafluorene ligand (diaz) has been shown to selectively perturb LF states while leaving the energy of any MLCT states nearly unchanged.⁶ However, for $\text{Ru}(\text{bpy})_2\text{diaz}^{2+}$ over the temperature range of 250–350 K, the observed temperature dependence yielded a value of 3450 cm^{-1} for ΔE , very similar to that observed for $\text{Ru}(\text{bpy})_3^{2+}$.⁷ Another example is $\text{Ru}(\text{bpy})_2(\text{py})_2^{2+}$ (py = pyridine). Certainly pyridine is lower in the spectrochemical series than bipyridine, and the LF state is

expected to occur at a lower energy. Again, the value of ΔE has been evaluated over the 250–350 K temperature range and found to be 3410 cm^{-1} .⁸ Since the energy of the ³MLCT (relative to $\text{Ru}(\text{bpy})_3^{2+}$ is essentially constant ($E_{\text{em}}(0-0)$ varies by only 40 cm^{-1}), this value of ΔE suggests little change in the energy of the presumed LF state. Clearly, the ligand field trends so apparent in other metal complexes were absent in the behavior of this presumed LF state.

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