Scheme IV

$$Co(en)_2(OH_2)_2{}^{3+} + 2SO_2 \underset{K'}{\overset{-2H^+}{\rightleftharpoons}}$$

$$Co(en)_2(OSO_2H)_2{}^+ \underset{+H^+}{\overset{-H^+,\ K_8}{\rightleftharpoons}}$$

$$Co(en)_2(OSO_2)(OSO_2H) \overset{-H^+,\ K_9}{\rightleftharpoons} Co(en)_2(OSO_2)_2{}^-$$

$$\Big\downarrow k_{red}$$

$$Co^{II}(en)_2(O_2S^VO)(O_2S^{IV}O)^-$$

$$fast \Big\downarrow {}^{+Co^{III}(en)_2(O_2S^{IV}O)_2{}^-}$$
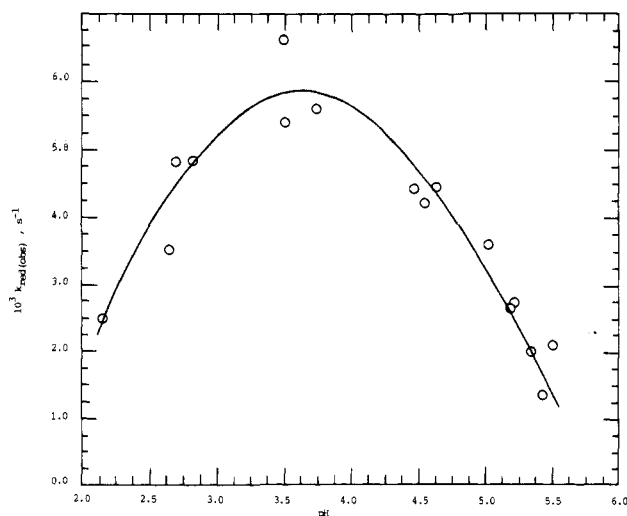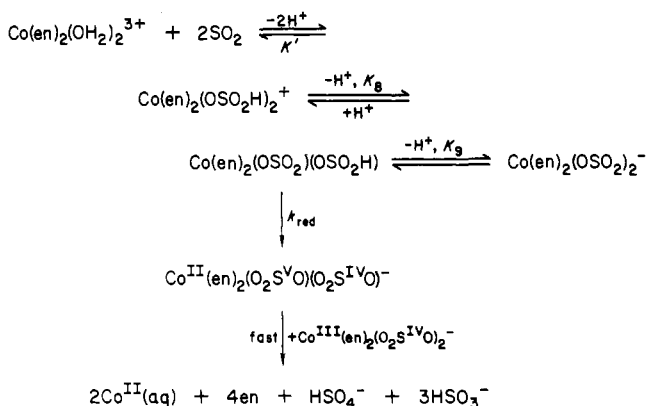
$$2Co^{II}(aq) + 4en + HSO_4{}^- + 3HSO_3{}^-$$

Figure 2. Variation of the observed rate constant k_{red}(obsd) for the reduction of bis(sulfito-O)cobalt(III) with pH at 25 °C (data of Table VII).

if $[H^+]^4$ is neglected. This situation is achieved if it is assumed that when the metabisulfite is added to the trans-diaquo and -aquo hydroxo equilibrium mixture, the cobalt(III) species are completely converted to the disulfito complex $Co(en)_2(OSO_2H)_2$. This latter complex then takes the three equilibrium forms given in Scheme IV, in which the monoprotonated species is the one that undergoes reduction to cobalt(II).

Rearrangement of eq 31 gives

$$\frac{[H^+]}{k_{red}(obsd)} = \frac{K_9}{k_{red}} + \frac{[H^+]}{k_{red}} + \frac{[H^+]^2}{k_{red}K_8} \tag{32}$$

A least-squares fit of the experimental data to the form of eq 32 gave $k_{red} = (6.5 \pm 0.3) \times 10^{-3}\ s^{-1}$, $K_8 = (4.4 \pm 0.6) \times 10^{-3}$ M, and $K_9 = (1.2 \pm 0.4) \times 10^{-5}$ M. These parameters gave a very satisfactory fit of all the experimental data as shown in Figure 2. The K values are in the range to be expected, since studies of an analogous cobalt(III) system[26] suggested a similar order of magnitude for K_8, while one would expect K_9 to be at least 1 order of magnitude smaller than K_8, due to the considerably decreased positive charge on the monoprotonated bis(sulfito) species relative to the diprotonated one.

Registry No. *trans*-[Co(en)$_2$(OH$_2$)(OH)]$^{2+}$, 24458-51-3; *trans*-[Co(en)$_2$(OH)$_2$]$^+$, 21772-94-1; *trans*-[Co(en)$_2$(OSO$_2$H)$_2$]$^+$, 100021-53-2; *trans*-[Co(en)$_2$(OH$_2$)(OH)](ClO$_4$)$_2$, 14099-22-0; SO$_2$, 7446-09-5.

(26) El-Awady, A. A.; Harris, G. M. *Inorg. Chem.* **1981**, *20*, 4251.

The Basis of Aryl Substituent Effects on Charge-Transfer Absorption Intensities

Carol C. Phifer and David R. McMillin*

Mulliken's theory for donor–acceptor interactions is used to rationalize the effects of aryl substituents on the intensities of the metal-to-ligand charge-transfer absorptions that are characteristic of Cu(I) complexes with phenanthroline ligands. Depending on the positions of the aryl substituents, the absorption intensity is enhanced or diminished with respect to the unsubstituted complex. The analysis verifies that the transition dipole length is approximately given by the separation between the charge centroids of the donor and acceptor orbitals. In the absence of steric complications, this means that the aryl substituent effects can be traced to readily envisioned resonance interactions. When conjugation with the π system of the substituents extends the acceptor orbital out away from the metal center, the transition dipole length is increased and the intensity is enhanced. Conversely, a decreased transition dipole length results when the substituent spreads the acceptor orbital in a direction opposite to that of the optically induced charge transfer.
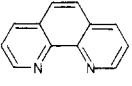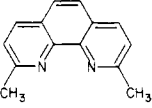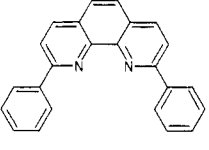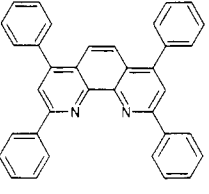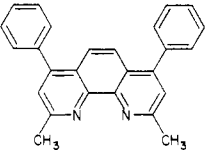
Introduction

Although relatively few studies have focused on the origins of absorption intensities, the absorption spectra of complexes of organic ligands with transition-metal ions often show distinct connections between intensity and ligand structure. An understanding of the basis of these effects would aid in the design of more effective ligands for colorimetric analysis as well as in the

adjustment of the photochemical and photophysical properties of the complexes themselves. For example, ligand modifications that improve the light-gathering characteristics of a complex enhance its potential for energy-conversion applications.

The charge-transfer (CT) absorption intensities of 1,10-phenanthroline (phen) complexes of copper(I) and iron(II) reveal the dramatic influence that perturbations in ligand structure can

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Table I. CT Data for Copper(I) Phenanthrolines

ligand	complex	λ_{max}, nm	ϵ_{max}, M^{-1} cm^{-1}	$\nu \int \epsilon(\nu)\, d\nu$, arbitrary units	
				exptl	calcd
(structure)	Cu(phen)$_2^+$	435	7000[a]	440	550
(structure)	Cu(dmp)$_2^+$	455	7950[a]	540	500
(structure)	Cu(dpp)$_2^+$	441	3620[a]	290	360
(structure)	Cu(tpp)$_2^+$	450	6400[b]	460	460
(structure)	Cu(bcp)$_2^+$	479	14200[a]	730	610

[a] Schilt, A. A. *Analytical Applications of 1,10-Phenanthroline and Related Compounds*; Pergamon: New York, 1969; pp 55–56. [b] Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P.; Kirchhoff, J. R.; McMillin, D. R. *J. Chem. Soc., Chem. Commun.* **1983**, 513–515.

have on the electronic spectrum. For example, phenyl substituents in the 4,7-positions of 1,10-phenanthroline lead to large enhancements in the absorptivity (Table I). Some years ago Smith attributed this effect to the relatively large charges that are indicated for the 4,7-positions by molecular orbital calculations of the π-electron system.[1] However, comparable charges are calculated for the 2,9-positions, and 2,9-phenyl substitution results in a sharp *decrease* in the molar absorptivity (Table I). To account for the reversal, Smith suggested that aryl substituents at the 2,9-positions would be likely to hinder the approach of the ligand to the metal ion, thereby limiting the development of charge-transfer intensity.

Some time ago, Day and Sanders showed that Mulliken's theory of CT interactions[2,3] could be used to explain the effects of methyl substituents on the CT absorption intensities of phenanthroline complexes.[4] Here we extend the analysis to aryl-substituted systems. This extension of the model is worthwhile because it provides convincing experimental support for the theory and because it resolves the anomalies originally noted by Smith.[1]

Theory

During a metal-to-ligand CT absorption, an electron is excited from a molecular orbital Ω_D, centered mainly on the metal, to an orbital Ω_A, centered mainly on the ligand. Correct to first order, the relevant wave functions are

$$\Omega_D = \phi_d + \lambda_{ad}\pi_a^* \tag{1a}$$

$$\Omega_A = \pi_a^* + \lambda_{da}\phi_d \tag{1b}$$

where ϕ_d is a d orbital of the metal, π_a^* is a π-antibonding molecular orbital of the phenanthroline ligand, and λ_{ad} and λ_{da} are mixing coefficients.[2] The transition moment $\vec{\mu}_{DA}$ is given by

$$\vec{\mu}_{DA} = \langle\Omega_D|-e\vec{R}|\Omega_A\rangle = -e\vec{R}_{DA} \tag{2}$$

where $e\vec{R}$ is the dipole moment operator, and e is the charge on the electron. Although eq 2 expands into a number of terms, Mulliken[2] and others[3,5] have shown that the transition moment is approximately given as

$$\vec{\mu}_{DA} = -e\lambda_{ad}\langle\pi_a^*|\vec{R}|\pi_a^*\rangle = -e\lambda_{ad}\vec{R}_{aa} \tag{3}$$

where $\vec{R}_{aa}$ is the vector between the metal nucleus, which we take to be the origin of our coordinate system, and the mean position of the electron in the acceptor orbital of the ligand. This result is very intuitive: the dipole length of the CT absorption can be taken as the distance between the centers of the orbitals involved. It follows that changes in ligand structure that affect the extension of the acceptor orbital will also influence the transition dipole and, hence, the absorption intensity.

The theoretical measure of absorption intensity is the oscillator strength, which depends on the square of $\vec{\mu}_{DA}$ and on ν_{av}, the average transition energy.[6] The value of $\vec{\mu}_{DA}$ is readily calculated from eq 3 when the Wolfsberg–Helmholtz approximation is used to obtain λ_{ad}.[4] Since the oscillator strength is also proportional to the integrated area under the absorption envelope,[6] we can equate the theoretical and experimental expressions for the intensity to obtain the following useful expression:

$$\nu_{av}\int\epsilon(\nu)\,d\nu = KC_{Na}^2 S_{MN}^2 \vec{R}_{aa}^2 \tag{4}$$

Here K represents a product of numerical factors, ν_{av} is the average transition energy, $\epsilon(\nu)$ is the molar absorptivity at frequency ν, C_{Na} is the coefficient of the pπ orbital of nitrogen in π_a^* and S_{MN} is the overlap integral between ϕ_d and the pπ atomic orbital of nitrogen.

Application to Copper(I) Phenanthrolines

Copper(I) systems are useful in the analysis of aryl substituent effects because the low coordination numbers and pseudotetra-

(1) Smith, G. F. *Anal. Chem.* **1954**, *26*, 1534–1538.
(2) Mulliken, R. S. *J. Am. Chem. Soc.* **1952**, *74*, 811–824.
(3) Murrell, J. N. *Q. Rev., Chem. Soc.* **1961**, *15*, 191–206.
(4) Day, P.; Sanders, N. *J. Chem. Soc. A* **1967**, 1536–1541.

(5) van der Avoird, T.; Ros, P. *Theor. Chim. Acta* **1966**, *4*, 13–21.
(6) Calvert, J. G.; Pitts, J. N., Jr. *Photochemistry*; Wiley: New York, 1966; pp 170–173.
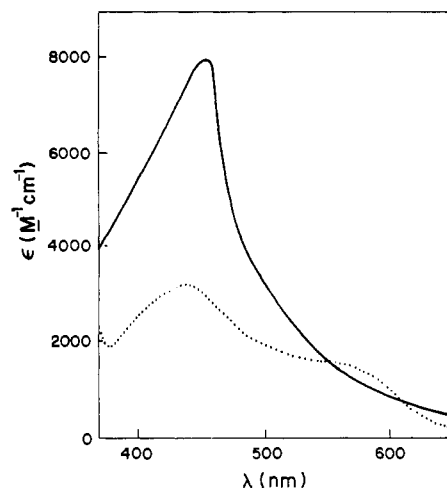
Figure 1. Visible absorption spectra of $Cu(dmp)_2^+$ (–) and $Cu(dpp)_2^+$ (···) in methylene chloride at 20 °C.
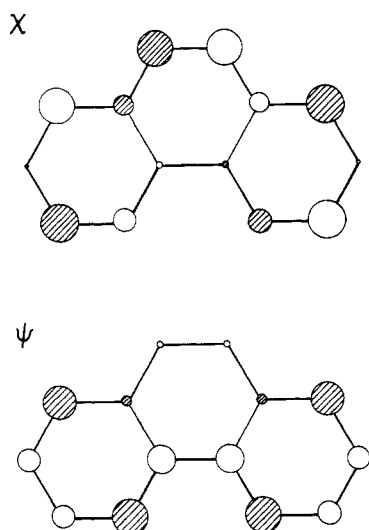

Figure 2. Schematic representation of the relative weights of the constituent $p\pi$ atomic orbitals in ψ and χ, the lowest unoccupied π^* orbitals of 1,10-phenanthroline. Where shaded, the relative phases are negative.

hedral coordination geometries around copper(I) present minimum steric complications. The bis-chelate complexes selected for detailed analysis are listed in Table I. Representative CT absorption spectra are presented in Figure 1. The relative CT intensities are compiled in Table I and have been obtained by integration of the experimentally measured spectra.

Although the theory outlined above pertains to a mono-ligated metal center, it carries over to the bis-chelated systems, as discussed in Appendix I. A complication intrinsic to the phenanthroline ligand is the fact that there are two low-lying π^* molecular orbitals involved in the CT absorption (Figure 2). The orbitals are denoted as ψ and χ, where ψ is antisymmetric with respect to the C_2 operation of the free ligand and χ is symmetric with respect to the same operation.[4,7] The ψ and χ orbitals have similar energies, and there is general agreement that transitions to both orbitals occur in the visible spectra of these complexes.[8,9] If we include terms for both transitions, the following equation (a generalization of eq 4) describes the integrated intensity of the CT spectrum:

$$\nu_{av}\int \epsilon(\nu)\; d\nu = K'[C_{N\psi}^2 S_{MN}^2 \vec{R}_{\psi\psi}^2 + C_{N\chi}^2 S_{MN}^2 \vec{R}_{\chi\chi}^2]. \quad (5)$$

Table II. Calculated Results

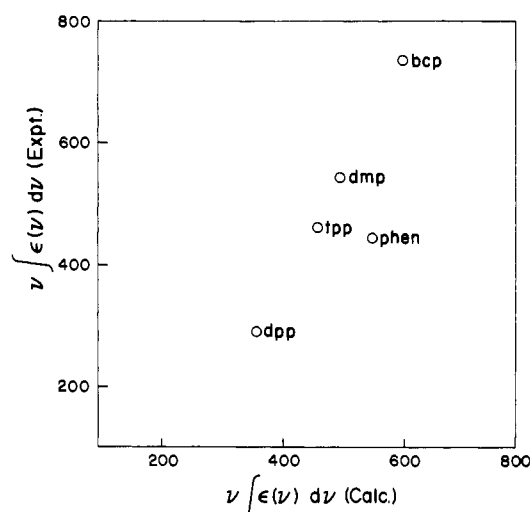| ligand	$C_{N\psi}$	$R_{\psi\psi}$, Å	$C_{N\chi}$	$R_{\chi\chi}$, Å
phen	0.4376	2.598	0.2659	3.287
dmp	0.4135	2.654	0.2442	3.303
dpp	0.4211	2.304	0.2422	2.450
tpp	0.3927	2.823	0.2309	2.902
bcp	0.3826	3.174	0.2284	3.824

Figure 3. Graphic display of the fit of the experimental data. If there were no errors in either theory or experiment, all points would lie on a line with unit slope.

In this approximation ν_{av} represents an average transition energy of the CT envelope.

The parameter K' in eq 5 can be regarded as a scale factor that can be estimated from a least-squares fit of the calculated and observed intensities. The C_{Ni} and the R_{ii} values, where $i = \psi$ or χ, are available from extended-Hückel calculations (Appendix II). Because of the C_2 symmetry axis that passes through the ligand, the only nonvanishing displacement occurs in the z direction. Hence, the vector notation can be dropped. The R_{ii} values are calculated from the extended-Hückel output by

$$R_{ii} = \sum_j C_{ji}^2 z_j + \sum_j \sum_k C_{ji} C_{ki} S_{jk}(z_j + z_k), \quad (6)$$
$$(j < k)$$

where z_j is the z component of the distance from the jth atom of the phenanthroline derivative to the copper center, S_{jk} is the overlap integral between the $p\pi$ orbitals of atoms j and k, and C_{ji} is the coefficient of the $p\pi$ orbital of the jth atom in the ith molecular orbital. On the basis of studies of the nuclear Overhauser effect in fluid solution[10] and crystal structure data,[11] the angle between the planes of the phenyl substituents and the phen core was assumed to be 45° in all cases. The quantity S_{MN} of eq 5 is obtained from a separate extended-Hückel calculation. A summary of the calculated values are presented in Tables I and II, and a graphical representation of a fit of the experimental data is provided in Figure 3.

Day and Sanders found that methyl groups exert an influence on R_{ii} by a redistribution of electron density within the phenanthroline framework.[4] In contrast, we find that the presence of phenyl substituents hardly changes the distribution of the ψ or χ orbitals within the phenanthroline core. Specifically, if the contributions of the atomic orbitals of the phenyl groups are ignored in the evaluation of eq 6, the transition dipole lengths $R_{\psi\psi}$ and $R_{\chi\chi}$ change by no more than about 5% as compared with those of unsubstituted phenanthroline. The sensitivity of the dipole lengths to the presence of phenyl substituents is instead due to the *delocalization* of the π system out onto the phenyl groups.

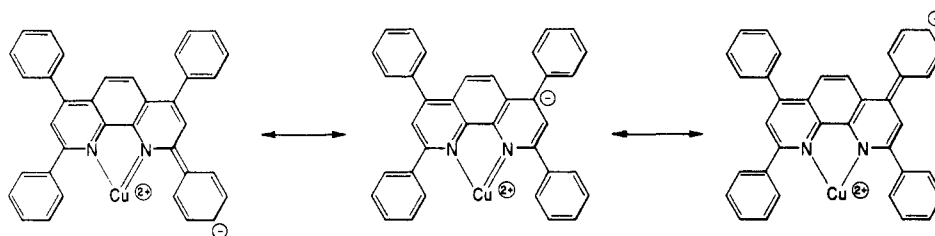(7) Orgel, L. E. *J. Chem. Soc.* **1961**, 3683–3686.
(8) Ceulemans, A.; Vanquickenborne, L. G. *J. Am. Chem. Soc.* **1981**, *103*, 2238–2241.
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(10) Dietrich-Buchecker, C. O.; Marnot, P. A.; Sauvage, J. P.; Kintzinger, J. P.; Maltese, P. *Nouv. J. Chim.* **1984**, *8*, 573–582.
(11) Green, B. E.; Kennard, C. H. L.; Smith, G.; Elcombe, M. M.; Moore, F. H.; James, B. D.; White, A. H. *Inorg. Chim. Acta* **1984**, *83*, 177–189.

Scheme I

Simple geometric considerations show that the presence of phenyl substituents at the 4,7-positions will extend the π system out away from the metal center. This increases the transition dipole length and enhances the absorption intensity. On the other hand, delocalization onto phenyl substituents in the 2,9-positions *decreases* the dipole length. When all four positions carry phenyl groups, the substituent effects almost cancel each other (Table II).

Generalization of Results

The transfer term, a name applied to the right-hand side of eq 3, appears in the expression for the transition moment because of the transfer of charge which occurs in the ground state due to the mixing of donor and acceptor orbitals.[2,3] Valence bond theory can be used to understand the ground-state charge distribution,[12] as illustrated by the three contributing resonance structures depicted in Scheme I. (Note that the formal charges resulting from coordinate–covalent bond formation are ignored.) From such diagrams it is easy to predict whether particular aryl groups will increase or decrease the distance between the charge center of the ligand orbital and the metal ion. Again, an increased separation means that the CT absorption intensity will increase.

A survey of the data in Table III, where the molar absorptivitiy at the absorption maximum is taken as a crude measure of absorption intensity, demonstrates that this "rule of thumb" is very useful in a qualitative sense. The last entry appears to be anomalous, but it actually reveals an important point. A comparison of the two systems with trimethoxyphenyl substituents reveals that ϵ_{max} is enhanced when the methoxy groups are found in the 3″,4″,5″ positions of the substituent (as expected) but that there is no such enhancement of ϵ_{max} in the 2″,4″,6″-trimethoxyphenyl derivative. We attribute the latter irregularity to steric interactions between the 2″,6″-methoxy groups and the 3,5-hydrogens of the bipyridine moiety. These interactions cause the phenyl group to rotate well out of the plane of the attached pyridine ring, thereby destroying conjugation.

Limitations of the Model

While the present treatment provides useful insight into aryl substituent effects, the shortcomings of the model are evident. For example, our model predicts a greater absorption intensity for the phen complex than for the dmp complex, in contrast with experimental results. Although our calculations predict that $R_{\psi\psi}$ and $R_{\chi\chi}$ are larger for dmp than for phen, the decrease in the $C_{N\psi}$ and $C_{N\chi}$ values is an overriding effect. In regard to the copper series, one problem is that we have been forced to use ν_{av} for the absorption envelope in eq 5. As detailed in Appendix I, multiple transitions are involved, and each has its own ν_{max}. Another problem is that important structural data are lacking; thus, we have had to assume a constant Cu–N distance and a fixed twist angle for the phenyl substituents.

In more general terms, the wave functions are deficient even within the context of a one-electron model. A more realistic version of Ω_D is given by

$$\Omega_D = \phi_d + \lambda_1 \pi^* + \lambda_2 \pi + \lambda_3 \phi_p \qquad (7)$$

where π^* indicates an empty π-antibonding orbital of the free ligand, e.g. ψ or χ, π is a filled π-bonding orbital of the ligand, and ϕ_p is a 4p orbital of copper. An analogous expansion can be written for Ω_A. As discussed by Day and Sanders,[4] these wave functions would give rise to metal-centered (3d → 4p), ligand-

Table III. Molar Absorptivities for Selected Metal-to-Ligand Charge-Transfer Transitions

ligand	complex	ϵ_{max}, M^{-1} cm^{-1}	ref
	RuL$_2^+$	16100	a
	RuL$_2^+$	6570	b
	RuL$_2^+$	38400	a
	CuL$_2^+$	6570	c
	CuL$_2^+$	10350	c
	CuL$_2^+$	4950	c

a Stone, M. L.; Crosby, G. A.; *Chem. Phys. Lett.* **1981**, *79*, 169–173. *b* Kirchhoff, J. R.; McMillin, D. R.; Marnot, P. A.; Sauvage, J. P.; *J. Am. Chem. Soc.* **1985**, *107*, 1138–1141. *c* Kröhnke, F. *Synthesis* **1976**, 1–24.

centered ($\pi \rightarrow \pi^*$), and interligand charge-transfer contributions to the absorption intensity. The latter terms could be significant when 2,9-diphenyl substituents are present since interligand stacking interactions are likely to occur.[13] Finally, electron-electron interactions, orbital relaxation effects, etc., have been ignored altogether.

Conclusions

From a systematic application of the CT model of Mulliken, we have been able to correlate the effects of aryl substituents on the absorption intensities of CT bands exhibited by copper(I) phenanthrolines. In the absence of steric problems, the primary effect of an aryl substituent arises from resonance interactions with the phenanthroline core. The result is that the average
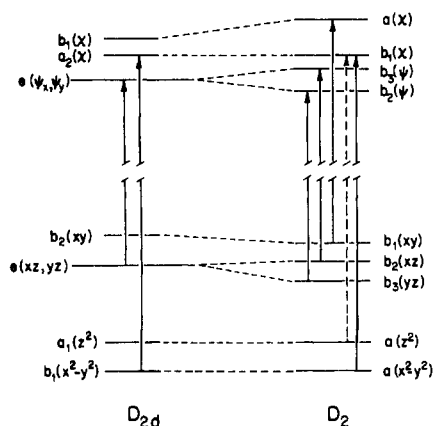
(12) Dewar, M. J. S. *J. Am. Chem. Soc.* **1984**, *106*, 669–682.

(13) Cesario, M.; Dietrich-Buchecker, C. O.; Guilheim, J.; Pascard, C.; Sauvage, J. P. *J. Chem. Soc., Chem. Commun.* **1985**, 244–247.

Figure 4. One-electron energy levels for $Cu(phen)_2{}^+$ in D_{2d} and D_2 symmetries. The arrows indicate the orbital excitations that carry intensity from the transfer term. In D_{2d} symmetry the state assignment for these transitions is $^1B_2 \leftarrow {}^1A_1$. In D_2 symmetry it is $^1B_1 \leftarrow {}^1A$.

displacement of a charge in the ligand acceptor orbital is either increased or decreased in relation to the metal center, depending on the position of substitution. In turn, this influences the dipole length of the CT absorption. Previously the relatively low ϵ_{max} value of $Cu(dpp)_2{}^+$ was attributed to a steric effect;[1] our results show that low intensity is expected even at a "normal" Cu–N distance. In fact, it is remarkable that good agreement between experimental and calculated results was found even though the compounds were artificially constrained to be alike in many ways: e.g., Cu–N length, dihedral angles of the phenyl groups, and phenanthroline core geometry. As shown by elementary valence bond considerations, these conclusions can be applied to a variety of other systems.

Acknowledgment. This work was supported by NSF Grant Nos. CHE-8105003 and CHE-8414267. We would like to thank Daniel L. Severance and Lawrence L. Halcomb for their valuable assistance.

Appendix I

The purpose of this section is to point out some of the subtleties that arise in the treatment of bis-chelate complexes and to justify the use of eq 5 in correlating the oscillator strengths of these systems. If, in the bis chelate, the CT transitions terminate on orbitals that are localized on particular ligands, it is easy to accept that the integrated CT intensity of the system with two ligands should be twice that of the related mono-chelated complex. It can be shown that this is also true, to a first approximation, if the acceptor orbital is viewed as being delocalized over both ligands.[4,14,15] In fact, an analysis based on the method of

Ceulemans and Vanquickenborne[8] shows that the total intensity is independent of the value of the dihedral angle between the two ligands.[17] However, the *number* of transitions over which the intensity is distributed does vary with the angle. A one-electron energy level scheme appropriate for the D_2 symmetry of $Cu(phen)_2{}^+$ (a flattened tetrahedron) is included in Figure 4, where arbitrary, but convenient, basis functions have been chosen to reflect the symmetry properties of the individual levels. For this particular basis set, only four of the five z-polarized transitions carry intensity from transfer terms because the d_{z^2} orbital is orthogonal to both ψ and χ. Actually, since it is likely that both of the totally symmetric wave functions contain some $d_{x^2-y^2}$ character, all five transitions should be allowed. In D_{2d} symmetry only two transitions can carry intensity from transfer terms (Figure 4). Consequently, the appearance of the CT spectra might be quite different in the two symmetries, but the integrated absorption intensity would be the same. It is possible that the complexes with phenyl groups in the 2,9-positions are further removed from D_{2d} symmetry than the other complexes considered, because the CT spectrum of the former is spread over a broader range of wavelengths.

Appendix II

A standard extended-Hückel program was used to perform calculations. The Cu(I) parameters were chosen as in Mehrotra and Hoffmann.[18] The bond lengths and bond angles assumed for the phenanthroline core were based on X-ray crystallographic data for $Cu(dmp)_2{}^+$.[19,20] Small adjustments were made to impose C_{2v} symmetry on the ligand framework. The substituent phenyl groups were assumed to be hexagonal with C–C bond lengths of 1.40 Å and C–H bond lengths of 1.08 Å. A length of 1.46 Å was used for the C–C bond connecting the phenyl group to phenanthroline. The phenyl substituents were rotated in a conrotatory fashion in order to preserve the C_2 symmetry axis of the ligand. The Purdue CDC 6000 series computers and Cyber 205 supercomputer were used for the calculations.

(14) Murrell, J. N. *The Theory of the Electronic Spectra of Organic Molecules*; Methuen: London, 1963; Chapter 7.

(15) The comparison is with an idealized monoligand complex that involves the same metal hybridization, CT energy, etc. as exhibited by the bis chelate. In practice the monoligand complex has its own identity.[16]

(16) Atkins, C. E.; Park, S. E.; Blaszak, J. A.; McMillin, D. R. *Inorg. Chem.* **1984**, *23*, 569–572.

(17) Phifer, C. C.; McMillin, D. R., unpublished results. The analysis assumes that the average transition energy and the Cu–N distance are independent of the dihedral angle relating the ligands.

(18) Mehrotra, P. K.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187–2189.

(19) Dessy, G.; Fares, V. *Cryst. Struct. Comm.* **1979**, *8*, 507–510.

(20) Hämäläinen, R.; Ahlgrén, M.; Turpeine, U.; Raikas, T. *Cryst. Struct. Commun.* **1979**, *8*, 75–80.