$$\underset{\mathbf{2}}{\mathrm{Ru^{VI}TMP(O)_2}} + 4\mathrm{P(OCH_3)_3} \rightarrow \underset{\mathbf{3}}{\mathrm{Ru^{II}TMP[P(OCH_3)_3]_2}} + 2\mathrm{OP(OCH_3)_3} \quad (1)$$

porphyrins, **4** and **5**, that lacked infrared bands between 700 and 900 cm^{-1} assignable to Ru═O. Further, **5** did not react with trimethyl phosphite at 25 °C. The ^{1}H NMR spectrum of **5** was completely consistent with the formulation O-$[\mathrm{Ru^{IV}TMP(mCB)}]_2$, and the conversion of **4** to **5** upon the addition of mCBA suggested $\mathrm{O[Ru^{IV}TMP(OH)]_2}$ for **4**. Accordingly, the stability of **2** with respect to these dimers is dependent upon the steric hindrance of the ortho methyl groups of the mesityl substituents.[15]

The cyclic voltammetric behavior of **2** indicated that formal oxidation states higher than Ru(VI) are chemically available with this system. The cyclic voltammogram of **1** in methylene chloride (0.1 M tetrabutylammonium perchlorate) shows reversible potentials at 0.60 and 1.08 V vs. SCE. Similar results have been reported for RuTPP(CO) at slightly higher potentials.[16] By contrast, a single reversible oxidation wave was observed for **2** at 1.12 V. Electrolysis of **2** in a thin-layer spectroelectrochemical cell at 1.3 V generated a new species, **6**, with absorption maxima at 412 and 609 nm and a 60% decrease in absorbance of the Soret band relative to **2**. Applying a potential of 0.75 V regenerates **2** nearly quantitatively, implying that degradation of the porphyrin or loss of oxo ligands does not occur upon formation of **6**. The visible spectrum of **6** is similar to those of several Ru(II) porphyrin cation radical complexes,[17] especially with regard to the significant decrease in absorbance at the Soret band relative to the unoxidized complex. Hence, it is reasonable that the site of oxidation of **2** is the porphyrin rather than the metal and that **6** is best formulated as a porphyrin cation radical complex, $\mathrm{Ru^{VI}TMP(O)_2{}^+ClO_4{}^-}$. The spectroscopic characterization of **6** and the reactivity of **2** and **6** in oxygen-transfer reactions are under study.

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Registry No. **1**, 92669-43-7; **2**, 92669-44-8; **3**, 92694-64-9; **4**, 92694-65-0; **5**, 92694-66-1; **6**, 92669-46-0; Ru$^{\mathrm{II}}$TTP(CO), 75888-64-1; $\mathrm{P(OCH_3)_3}$, 121-45-9.

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(15) Visible spectral transients observed immediately upon addition of mCPBA to Ru$^{\mathrm{II}}$TTP(CO) indicated that a species analogous to **2** is formed prior to **4** and **5**.

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Articles

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Redirected Ligand-Field Analysis. 1. Ligand Fields of Coordination Voids and "Semicoordination" in Copper(II) Complexes

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The electronic d–d spectra of 11 complexes of copper(II) are analyzed within the angular-overlap model (AOM) formalism. Two analyses are reexaminations of tetrahedral $[\mathrm{CuCl_4}]^{2-}$ and trigonal-bipyramidal $[\mathrm{CuCl_5}]^{3-}$ ions in terms solely of traditional e_σ and e_π parameters taking normal values. The remaining nine studies demonstrate how e_σ values for the axial ligands, or lack thereof, in essentially tetragonal systems range from positive to negative as the axial interactions weaken. The significance of this variation and its relationship with variable equatorial AOM parameters in the complexes are discussed in terms of the new ligand-field formulation of the AOM. The concept of a "global overlay" upon the AOM definition of "local" chemical functionality in ligand-field theory is demonstrated. An incidental feature of the analyses is an evident irrelevance of ESR g values in these, and possibly other, copper(II) complexes.

Introduction

Although ligand-field theory did not begin or evolve within the mainstream chemical literature, that is where most attempts to exploit it are to be found. At the outset, therefore, it is right for us to emphasize that this subject is properly directed toward the formulation and clarification of concepts of chemical bonding and electron distribution in complexes. The reproduction of experimental ligand-field properties by quantum-mechanical models, which must always be done with care and technical skill, is merely a means toward an essentially chemical goal. If not, then however important or beautiful a study may be, it is surely not part of the chemical discipline. Too often in the past, research of this kind has purported to address chemical issues and its transparent failures to do so have engendered a rather widely held indifference to an "over-technical, irrelevant and passê" area of chemical endeavor.[1] Our own view now is that a new version of the angular-overlap model (AOM) provides the means by which ligand-field studies might be properly redirected. The formalism and theoretical structure of the approach have been

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fully described,[2-5] recently, and the efficacy of the model has been attested by several analyses of quite diverse systems.[4,5] In the present series of papers, we seek to develop further our understanding of the significance of AOM parameters and modeling but always with chemical bonding issues to the fore. We focus on a different main theme in each paper.

The central attraction of the AOM always has been its promise to establish measures of *local* chemical functionality within a transition-metal (or lanthanide) complex.[6,7] In bringing the functional group into ligand-field studies, it proposed a separation of radial, "bonding" factors from angular features of the overall coordination geometry. For some, there arose an exciting possibility of constructing "inner" spectrochemical series for separate σ and π interactions that would provide transferable quantities from complex to complex and from geometry to geometry. But this was surely never a worthwhile ambition, for the empirical variations that actually defeat such a project simply reveal the very stuff of chemistry, for we do not expect the bonding and electron distribution in any given M–L moiety to be independent of the remaining molecular environment. If it is argued here that "roughly" and "on average" such parameter series might still be constructed, one can only observe that, beyond confirming an overall relevance of the approach yet again, all vigor would thereby be leached out of the subject. What *is* undoubtedly exciting and chemically important about the new AOM is the possibility of monitoring the interplay of bonding forces within a molecule as a whole in satisfying the exigencies of the electroneutrality principle. What this means, however, is that "local" M–L interactions, and their attendent parameters, take on a global complexion. We are reminded, once more, that an *interaction* involves both partners—the ligand and the rest. This theme will be developed in this and the following papers from very different points of view. We begin by tracing the connection between weak or "semi" coordination and the ligand fields of voids in a coordination shell.

Some time ago, Smith[8] observed that the ligand-field, d–d spectra of several copper(II) complexes could not be reproduced or parameterized completely within contemporary crystal-field or angular-overlap models. The problem concerned the energy of the d_{z^2} orbital in planar four-coordinated complexes, which was typically placed some 5000–6000 cm^{-1} higher than that experimentally observed by all ligand-field calculations which simultaneously reproduced the relative energies of the remaining d orbitals. Since then, similar anomalously low d_{z^2} orbital energies have been identified in planar complexes of iron(II),[9] cobalt(II),[10,11] and nickel(II)[12] as well as copper(II).[13] Smith sought to account for the depression of the d_{z^2} orbital energy in terms of a new parameter, e_{ds}, of the AOM arising out of an interaction between the $3d_{z^2}$ and higher lying 4s orbitals, which transform similarly in the planar D_{4h} environment. He thus considered the inability of current ligand-field models to account for the complete d-orbital energy manifold as a failure of ligand-field theory itself for, by the introduction of the d–s interaction, Smith had explicitly enlarged his orbital basis from the usual ligand-field d set. On the other hand, he considered that this change of basis posed no problems for the AOM, as current understanding of that model characterized it as a molecular orbital scheme. However, a number of serious and, indeed, fundamental objections can be made against a molecular orbital based AOM and we have argued[4] extensively recently for an approach that characterizes the AOM wholly within ligand-field theory. The localized potential model of the ligand field that we espouse involves a cellular decomposition of an effective ligand-field potential within a pure d basis and is parameterized by quantities that map closely onto the traditional AOM quantities e_λ ($\lambda = \sigma, \pi$). It is an approach that bears a *defined* relationship with quantum chemistry at large and so is in sharp contrast with the flawed molecular orbital version of the AOM. The anomalous d_{z^2} energies of planar molecules are accommodated within the new AOM by assigning negative values of e_σ to the coordinationally void sites above and below the ligation plane (since a negative e_λ value parameterizes a decrease in energy of the appropriate metal orbital, the low energy of the d_{z^2} orbital follows immediately). This rather strange idea of assigning a (negative) ligand-field strength to a region devoid of ligands is *no failure* of the AOM, however, but is required, a priori, for the internal consistency of the approach.[2-5] It arises ultimately from the perturbation of the basis d orbitals by higher lying metal s orbitals: thus Smith's basic idea is recovered but without the theoretical inconsistencies inherent in the molecular orbital scheme. The proposition that d–s interactions affect ligand-field properties is much older, of course. In 1958, Griffith[14] invoked such mixing to explain widely varying, and also negative, values of the Fermi contact parameter κ that had been observed in the ESR hyperfine spectra of some cobalt(II) species, and further evidence for the effect has been provided[10,11,15] at intervals since then. Smith's contribution,[8] however, was to propose that such mixing could be responsible for the large anomaly in the ligand-field d_{z^2} eigen*value* as well: despite the ESR evidence on the mixed nature of molecular orbital eigen*vectors*, the connection with marked eigenvalue shifts does not seem to have been made before.

Typical values for e_σ(void), determined from studies of planar systems, are about -3000 cm^{-1}. As yet no estimates for this quantity in molecules with other coordination geometries are available and generally we have no quantitative appreciation of the ligand-field roles of coordination voids in systems of varying coordination number and geometry. The notion of d–s mixing in other copper(II) systems has been invoked *qualitatively* on several occasions, of course. For example, it has been claimed to account for the predominant sense of tetragonal Jahn–Teller distortion of octahedral copper(II) systems being elongation rather than compression:[16] but the discussion was couched in only qualitative terms. It appears that the idea of d–s mixing in ligand-field studies of complexes with geometries other than planar coordination has only been entertained in a limited group of chlorocuprate species—by Smith in his original paper.[8] However, he extended his ideas to include d–p mixing and proposed a series of molecular orbital type AOM parameters, labeled in a self-evident manner as $e_{dp\sigma}$ and $e_{dp\pi}$. Within the prevelent MO formalism[6,7] of the AOM, these extensions seem logical: they are *not* required, however, within the ligand-field-based version[2-5] of the AOM. Further, we present analyses of the d–d spectra of tetrahedral $[CuCl_4]^{2-}$ and trigonal-bipyramidal $[CuCl_5]^{3-}$ ions in the next section that demonstrate the total

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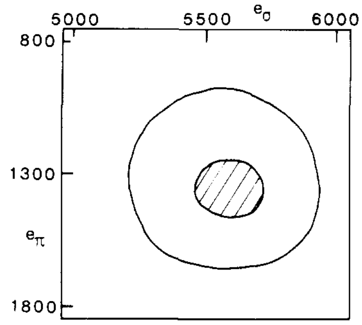

Figure 1. Reproduction of the crystal spectrum[21] of Cs_2CuCl_4 by variation of e_σ(Cl) and e_π(Cl) (ζ = 700 cm^{-1}). All calculated transition energies are within 250 cm^{-1} of the observed band maximum in the hatched area and within 500 cm^{-1} in the annulus.

lack of empirical need for any parameters referring to either d–s or d–p mixing in these systems. Altogether, therefore, while the relevance of coordination voids and d–s mixing in planar systems is well established, there appears to be no good evidence to date substantiating the idea in complexes with other geometries. In addressing this feature of ligand-field analysis, we present modern AOM studies of the d–d spectra of a series of copper(II) complexes possessing approximate fourfold symmetry in which coordination along the tetragonal *z* axis ranges from nothing, through square pyramidal and "semicoordinated" octahedral, to "fully" coordinated, but distorted, octahedral.

Analyses

In this section we report the reproduction of observed d–d spectral bands within the AOM, using standard conventions[5] and established computing facilities:[17] in each of the 11 analyses described, published details of the coordination geometry have been used as cited where appropriate. We comment on the use of ESR *g* values later. Beginning with the "normal" systems involving tetrahedrally and trigonal-bipyramidally coordinated copper(II) ions, we demonstrate the lack of need for any further AOM parameters like e_{ds} or e_{dp}.

Tetrahedral $[CuCl_4]^{2-}$. The electronic properties of Cs_2CuCl_4 have been investigated many times,[18] though several detailed studies used an earlier X-ray crystal structure analysis[19] that described the compressed-tetrahedral coordination as possessing near-D_{2d} symmetry. The present AOM analysis is based on the later work of McGinnety,[20] in which the molecular geometry is better described as of C_s symmetry. Nevertheless, we retain the approximation of assuming equal Cu–Cl parameters in view of the closely similar bond lengths: 2.220 (two), 2.235, and 2.244 Å. We have sought to reproduce the electronic spectrum published by Ferguson,[21] based on polarized absorption at 20 K. The spin–orbit coupling parameter was held fixed in this, and all other, studies to be described in this part, usually at the nominal value of 700 cm^{-1}. Variations in this value by 100 or 200 cm^{-1} yield changes in eigenvalues of a similar magnitude which are unimportant in these spectral analyses, doubly so as we attempt at all times to reproduce observed spectral bands (which are usually very broad) by the means of spin–orbit pairs of levels, as appropriate. Then, using the two-parameter model—e_σ(Cl), e_π(Cl)—we may define good "fits" to experiment as shown in Figure 1. The agreement between calculated eigenvalues and Ferguson's spectrum for "central" parameters, e_σ(Cl) = 5600 cm^{-1}, e_π(Cl) = 1350 cm^{-1}, is (all values in cm^{-1}, for transitions from *xy* to the indicated levels)

	xz, yz	x^2-y^2	z^2
obsd	4800, 5550	7900	9050
calcd	4998, 5610	7864	8793

Smith[8] employed the parameter set e_σ, e_π, e_{ds}, $e_{dp\sigma}$, $e_{dp\pi}$ but defined values for all but $e_{dp\sigma}$ by recourse to calibration charts and a relationship between AOM parameters and overlap integrals that belongs in semiempirical molecular orbital theory. Using this "one-parameter" model (but with an extensive set of assumptions), he calculated the energies of the three highest energy bands as 5950, 7630, and 9310 cm^{-1} with the parameter values e_σ (5780 cm^{-1}), e_π (1010 cm^{-1}), e_{ds} (1700 cm^{-1}), $e_{dp\sigma}$ (750 cm^{-1}), and $e_{dp\pi}/e_{dp\sigma}$ (0.082). As outlined in the introduction and discussed in full elsewhere,[5] the ligand-field version of the AOM should be parameterized freely, so that the two-parameter model we describe here suffices.

Trigonal-Bipyramidal $[CuCl_5]^{3-}$. Allen and Hush[22] have reported the d–d spectrum of $[Cr(NH_3)_6]^{3+}[CuCl_5]^{3-}$, crystals of which have been reported as containing exactly trigonal-bipyramidal (TBP) copper(II) ions with axial and equatorial bond lengths of 2.30 and 2.39 Å, respectively. Since then, evidence has been presented[23] of fluxional behavior in these ions, presumably arising from second-order Jahn–Teller effects, but in order to make a comparison with Smith's earlier AOM study[8] of this complex, we have analyzed the system within the original "static" description. Two spectral bands, at 8700 and 10 800 cm^{-1}, are assigned as $^2A_1 \rightarrow {}^2E'$ and $^2A_1 \rightarrow {}^2E''$ in D_{3h} symmetry. Ignoring spin–orbit coupling, and using analytical AOM expressions given by Smith,[8] we establish values for e_σ and e_π parameters for both axial and equatorial sites. This could only be done, of course, provided supplementary conditions were imposed to reduce the number of variables from four to two. In other analyses this procedure might be undesirable: here we are merely concerned to demonstrate the efficacy or otherwise of a "standard" AOM scheme which does not involve e_{ds} or e_{dp} parameters. For illustrative purposes, therefore, we assume $e_\sigma = 4e_\pi$ for both axial and equatorial ligands, this ratio being very approximately in line with experience in other systems and with overlap calculations—however ill advised. While different ratios for axial and equatorial sites might be proper, we have no way of establishing what they may be from present analysis, not least because of uncertainties in the detailed molecular structure as noted above. With use of this selected ratio, exact reproduction of the spectral peaks is then obtained with e_σ(ax) = 6060 cm^{-1} and e_σ(eq) = 4560 cm^{-1}. Insofar that we may compare this molecular ion with the known TBP structures reported in the following paper, these absolute and relative e_σ values appear unexceptional. We conclude, therefore, that a "normally" parameterized model employing e_σ and e_π parameters (but in fixed, though typical, ratio) for independent axial and equatorial TBP sites reproduces the experimental spectrum with values that accord well with precedent: a need for extra AOM parameters is not established.

Planar $[CuCl_4]^{2-}$. We now consider the first of the present series of systems where d–d spectra cannot be reproduced within the "standard" AOM framework. Crystals of the complex $[C_6H_5(CH_2)_2NH_2CH_3]^+{}_2[CuCl_4]^{2-}$ contain[24] planar-coordinated copper(II) ions. The centrosymmetric planar molecules have effectively equal Cu–Cl bond lengths (pairs of 2.281 and 2.248 Å), and the nearest contact normal to the coordination plane is more than 3.5 Å. Hitchman and Cas-

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sidy[13] have reported the single-crystal polarized electronic spectrum at ca. 10 K, summarized below. With use of only e_σ(Cl) and e_π(Cl), together with ζ held fixed at 700 cm^{-1} as discussed earlier, it proves impossible to reproduce the observed spectral bands (the same is true even if we take $e_{\pi\parallel} \neq e_{\pi\perp}$, where $\parallel$ and $\perp$ refer to the "tetragonal" axis). Typically, the $^2A_g \rightarrow {}^2A_g$ (D_{4h}) transition at 17 000 cm^{-1} is calculated 5000–6000 cm^{-1} too low (corresponding to the d_{z^2} *orbital* being calculated too high): this situation was originally reported by Hitchman and Cassidy. We therefore introduce the extra parameter e_σ(void) to represent the ligand-field experienced by the copper atom above (or below) the coordination plane. Optimizing the three-parameter model yields an essentially unique "best-fit" (all values in cm^{-1}, for transitions from $x^2 - y^2$ to the indicated levels)

	xy	xz	yz	z^2
obsd	12 500	14 050	14 450	17 000
calcd	12 224	13 992	14 205	16 955

with use of e_σ(Cl) = 5300 cm^{-1}, e_π(Cl) = 900 cm^{-1}, and e_σ(void) = −3000 cm^{-1} (and ζ = 700 cm^{-1}). Equally satisfactory agreement is obtained with parameter values lying within the ranges ±250, ±200, and ±500 cm^{-1} for e_σ(Cl), e_π(Cl), and e_σ(void), respectively. Earlier, Smith[8] had reproduced the spectrum with the parameter set e_σ(Cl) = 5370 cm^{-1}, e_π(Cl) = 900 cm^{-1}, and e_{ds} = 1540 cm^{-1}. Note that $e_\sigma(\text{void}) \equiv -2e_{ds}$. We thus confirm Smith's results but with a modified interpretation.

In view of our opening remarks about the interactive nature of AOM parameters, it is entirely possible that $e_{\pi\parallel}$(Cl) and $e_{\pi\perp}$(Cl) may differ, in reflection of the very different ligand fields represented by axial and equatorial e_σ values. Such a possibility must be entertained notwithstanding the conventional designation of monoatomic ligands as "linear ligators". It has proved impossible so far for us to demonstrate such an effect, however, from various AOM analyses. The problem is essentially one of resolution in that experimental data have been insufficiently numerous or exact to establish clear values for more heavily parameterized models. As argued extensively elsewhere,[5] the AOM is generally most effective when applied to molecules of low symmetry: the analyses presented in the following paper illustrate the point. The present close approach to tetragonal symmetry effectively forestalls any possibility of discriminating anisotropic e_π(Cl) values.

Egyptian Blue. The sheet-structured silicate $CaCuSi_4O_{10}$ incorporates copper(II) ions coordinated by silicate oxygen atoms at 1.91 Å in exact square array.[25] Clark and Burns[26a] have reported three d–d transitions in the reflectance electronic spectrum, and Ford and Hitchman[26b] describe single-crystal data. As for the planar chlorocuprate above, the large energy splitting of the higher lying bands—assigned as transitions to components of the $^2T_{2g}$ term of the formal octahedral precursor—clearly establishes a significant M–L π interaction. Once again, however, the high molecular symmetry, at least, hinders any attempt to distinguish anisotropic Cu–O π interactions. A full modeling of the Cu–O ligand field would include $e_{\pi x}$, $e_{\pi y}$, and appropriate $e_{\pi\sigma}$ parameters as well as e_σ, in recognition of the influence of the oxygen lone pairs, as discussed elsewhere.[4,5] A resolution of such features is not pursued in the present analysis, and fixed relationships between such parameters are taken: we consider here the use of an isotropic e_π(O) parameter as an acceptable compromise. Satisfactory reproduction of all three spectral bands is quite impossible without explicit recognition of the coordination voids in this planar complex, as implicitly recognized by Mackey et al.[9] On the other hand, excellent and essentially unique reproduction of the experimental spectrum is obtained with the parameter set e_σ(O) = 6200 cm^{-1}, e_π(O) = 1400 cm^{-1}, e_σ(void) = −3250 cm^{-1}, and ζ = 700 cm^{-1} (all values in cm^{-1}, for transitions from $x^2 - y^2$ to the indicated levels):

	xy	xz, yz	z^2
obsd	12 900	15 800	18 800
calcd	12 982	15 623, 15 956	19 197

Equally acceptable fits are possible with AOM parameter values within 300, 250, and 600 cm^{-1} of the quoted values, respectively.

Square-Pyramidal $[Cu(NH_3)_5]^{2+}$. In the first of a series of seven amine complexes, we consider a system with one coordinationally void cell rather than two. Crystals of the salt $K^+[Cu(NH_3)_5]^{2+}(PF_6^-)_3$ contain square-pyramidal pentaamminecopper(II) ions with rigorous C_{2v} symmetry.[27] The basal Cu–N bond lengths form two sets of 2.010 and 2.048 Å (twice each), and the axial bond length is 2.193 Å. Typically, the metal atom lies above the plane of the basal nitrogen atoms, the N_{ax}–Cu–N_{eq} bond angles being ca. 98°. Hathaway and Tomlinson[28a] have reported the room-temperature, single-crystal polarized spectrum of this[28b] compound as characterized by a relatively intense single absorption in xy polarization at 15 000 cm^{-1} and by two less intense maxima in z polarization of 11 400 and 14 800 cm^{-1}. With ζ fixed again at 700 cm^{-1}, we have employed a two-parameter AOM, presuming zero copper–ammonia π interaction: the essentially unsplit nature of the higher lying components of the $\rightarrow {}^2T_{2g}$ (O_h) transitions observed in this, and indeed all the tetragonal amine complexes that follow, provides direct support for this assumption. Values for e_σ(eq) in the range 3000–8000 cm^{-1} were considered, together with ones ranging +2000 to −3000 cm^{-1} for e_σ(ax). An essentially unique fit was obtained (all values in cm^{-1}, for transitions from $x^2 - y^2$ to the levels indicated)

	z^2	xz, yz, xy
obsd	11 400	15 000
calcd	11 406	14 555, 15 654, 15 945

for the parameter values e_σ(eq) = 5400 cm^{-1} and e_σ(ax) = −750 cm^{-1} (ζ = 700 cm^{-1}). Satisfactory fits are obtained also with use of parameter values within 200 and 500 cm^{-1} of those quoted, respectively.

Tetragonal-Octahedral $Cu(NH_3)_4(SCN)_2$. These neutral copper(II) molecules have been described as centrosymmetric and tetragonal with four equatorial Cu–N bond lengths of 2.08 Å and two axial Cu–S bonds of 3.00 Å: two X-ray analyses[29,30] of the compound have been reported by Porai-Koshits, but some uncertainty still attaches to the accuracy of the quoted bond lengths. Tomlinson et al.[31] report two bands in the d–d spectrum, at 14 300 and 17 500 cm^{-1}, which we label ν_1 and ν_2, respectively. If spin–orbit coupling is ignored, these transitions may be fitted exactly with use of the analytical AOM expressions

$$\nu_1 = 2e_\sigma(\text{eq}) - 2e_\sigma(\text{ax}) \qquad \nu_2 = 3e_\sigma(\text{eq}) \tag{1}$$

to yield the parameter values $e_\sigma(NH_3)$ = 5833 cm^{-1} and e_σ(SCN) = −1317 cm^{-1}. Again no π interaction is assumed between the copper atom and the ammonia ligands nor with the very distant thiocyanates.

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Tetragonal-Octrahedral $Cu(NH_3)_4(NO_2)_2$. Analogous to the thiocyanate complex is this trans-dinitro species. The equatorial Cu–NH_3 bond lengths[29] are 1.99 Å and the axial Cu–N distances 2.65 Å. Tomlinson et al.[31] report d–d transitions as 13 400 and 17 100 cm^{-1}. With use of relationships 1 above, exact reproduction of the spectral peaks is obtained for $e_\sigma(NH_3) = 5700\ cm^{-1}$ and $e_\sigma(NO_2) = -1000\ cm^{-1}$, π interactions being ignored once more.

Tetragonal-Octahedral $[Cu(NH_3)_4]L$; L = NH_3, H_2O. X-ray crystal structure analyses[32] of a pair of isomorphous compounds, $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]L$ (L = NH_3, H_2O), involve square-planar $[Cu(NH_3)]_4$ moieties continuously bridged along the tetragonal axis by either ammonia or water molecules. The bridging groups lie on crystallographic inversion centers and must therefore be disordered in some way: in the ammonia case, inversion and rotation have been suggested to take place.[32] The equatorial Cu–NH_3 bond lengths are 2.01 Å in the ammonia-bridged complex and probably similar[32] in the other. The copper atoms lie 2.88 Å from the inversion centers on the tetrad, so that axial bond lengths are around 2.9 Å. The electronic spectra of each compound comprise two bands: at 13 600 and 17 400 cm^{-1} for L = NH_3 and at 18 400 and 19 200 cm^{-1} for L = H_2O. Analytical reproduction of these transition energies using eq 1 above, together with the neglect of spin–orbit coupling and of any metal–ligand π interactions, yields the parameter sets $e_\sigma(eq) = 5800\ cm^{-1}$ and $e_\sigma(ax) = -1000\ cm^{-1}$ when L = NH_3 and $e_\sigma(NH_3) = 6400\ cm^{-1}$ and $e_\sigma(H_2O) = -2800\ cm^{-1}$ when L = H_2O.

Tetragonal-Octahedral $[Cu(en)_2]^{2+}[BF_4^-]_2$. The centrosymmetric coordination of the copper ions in the complex comprise[33] four essentially equal Cu–N bonds (two each of 2.02 and 2.03 Å) from the equatorial ethylenediamine chelates and two long Cu–F contacts of 2.56 Å with the BF_4^- ions. The Cu–F bonds lie within 6° of the normal to the CuN_4 plane, and so the overall molecular geometry is quite closely tetragonal trans octahedral. Hathaway et al.[34] have reported the polarized single-crystal spectrum to comprise a single well-resolved band in *xy* polarization at 19 400 cm^{-1} together with less intense *z*-polarized bands at ca. 20 000 and 17 700 cm^{-1}. We avoid uncertainties of assignments based on vibronic analysis in this triclinic centrosymmetric system and so seek merely to reproduce two band maxima—at 19 400 and 17 700 cm^{-1}—as in the foregoing five analyses. Using a two-parameter model again, with ζ fixed, we considered parameter values in the range 3000–8000 cm^{-1} for $e_\sigma(en)$ and +2000 to −4000 cm^{-1} for $e_\sigma(F)$: a search through parameter space was carried out here using our usual nonanalytical computational methods,[17] in view of the inexact tetragonality of the molecular geometry. All calculations produced an eigenvalue pattern in the form of three more closely grouped bands at higher energy than the fourth, as expected in the absence of π perturbations. The single calculated level was assigned to the observed band at 17 700 cm^{-1} while the remaining three transitions were optimized within an envelope at 19 400 cm^{-1}. An essentially unique best fit was obtained (all values in cm^{-1}, for transitions from $x^2 - y^2$ to the level indicated)

	z^2	*xz, yz, xy*
obsd	17 700	19 400
calcd ($\zeta = 700\ cm^{-1}$)	17 660	18 977, 19 861, 20 842
calcd ($\zeta = 0$)	17 608	19 431, 19 431, 21 850

when $e_\sigma(N) = 6500\ cm^{-1}$ and $e_\sigma(F) = -2750\ cm^{-1}$. Satisfactory agreement is also obtainable with these parameters lying within the error ranges ±200 and ±500 cm^{-1}, respectively.

Tetragonal-Octahedral $[Cu(tach)_2]^{2+}$. The triamine 1,3,5-triaminocyclohexane (tach) forms essentially tetragonally distorted octahedral complexes of copper(II). Ammeter et al.[35] have made an extensive ESR study of the systems $[Cu(tach)_2]^{2+}X^-_2$ (X = NO_3, ClO_4) for they provide excellent examples of both static and dynamic Jahn–Teller effects. The ESR spectrum[35] of the dinitrate salt reveals a dynamic regime at higher temperatures that freezes out into a static distortion at lower temperatures. The perchlorate salt only displays static distortion and is thus the more suitable for the present ligand-field study. Ammeter et al.'s interest was in the determination of the coupling parameters that define the Jahn–Teller potential surfaces, having no concern with ligand-field parameters. The coordination geometry of the copper complex in the perchlorate salt is shown in Figure 2. The molecular ion is centrosymmetric with effectively equal equatorial Cu–amine bond lengths[35] of 2.061 and 2.078 Å (twice each) and with axial Cu–N distances of 2.353 Å. The axial ligators lie within 6° of the normal to the equatorial plane. Childers et al.[36] have reported a diffuse-reflectance spectrum with d–d transitions at 8790 and 15 750 cm^{-1}. Again, we have reproduced these band energies with a two-parameter model, holding ζ fixed and assuming no Cu–amine π interactions. The AOM parameters were varied in the following ranges: $e_\sigma(eq)$, 3000–7000 cm^{-1}; $e_\sigma(ax)$, +2000 to −3000 cm^{-1}. Effectively unique reproduction of the observed spectrum was obtained (all values in cm^{-1}, for transitions from $x^2 - y^2$ to the level indicated)

	z^2	*xz, yz, xy*
obsd	8790	15 750
calcd	8786	14 630, 15 730, 15 786

with $e_\sigma(aq) = 5100\ cm^{-1}$ and $e_\sigma(ax) = +700\ cm^{-1}$ ($\zeta = 700\ cm^{-1}$). Equally suitable parameter values lie within 300 cm^{-1} of these.

ESR g Values. Many ligand-field studies of d^9 complexes have included, or indeed centered upon, the measurement of ESR *g* values, often from careful single-crystal work. It was natural to expect that complete or even partial definition of a $\mathbf{g}^2$ tensor would furnish useful or even crucial data upon which to build a ligand-field analysis. The ESR technique has been applied to several of the present complexes. It is therefore disappointing to report that none of these studies appear to provide more than loosely confirmatory data. In each case, and in those TBP complexes described in the following paper, two general observations can be made. First, the *g* values fail to improve the ease in finding a ligand-field fit, either by themselves or in combination with the electronic spectrum. Second, they do not provide a means to refine the ligand-field parameters nor to establish values for either spin–orbit coupling or orbital reduction parameters. These last two quantities are widely correlated so that apart from being able to conclude that the *g* values are compatible with the various spectral analyses, nothing new can be learned from their measurement. We strongly suspect that this salutory warning will apply in many other d^9 systems also.

Discussion

In Figure 2 we summarize the ligand-field parameters determined by the foregoing analyses on planar and tetragonal copper(II) systems. A discussion of these values is best built around a brief review of our current understanding[4] of the

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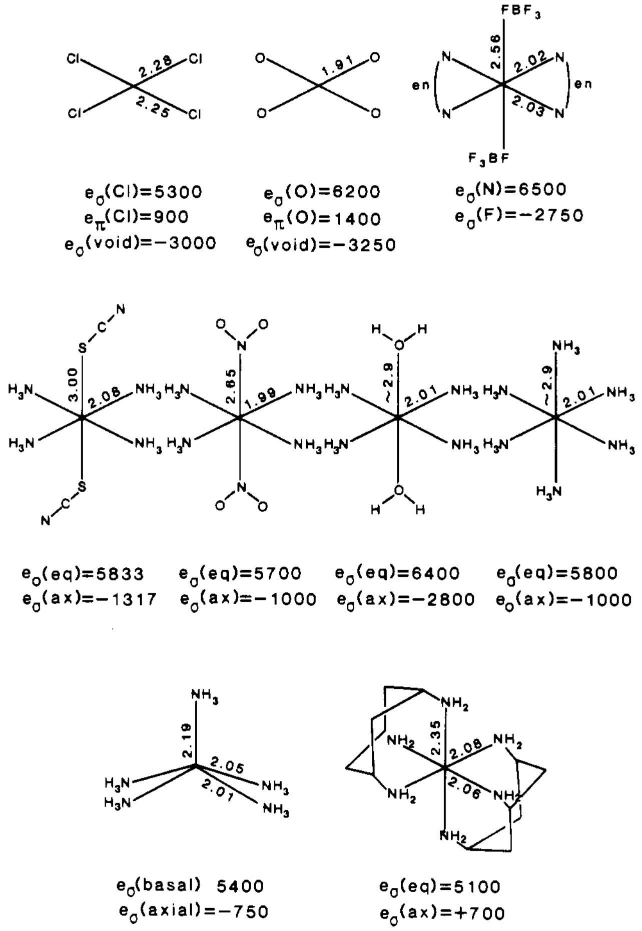

Figure 2. Summary of "best fit" AOM e parameter values (cm^{-1}) for planar and formal tetragonal copper(II) systems reported in this paper (bond lengths in Å).

angular-overlap modeling of the ligand field.

Ligand-field theory centers on the notion of an effective potential operating upon a pure d-orbital basis (for transition-metal ions; f for lanthanides). Within the ligand-field regime, all one-electron perturbations are sequestered within this effective potential (plus spin–orbit coupling, which can be ignored in the present discussion) while two-electron energies exclusively within the d basis are dealt with by using free-ion-like interelectron repulsion parameters. The radial properties of the d-orbital basis can be envisaged as optimally chosen so as to reflect the mean (spherical) potential in the system. All we need recognize at this point in the present sketch is that the radial form of the d basis is defined in principle but is unknown in practice. The effective potential V_{LF} arising in a typical ligand-field matrix element $\langle d_i|V_{LF}|d_j\rangle$ is constructed concomitantly with the d basis and again, while defined formally and of known structure,[2-5] is quantitatively unknown in any given system. These seemingly unhelpful caveats are made at the outset to emphasize that while a great deal can be said of the form of the potential and of the associated ligand-field matrix elements (parameters), a simple quantitative basis for computation should not be sought. This is part of the reason even approximate proportionality between AOM parameters and the squares of overlap integrals cannot be expected and is frequently not observed. Having said that, we note that the many structural similarities between the molecular orbital and ligand-field versions of the AOM are responsible for the very common, but only approximate, empirical validity of the early assertions of the original model.

The sources of the potential V_{LF} acting on the metal d electrons arise from *all* other charges in the system: the ligand nuclei and core electrons, the ligand valence electrons, *and* the metal nucleus, core, and higher valence electrons. Elsewhere,[2-5] we have identified two kinds of contribution to an AOM parameter, called "static" and "dynamic". The static contributions to other than e_σ parameters are negligible; even those to the σ perturbation are probably of second order. It suffices in the present summary to focus on the dynamic contribution to an e_λ parameter ($\lambda \equiv \sigma, \pi_x, \pi_y$), which has been shown[2-5] to be dominated by terms like $|\langle d_\lambda|v|\chi_\lambda\rangle|^2/(E_d - E_\chi)$ (expression I). In the cellular decomposition of the ligand field that we call the AOM, the function χ (of local symmetry λ) will be a "bond orbital" when the local AOM region or coordination cell is occupied by a ligand. We may visualize the dominant part of the local ligand-field potential, v, as arising from the electron density associated with the local M–L bond (of λ symmetry): note that, in this formalism, the bonding electrons enter expression I twice—once in χ_λ and once via the bond electron density implicit in v. Now the bond orbitals, expressing the full (λ contribution to) chemical bonding intended by the line in M–L, will consist predominantly of appropriate ligand (λ) functions together with metal s, and perhaps p, orbitals (nominally 4s and 4p for the first-row TM series). It is likely that metal (3)d orbitals enter only slightly into these bonds but, in any case, the formalism explicit in the full theoretical treatment[4] excludes those with energy E_d from χ_λ: this does *not* imply any further assumption or neglect, however. Although we have emphasized that the ligand-field and molecular orbital approaches to the AOM are fundamentally distinct, it remains perfectly legitimate to use qualitative molecular orbital concepts in order to help visualize the structure of the defined, ligand-field version of the AOM. So, considering a local M–L σ interaction, we would envisage χ_σ as the bonding MO between metal s (and possibly p) orbitals, lying higher in energy than the ligand-field d-orbital basis, and ligand σ orbitals (perhaps sp^3 for an amine). As a result of bond formation, E_χ will be less than E_d (for we are not concerned with the antibonding M–L orbital, which, being empty, cannot give rise to any potential): altogether, therefore, the resultant σ parameter—e_σ—is positive, this sign being determined by the denominator in expression I. Qualitatively, we observe that the greater the M–L interaction, the lower the value of E_χ and/or the greater the potential (and hence numerator in expression I) generated by the overlap bond electron density—hence, the larger is (the positive) e_σ. On the other hand, a quantitative appreciation of the magnitudes of e_λ parameters is not readily attainable, even though the formalism has been established theoretically.[2-5]

It will certainly not be given by porportionality to overlap integrals squared—even if it were known what functions were involved in the overlaps. We illustrate this empirically in the present systems by abstracting some e_σ values for Cu–N ligation as proposed by Smith.[37] Figure 3 shows such values as estimated relatively, by recourse to squares of overlap integrals, and absolutely, by empirical matching to experimentally determined values. Comparison of these values with those determined by the current analyses illustrates our assertion that the simple overlap procedure forms a totally inadequate basis for even a semiquantitative understanding of the AOM. We discern two general trends. These concern the variation of e_σ values for the various equatorial (or basal) sites in the amine complexes, on the one hand, and the wide-ranging e_σ values for the axial ligands, on the other. We take this latter feature first.

Consider progressively lengthening and weakening a particular M–L σ bond in a complex. The ligand field in the spatial region assigned to that interaction (the local cell) monitors the effect of the bond upon the metal d orbitals. The

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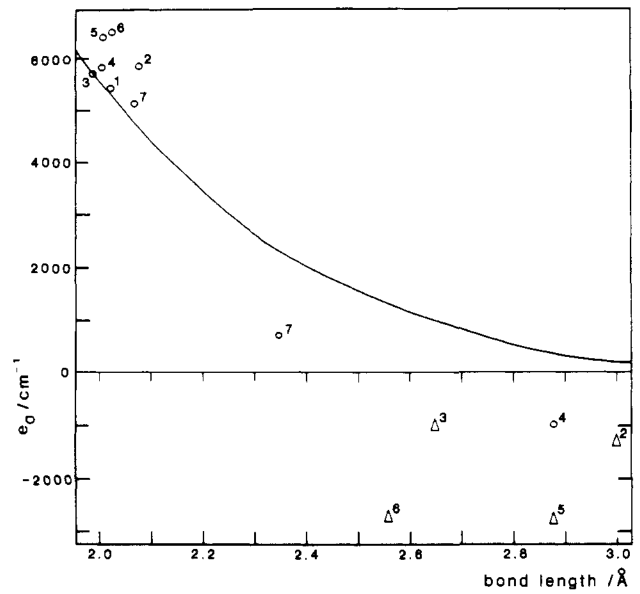

Figure 3. Cu–N and other e_σ values, determined in the present study, plotted with respect to bond lengths. The curve is derived from e_σ values predicted[37] from the variation of the squares of Cu–N overlap integrals. Experimental key: (1) $K[Cu(NH_3)_5](PF_6)_3$; (2) $Cu(NH_3)_4(SCN)_2$; (3) $Cu(NH_3)_4(NO_2)_2$; (4) $Na_4[Cu^{II}(NH_3)_4][Cu^I(S_2O_3)_2]_2{\cdot}NH_3$; (5) $Na_4[Cu^{II}(NH_3)_4][Cu^I(S_2O_3)_2]_2{\cdot}H_2O$; (6) $Cu(en)_2(BF_4)_2$; (7) $Cu(tach)_2(ClO_4)_2$; (○) Cu–NH_3 or Cu–amine interaction; (△) interactions of Cu with other groups.

ligand-field parameters probe or reflect the M–L bond. As discussed above, when the bond is "normal" and "strong", the charge overlap density lies appropriately between metal and ligand, and the bond orbital χ_σ housing it has an energy E_χ less than that of the d-electron (probe) orbitals: e_σ is large and positive. On removal of the ligand somewhat, the M–L interaction is weakened and the energy of the bonding molecular orbital is now not so low: at the same time, the bonding overlap charge is rather less concentrated in the region between metal and ligand, and e_σ becomes smaller. Weakening the bond further will produce a situation in which rather little overlap charge leaves either metal or ligand and the energy of the bonding orbital might easily be greater than that of the metal d orbitals. Now the denominator in expression I is negative and we observe small negative values for e_σ. Ultimately, we envisage a coordination void as the limiting case of an M–L interaction in which there is no overlap charge density at all. "Valence" electron density now resides partly in the metal (4)s orbitals and partly in the ligand (σ) orbitals. However, the dominant contribution to expression I now comes from that density—and, hence, potential—associated with the metal s orbital, for the ligand electrons are either too for away or, indeed, absent altogether. Herein lies the explanation of the negative e_σ values observed for coordination voids. Their numerical magnitudes depend upon the notional d–s promotion energy in the actual system and upon the electronic population of the higher lying s orbital. Both quantities are complex functions of the gross ligand fields present elsewhere in the molecule, for these help determine the mean spherical potential that defines E_d as well as establish the participation of the metal s orbitals within the bonding at large. The negative d–s contribution to e_σ(void) values does not carry over to ligand-occupied cells as an additive and hidden correction, of course, for the formation of M–L bonds in those cells effectively preempts the metal s-electron density, placing it in a different region of space and giving it a different energy.

The foregoing description graphically illustrates another aspect of the difference between ligand-field and molecular orbital theories. An MO description of the removal of a ligand to infinity would naturally suggest that e_σ values would decrease from substantial and positive values to zero. Yet, as summarized by Figure 4, the ligand-field version[2-5] of the AOM, which explicitly recognizes that d-orbital matrix elements are *not* directly bond energies but merely probes of the bonding, establishes a trend from substantial and positive to moderately large and negative for these same parameters. And, to reemphasize, none of this represents a failure of ligand-field theory by the rejection of a pure d-orbital basis. It arises naturally and consistently out of a proper conception of what kind of model ligand-field theory is.

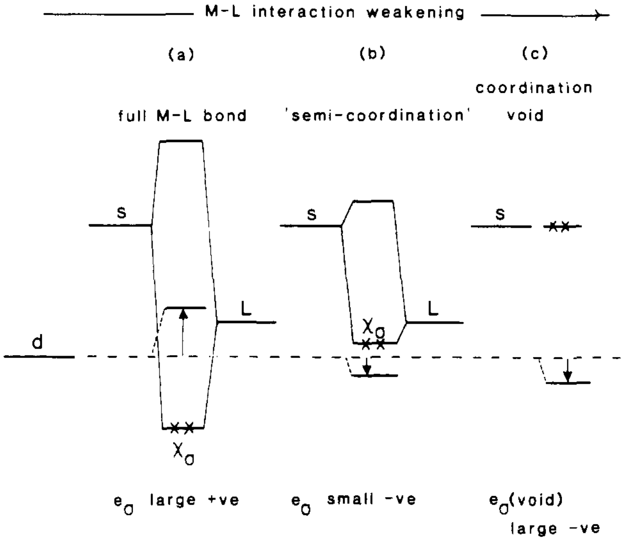

Figure 4. Illustration of how AOM e_σ parameters range from positive to negative values as an M–L bond in a complex is progressively lengthened and weakened.

One obvious limitation of diagrams like those in Figure 4 is their overdue attention to eigen*values*. However, our discussion also emphasized the spatial redistribution of "bond charge" and source of potential on progressive weakening of the M–L interaction. Hence, in a qualitative way at least, the magnitudes of AOM parameters provide some measure of charge redistribution, including that which reflects the operation of the electroneutrality principle. It was clear from Figure 3 that no simple rules based on additivity or proportionality of overlap integrals was to be expected nor observed to be useful. On the other hand, some rough additivity of AOM *parameters* might be expected to sequester, inter alia, the effects of charge redistribution and the electroneutrality principle. In the present series of seven amine complexes, we note that the gross, algebraic sums of AOM e_σ parameters are about equal (at ca. 21 000 cm^{-1}). It appears that the considerable variations in equatorial (or basal) e_σ(N) values, summarized in Figure 2, for Cu–N bond lengths which vary relatively little, reflect the extent of bond formation with the various axial ligands. Again, the latter seems to be monitored rather better by the signs and magnitudes of the e_σ(ax) parameters than by bond lengths. This might be doubly welcome for those who share a distaste for the "semicoordination" concept in copper(II) complexes, preferring simply to recognize a continuous gradiation in axial bond strengths. Anyway, it appears from our current data that the bond "strengths" of axial copper–nitrite at 2.56 Å and copper–S̲CN at 3.00 Å are comparable, while those of bridging ammonia and water ligands at about 2.8 Å are substantially different. Insofar that a value of −3000 cm^{-1} for e_σ(void) appears to represent the situation of "no bond" (for copper(II) complexes, anyway), the $e_\sigma(H_2O)$ value of −2800 cm^{-1}, and of −2750 cm^{-1} for BF_4^- in the ethylenediamine complex, might be indicative of merely vestigial axial bonding in those systems. Certainly, comparison of the bridging ammonia and water complexes suggests that, at those large distances at any rate, nitrogen is a considerably better σ donor than is oxygen. Whether or not this may be taken as support for the relative placement of these ligands in the spectrochemical series is not clear, for at more normal bonding distances, the π-donor role of water and other oxygen ligators serves to diminish Δ_{oct} and so confuse the issue.

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Registry No. Cs_2CuCl_4, 35637-99-1; $[Cr(NH_3)_6]^{3+}[CuCl_5]^{3-}$, 92346-76-4; $[C_6H_5(CH_2)_2NH_2CH_3]^+{}_2[CuCl_4]^{2-}$, 51751-77-0; $K^+[Cu(NH_3)_5]^{2+}(PF_6)^-{}_3$, 92346-77-5; $Cu(NH_3)_4(SCN)_2$, 92419-35-7; $Cu(NH_3)_4(NO_2)_2$, 92419-36-8; $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]NH_3$, 27735-97-3; $Na_4[Cu(NH_3)_4][Cu(S_2O_3)_2]H_2O$, 27735-96-2; $[Cu(en)_2]^{2+}[BF_4]^-{}_2$, 92419-37-9; $[Cu(tach)_2](ClO_4)_2$, 31220-63-0; Egyptian blue, 10279-60-4.

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Redirected Ligand-Field Analysis. 2. Asymmetric Chelation in Trigonal-Bipyramidal Copper(II) Complexes

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The electronic d–d spectra of three formally trigonal-bipyramidal (TBP) complexes have been analyzed within the angular-overlap model (AOM). In two molecules—$[Cu(bipyridyl)_2I]^+I^-$ and $[Cu(phenanthroline)_2H_2O]^{2+}(NO_3)^-{}_2$—the ligand-field parameters describe markedly different Cu–N interactions in axial and equatorial sites of these structures, despite the near-equality of the relevant bond lengths. These circumstances are considered to arise from the steric activity of the d^9 shell of the copper ion while more detailed differences between the AOM parameter values for the two complexes are associated with a ligand-field activity of the coordinationally void region opposite the water ligand in the phenanthroline complex, whose structure tends somewhat toward square-pyramidal geometry. A further analysis of the structurally similar complex Cu(tet-b)(*o*-mercaptobenzoate) (tet-b = *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane) confirms the overall interpretation, especially with respect to the π-bonding roles of the phenanthroline and bipyridyl ligands in the other systems. Published ESR *g* values for each of the three complexes do not assist the analyses but are not inconsistent with them.

Introduction

That ligand-field parameters reveal the interactive nature of bonding in metal complexes is an important theme of the present paper. The idea that "local" AOM parameters are modified by a "global overlay" representing the interplay of bonding forces and charge redistribution in complexes is as natural to mainstream chemical thinking as it is relatively unexplored in ligand-field analysis. Some evidence for the relevance of this view was provided by studies of a series of tetragonal copper(II) complexes in the preceding paper.[1] Here we characterize another interesting feature of copper(II) coordination that complements more familiar features arising out of the Jahn–Teller effect. It is revealed by a short series of d^9 complexes possessing nominal trigonal-bipyrimidal (TBP) coordination geometry.

The complex $[Cu(bpy)_2I]^+I^-$, where bpy = 2,2′-bipyridyl, is just one of an extended series with the general formula $[Cu(bpy)_2X]^{n+}Y^{n-}$, $n = 1$ or 2, that has been the focus of crystallographic and spectroscopic study. Hathaway[2] has been concerned to establish an empirical criterion of structure in this series, defining geometries along a "vibration-mode pathway" between idealized trigonal-bipyramidal and square-pyramidal precursors as correlated with splittings in the electronic d–d spectra. The ligand-field properties of the iodo complex have been investigated in more detail than those of other members of the series, however, published single-crystal optical[3] and electron spin resonance[3] spectra offering a substantial database for detailed analysis. It has been concluded[3] from a spectral polarization analysis of the complex that the energies of the parent e′ and *e″* orbitals arising in ideal TBP symmetry, to which this geometry approximates, are reversed with respect to those predicted by point-charge and "numerous (other) ligand-field calculations". However, simple AOM computations, in which the obvious and clearly implicit assumption of symmetric chelation of the bipyridyl ligands is made, not only fail to reproduce the observed polarization scheme but also predict wholly incorrect transition energies. We therefore address two important questions: is it reasonable, or indeed efficacious, to entertain the notion of markedly different ligand-field perturbations upon the copper ion from the two ends of the otherwise symmetrical bipyridyl ligand, and was the original processing[3] of the experimental spectral data of this triclinic system beyond reproach?

A closely similar TBP system is presented by the species $[Cu(phen)_2X]^{2+}Y^{2-}$ (phen = 1,10-phenanthroline). The series has been somewhat less extensively studied, and once again it appears that only one member—$[Cu(phen)_2H_2O]^{2+}(NO_3)^-{}_2$—has been the subject of both single-crystal optical and ESR studies. Bencini and Gatteschi[4] reached two main conclusions in their study: first, that the experimental $\mathbf{g}^2$ tensor can be reproduced well by their model, a successful result to which some measure of significance and importance was attached, and second, that an AOM scheme in which axial and equatorial phenanthroline nitrogen atoms are assigned dissimilar values reproduces the electronic (and ESR) spectra in a manner that corresponds to the e′ and e″ orbitals of the TBP percursor being assigned in the normal or regular way, with the d-orbital sequence $E(a_1) < E(e') < E(e'')$. For the moment, their parameter values may be summarized by the list $e_\sigma(ax) = 6000$ cm^{-1}, $e_\sigma(eq) = 5400$ cm^{-1}, $e_{\pi\perp}(ax) = 150$ cm^{-1}, and $e_{\pi\perp}(eq) = 1300$ cm^{-1} for AOM parameters labeled

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