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.

Acknowledgment. It is a pleasure to acknowledge the interest of, and useful discussions with, Dr. R. G. Woolley.

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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[1] Deeth, R. J.; Gerloch, M., *Inorg. Chem.*, preceding paper in this issue.
[2] Harrison, W. D.; Kennedy, D. M.; Power, M.; Sheehan, R.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1557.
[3] Hathaway, B. J.; Billing, D. E.; Dudley, R. J.; Fereday, R. J.; Tomlinson, A. A. G. *J. Chem. Soc. A* **1970**, 806.
[4] Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1977**, *16*, 1994.

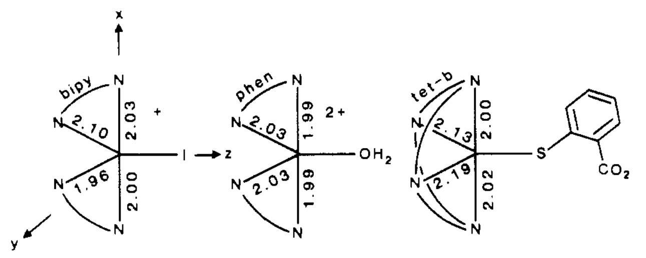

Figure 1. Approximate trigonal-bipyramidal geometries of the bpy, phen, and tet-b copper(II) complexes.

according to standard conventions, where ax ≡ axial N, eq ≡ equatorial N of the formal TBP, and ∥ and ⊥ refer to directions normal to and in the planes of, the chelates. (The Cu–N bond lengths[5] are only slightly different, being 1.99 Å for the axial sites and 2.03 Å for the equatorial ones.) Any disquiet that one may feel about these values pales in comparison with that engendered by the reported negative $e_\pi(H_2O)$ values, implying a π-acid role for the water ligand. Bencini and Gatteschi were aware of the problem, however, observing that the parameter values "may not be satisfactory in a chemical sense...but can reproduce the data. The chemical meaning of ligand-field parameters", they continued, "is an open problem and particularly in the case of copper(II) complexes it is not uncommon to find values of parameters which do not appeal to chemical sense but are, however, useful, at least in a bookkeeping sense, to interpret the spectra." *We* take great exception to this whole philosophy, and a continuing strand throughout this and our recent work[1,6–9] in this area is to show that the AOM provides a *meaningful* and *valid* approach to the analysis of electronic properties of transition-metal complexes. If bookkeeping were all that one could claim, why not simply report the observed transition energies that constitute directly observed data and are, incidentally, fewer in number? We report below, therefore, a new, detailed, and thorough AOM analysis of both bipyridyl and phenanthroline systems.

A major conclusion to arise from these analyses is the demonstration of markedly asymmetric chelation by the otherwise equivalent ligating atoms in both phenanthroline and bipyridyl ligands. A feature of immediate relevance is the close similarity of the axial and equatorial Cu–N bond lengths. The correlation we shall discuss is augmented by one further analysis, this time concerning a TBP structure involving a cyclic tetraamine—[*rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane]copper(II) *o*-mercaptobenzoate hydrate—Cu(tet-b), for short. Hughey et al.[10] report an X-ray diffraction analysis of the crystal and molecular structure of the compound, together with powder and solution charge-transfer and d–d electronic transition energies and powder ESR *g* values. These authors' interest lay mostly in the sulfur ligand, and while no detailed ligand-field analysis was reported, they claim that the ligand-field and charge-transfer data are consistent with a description of the sulfur ligand as a mercaptide. In the present paper, we focus rather more on the nitrogen donor set of the tet-b ligand, which, as in the bipyridyl and phenanthroline systems above, comprises a pair of TBP axial nitrogen atoms and a pair of equatorial ones. In this case the equatorial bond lengths are noticeably longer than the axial. The molecular structures of the three molecules we analyze in the following section are shown in Figure 1, together with a common coordinate frame.

Analyses

We have argued at length recently[6–9] for the theoretical validity of the AOM within ligand-field theory and have demonstrated its consistency and utility in providing ready chemical insight into the electron distribution is transition-metal complexes. A parametric model of this kind can only command respect if, while satisfactorily reproducing experimental data, it yields parameter values that are comprehensible and chemically informative rather than inconsistent, puzzling, or uninterpretably counterintuitive. It is also of central importance that the analytical processes involved in any study should be sufficiently comprehensive and, furthermore, be seen to be so. This attitude has guided the AOM ligand-field analyses we now report. While the geometries of the present complexes approximate TBP, their detailed symmetry is sufficiently low as to permit partial definition, at least, of more bonding features than was possible in the near-regular tetragonal octahedra of the preceding paper.

$[Cu(bpy)_2I]^+$. We begin with an examination of the reported d–d spectrum,[3] leaving ESR *g* values[3] till later. Our ligand-field schemes are therefore defined by AOM parameters together with a nominal value only for the spin–orbit coupling parameter ζ (taken as 700 cm^{-1}). All computations have been performed within the d^9, ^2D basis with use of the J,M_J quantization scheme and the CAMMAG computing package.[11]

The compound $[Cu(bpy)_2I]^+I^-$ crystallizes in the triclinic system.[12] Hathaway et al.[3] have recorded the crystal absorption spectrum in polarized light, but no presentation of the raw data was made. Instead, the results of some data processing procedures were given and, with respect to molecular Cartesian axes defined as in Figure 1, may be summarized as follows: only one absorption is observed in light polarized parallel to z, at 13 800 cm^{-1}, only one in y polarization, at 12 700 cm^{-1}, and one in x-polarized light, at 10 800 cm^{-1}. It was also claimed that there was evidence—from Gaussian analysis—of a very weak, fourth transition at ca. 9300 cm^{-1} in x poalrization, but its reality must be doubted. Altogether, therefore, the experimental spectrum furnishes three clear pieces of data (transition energies) of uncertain (as we shall argue) polarization character. As will become clear, we shall also exploit the "window" between the instrumental lower limit (ca. 5000 cm^{-1}) and the lowest energy band.

Given this limited database, we felt obliged to investigate first a parameterization scheme that constrained the ligand fields of axially and equatorially coordinated ends of each bipyridyl ligand to be equal. Although each nitrogen atom in the system is crystallographically independent,[12] the free bipyridyl ligands are surely symmetric and the observed Cu–N bond lengths in the complex vary little, being 2.00 and 2.03 Å for the axial contacts and 1.96 and 2.10 Å for the equatorial. The mean axial and equatorial Cu–N distances are thus not significantly different, though in other X-ray analyses of related $[Cu(bpy)_2X]^{n+}Y^{n-}$ systems reported,[13,14] the mean axial bond lengths are very slightly shorter than the equatorial. Similarly, the iodine ligand in the TBP structure is considered to act as a linear ligator so leaving the four variables $e_\sigma(N)$, $e_{\pi\perp}(N)$, $e_\sigma(I)$, and $e_\pi(I)$. In this and all subsequent parameterization schemes, metal–nitrogen π interaction parallel to the planes of the chelating ligands was not entertained, and

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(5) Nakai, H.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2557.
(6) Woolley, R. G. *Mol. Phys.* **1981**, *42*, 703.
(7) Gerloch, M.; Harding, J. H.; Woolley, R. G. *Struct. Bonding (Berlin)* **1981**, *46*, 1.
(8) Gerloch, M.; Woolley, R. G. *Prog. Inorg. Chem.* **1983**, *31*, 371.
(9) Gerloch, M. "Magnetism and Ligand-Field Analysis"; Cambridge University Press, New York, 1983.
(10) Hughey J. L., IV; Fawcett, T. G.; Rudich, S. M.; Lalancette, R. A.; Portenza, J. A.; Schugar, H. J. *J. Am. Chem. Soc.* **1979**, *101*, 2617.
(11) "CAMMAG", a FORTRAN program by D. A. Cruse, J. E. Davies, M. Gerloch, J. H. Harding, D. J. Mackey, and R. F. McMeeking.
(12) Barclay, D. G. J.; Hoskins, B. F.; Kennard, C. H. L. *J. Chem. Soc.* **1963**, 5691.
(13) See ref 2 for citations.
(14) See citations in: Tyagi, S.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1983**, 199.

$e_{\pi\parallel}$(N) was held fixed at zero. Calculations have been performed for extensive variations in the parameter values: e_σ(N) ranging from 4000 to 8000 cm^{-1}, e_σ(I) from 1000 to 5000 cm^{-1}, $e_{\pi\perp}$(N) from −3000 to +3000 cm^{-1}, and e_π(I) from 0 to 2500 cm^{-1}. No parameter combinations within these wide ranges enabled us to reproduce the reported electronic spectrum satisfactorily, and this includes the special case for $e_{\pi\perp}(N) = e_\pi(I) = 0$, corresponding to a σ-bond-only model, which may, of course, be equivalenced by a crystal-field point-charge calculation. The nature of the failure of this scheme to reproduce experiment is twofold. Even when calculated transition energies coincide with the three spectral maxima, the polarization pattern was incorrect—as judged by electric dipole selection rules in the idealized C_{2v} symmetry group chosen[3] for this exercise. However, as will be clarified shortly, no ligand-field model appears capable of reproducing the reported polarization pattern. By far the more important failure of the scheme described is the inevitable prediction of a transition in the range 4000–6500 cm^{-1} that is *not* orbitally forbidden (i.e. *not* $A_1 \rightarrow A_2$ in C_{2v} symmetry, the principal rotation axis taken parallel to Cu–I). The complex is reported to be transparent from $\lesssim$5000 to ca. 9000 cm^{-1}. It is upon this finding that our assertion of unsymmetrical chelation by the bipyridyl ligands ultimately rests. In passing, we note that Hathaway's claim[3] that Cu–I π bonding could be responsible for his assignment within a scheme arising from TBP with $E(a_1) < E(e'') < E(e')$ cannot be supported.

We considered next more freely parameterized AOM schemes in which the axial and equatorial nitrogen atoms are treated differently. An immediate objection to such schemes, of course, would be a charge of "over-parameterization". Our response to this must be that the failure of the constrained schemes to reproduce three experimental bands (plus a "window") defines a clear, positive result. Expressed otherwise: a many-parameter model in which several parameter values are fixed at zero, or made equal to others, is unsatisfactory. Moving to a freer scheme may well lead to ambiguous sets of "fitting parameters". Provided any such correlations are thoroughly investigated and reported, we shall be guilty of no misconduct.

Before constraints on both σ and π AOM parameters for equatorial and axial nitrogen ligators were removed, several calculations were performed in which either the e_σ values alone, or the $e_{\pi\perp}$ values alone, were allowed to differ. While not making much chemical sense, this stepwise approach helped the mundane practical aspects of acquiring a "feel" for the more heavily parameterized schemes and also enabled us to discover which equalizing constraint was the more significant in reproducing the spectrum. Relaxing the equality of the π parameters alone did not lead to the calculation of a "window" between 8000 and 9000 cm^{-1}. Only when $e_\sigma(N_{ax})$ was allowed to differ from $e_\sigma(N_{eq})$ was adequate reproduction of both spectral bands *and* the transparent region possible. The essence of the change brought about by the asymmetric bipyridyl σ bonding was the elevation of the lowest calculated band into the 10 000-cm^{-1} region without simultaneously predicting orbitally allowed transitions at energies higher than 14 000 cm^{-1}. Contrast the behavior of the "symmetric parameterization scheme" in which very large values of e_σ(N) can raise the energy of the lowest calculated transition to ca. 10 000 cm^{-1} but only by simultaneously raising the remaining levels into the range 20 000–25 000 cm^{-1}.

We therefore made a wide exploration of the chemically consistent scheme in which values for the six AOM parameters—$e_\sigma(N_{ax})$, $e_\sigma(N_{eq})$, $e_{\pi\perp}(N_{ax})$, $e_{\pi\perp}(N_{eq})$, e_σ(I), and e_π(I)— were freely varied. Many combinations of these parameter values led to satisfactory reproduction of the three reported band maxima, without any formally allowed band (i.e. in the C_{2v} idealization) appearing outside the range 10 000–14 000 cm^{-1}. Before describing these "best-fit" parameter combinations, however, we emphasize that none of them, in common with the more constrained schemes above, yielded the polarization pattern reported.[3] We consider that those polarization ratios are incorrect, for two main reasons. First, the unbroken series of successful and chemically sensible AOM analyses on other systems,[1,8,9] coupled with our recent theoretical analyses[6-9] of the AOM itself, make us reluctant to discard the model on this occasion. Second, the experimental determination of polarization ratios in triclinic crystals is known to be difficult.[15,16] The incident light is required to be polarized parallel to a principal axis of the absorption tensor, which is hopefully parallel to one of the indicatrix. Further, such directions may be frequency dependent. Only in studies of orthorhombic, or more highly symmetrical, zones is the polarization experiment at all simple, although some detailed experiments have been reported[4,17] in low-symmetry systems. However, no evidence was provided by Hathaway et al.[3] that the severe problems connected with polarization analysis in the triclinic system were overcome, so we prefer to base our AOM analysis upon the transition *energies* alone—which should be reliable—and pay no heed to the reported polarization ratios. Finally, if this argument is pursued, we must question whether it has been satisfactorily established that all three directions are spectroscopically distinct, as claimed.[3] If not, the point group C_2 might be considered to approximate the real geometry more correctly than C_{2v}, which was originally selected on the basis of "observed" differences between *x*- and *y*-polarized spectra. As we have made no attempt to match calculated and observed polarizations, based on electric-dipole selection rules or otherwise, our analysis is independent of the choice of idealized molecular symmetry. However, since a transition $A_1 \rightarrow A_2$ (C_{2v}) should be electric-dipole forbidden, and so possibly of relatively low intensity in C_2, our calculations aim not only at reproducing the other A_1 transitions but also at placing this calculated band within the general broad absorption envelope, that is, within 1000–1500 cm^{-1} of the highest or lowest observed band maxima.

Table I. Reproduction of the Transition Energies of $[Cu(bpy)_2I]^+I^-$ [a]

$e_\sigma(N_{ax})$	$e_\sigma(N_{eq})$	$e_{\pi\perp}(N_{ax})$	$e_{\pi\perp}(N_{eq})$	e_σ(I), e_π(I)
6000	2250	0	−1000	insensitive in the ranges 2000–3500 (e_σ(I)) and 500–1000 (e_π(I))
6500	2500	500	−500	
7000	3000	1000	0	
7500	3500	1500	500	

[a] ζ is fixed at 700 cm^{-1}. AOM parameter values are in cm^{-1}.

In Table I are shown a selection of "good fit" parameter values satisfying these criteria. The entry with $e_\sigma(N_{ax}) = 6000$ cm^{-1} roughly describes a lower bound on this parameter. The last entry line does not represent an upper bound, however, except insofar that experience and prejudice might suggest so. The correlations in the table give rise to two main observations: (a) that e_σ values for the equatorial nitrogen ligators are rather less than half those for the TBP axially coordinated nitrogens and (b) that the $\pi_\perp$ perturbations describe a situation in which the axial nitrogens are algebraically better donors than the equatorial ones: it is even possible that the axial ends of the bipyridyl ligands act as π donors toward the copper atom while the equatorial ends behave as acceptors. In view of the asymmetric parameterization of the bipyridyl groups, the possibility of similarly asymmetric Cu–I π bonding must be

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(15) Hartshorn, N. H.; Stuart, A. "Crystals and the Polarizing Microscope", 3rd ed.; Edward Arnold: London, 1960.

(16) McKie, D.; McKie, C. H. "Crystalline Solids"; Nelson: London, 1974.

(17) Hitchman, M. A. *Inorg. Chem.* **1974**, *13*, 2218.

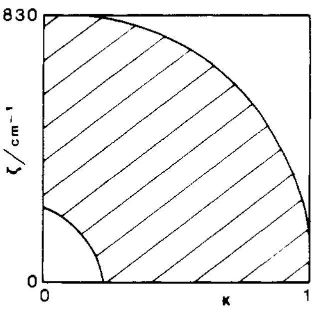

Figure 2. $[Cu(bpy)_2I]^+I^-$. With use of AOM parameter values that reproduce the optical spectrum, essentially perfect agreement with observed ESR *g* values is obtained for spin–orbit (ζ) and orbital reduction (k) parameters within the hatched area.

considered, notwithstanding the conventional view of such interactions as "linear ligation". However, we have not pursued this line in view of the already high degree of parameter correlation.

Actually, even wider correlations of the various parameter values yielding good reproduction of the spectral transition energies occur than are indicated in Table I. It is possible, for example, to hold $e_{\pi\perp}(N_{ax}) = e_{\pi\perp}(N_{eq})$ (=500 cm^{-1}, e.g.), but only if the value of $e_\sigma(N_{eq})$ is reduced further (by ca. 500 cm^{-1}). That is, a "bookkeeping" philosophy would record a fit in which the two ends of the bipyridyl ligands act similarly so far as π bonding is concerned, while the σ bonding functions are widely different. We argue that such fitting regions merely illustrate the unfortunate but necessarily overparameterized nature of the present analysis rather than provide any chemical insight.

We leave to the Discussion section the matter of the interpretation of the general assertations of the previous paragraph and comparisons with related molecules to which we shortly refer. Meanwhile, our analysis of the ligand-field properties of the bipyridyl complex ends with an examination of the ESR *g* values. We had hoped that such hard-won experimental data[3] might provide a means of sharpening our estimates of the parameter values, as is found to be the case in complexes of cobalt(II) for example. Figure 2, however, illustrates the typical situation that results when we take *any* reasonable combination of parameter values, as described above, and examine the ability of the model to reproduce *accurately* both magnitudes and directions of principal *g* values. The hatched area defines the region of parameter space, relating to spin–orbit coupling and Stevens' orbital reduction factor, in which essentially perfect agreement between observed and calculated $\mathbf{g}^2$ tensors is obtained. We have repeatedly observed this sort of correlation in analyses of a wide range of copper(II) complexes—including those tetragonal systems in the preceding paper,[1] as well as the present TBP structures. We must reluctantly conclude that ESR *g* values are frequently, if not always, uninformative in copper(II) single-center studies: hyperfine data may well present more useful data, of course. It should be obvious from Figure 2 that more "refined" computations involving anisotropic ζ and/or k values would merely enlarge the ambiguity. In passing, however, we note that the use of isotropic spin–orbit and orbital reduction parameters does not constitute an "ad hoc" assumption, as has been claimed,[4] but is theoretically far more defensible[7,9] than *any* other increase in the number of these parameters: "anisotropic" parameters have evolved from overrestricted molecular orbital models and then used inconsistently within the fundamentally, and practically, distinct ligand-field formalism.

$[Cu(phen)_2H_2O]^{2+}$. Bencini and Gatteschi[4] have made a detailed study of the electronic absorption spectrum of the monoclinic crystals of the dinitrate salt of this cation, at ca. 77 K. A careful polarization investigation, especially of the monoclinic zone, led to band assignments as follows (again with respect to the coordinate frame of Figure 1): band maxima at ca. 12 000 cm^{-1} in *z*-polarized light, assigned as $^2A_1 \rightarrow {}^2A_1$ (C_{2v}) or $^2A \rightarrow {}^2A$ (C_2); ca. 13 000 cm^{-1} in *y* polarization, $\rightarrow{}^2B_2$ or $\rightarrow{}^2B$ (in C_{2v} or C_2, respectively); ca. 15 000 cm^{-1}, $\rightarrow{}^2B_1$ or $\rightarrow{}^2B$ (C_{2v} or C_2). These authors also determined the single-crystal $\mathbf{g}^2$ tensor of the complex, and we shall refer to these ESR results later. Using the same basis and computing procedures as for the bipyridyl complex, our fitting investigations began with the simplest AOM parameterization schemes.

Various parameter constraints were considered, each based upon the notion of symmetric chelation by the phenanthroline ligand: (i) $e_\sigma(N)$, $e_\sigma(O)$ as the only non-zero AOM variables; (ii) $e_\sigma(N)$, $e_\sigma(O)$, $e_{\pi\perp}(N)$, $e_{\pi\perp}(O) = e_{\pi\parallel}(O)$ taking non-zero values; (iii) the same as (ii) but with $e_{\pi\perp}(O) \neq e_{\pi\parallel}(O) = 0$. As in the bipyridyl analysis these, and all other, schemes set $e_{\pi\parallel}(N) = 0$. The rationale behind the last variation (iii) lies in the observation, from the reported structural analysis,[5] that the water oxygen atom is hydrogen bonded to an oxygen atom of a nitrate anion in the lattice. The distance O(water)···O(nitrate) is 2.77 Å, and the angle Cu–O(water)···O(nitrate) is 121.3°. It thus appears highly probable that an essentially linear O–H···O hydrogen bond is present, associated with the water ligand in a formal trigonal planar, sp^2-hybridized state.

Calculations for each of these three schemes within the parameter ranges 4000–8000 cm^{-1} ($e_\sigma(N)$), 1000–5000 cm^{-1} ($e_\sigma(O)$), −2000 to +2000 cm^{-1} ($e_{\pi\perp}(N)$), and 0–3000 cm^{-1} ($e_\pi(O)$) revealed some common characteristics. Almost always, levels were calculated in the order A_1(ground) < A_1 < B_2 < B_1, A_2, assigned in C_{2v} symmetry. Typical best transition energies are 12 000, 13 000, 16 500, and 18 500 cm^{-1} if the lowest calculated energies are contrived to match the experimental bands, or 10 000, 11 000, 15 000, and 16 500 cm^{-1} if the 15 000-cm^{-1} band is held. By far the best fits were obtained for low values of $e_\sigma(O)$ and for ratios $e_\pi(O)/e_\sigma(O) \gtrsim 1$. Note that there was no difficulty in avoiding calculating bands in the transparent window between 5000 and 10 000 cm^{-1}. This behavior contrasts sharply with that observed for the bipyridyl complex and, in view of the overall similarity of the two chromophores, calls for an explanation. The reason evidently stems from differences in geometrical detail between these molecules. In particular, the angle N_{eq}–Cu–N'_{eq} is ca. 114° in the bipyridyl complex and ca. 140° in the phenanthroline complex: the angles N_{eq}–Cu–X (X = I, H_2O) are commensurate with this difference. A set of calculations undertaken to investigate the consequences of this difference in geometry show that the result of opening the N_{eq}–Cu–N'_{eq} angle is to raise all transition energies markedly so that the "troublesome" band calculated to lie in the bipyridyl window is now placed so as to correspond with the lowest observed phenanthroline band at ca. 12 000 cm^{-1}. Hence the gross differences between the spectra of these two complexes arise mainly from the greater distortion from ideal TBP found in the phenanthroline complex.

None of the constrained schemes i–iii lead to acceptable *quantitative* reproduction of the observed bands, the discrepancy arising in the calculated spread of transition energies being some 1500–2000 cm^{-1} too large. Despite the usual overparameterized situation, herein lies the basis of our claim for asymmetric chelation in the phenanthroline complex also. The assertion is not merely based on this negative evidence, however, as the following freely parameterized scheme demonstrates.

In extending the degree of parameterization to allow for $e_\sigma(N_{eq}) \neq e_\sigma(N_{ax})$, $e_{\pi\perp}(N_{eq}) \neq e_{\pi\perp}(N_{ax})$, we have mostly restricted calculations to those cases where $e_{\pi\perp}(O) = 0$. Our

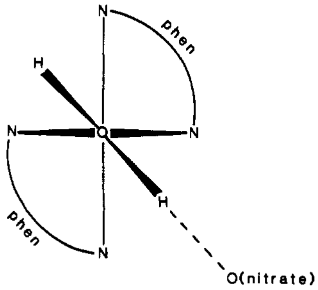

Figure 3. $[Cu(phen)_2H_2O]^{2+}$ ion viewed along the Cu–O bond (z axis) from the water ligand. Hydrogen bonding with the nitrate probably establishes the water orientation shown.

Table II. Main Perturbations on Globally Defined d Orbitals in $[Cu(phen)_2H_2O]^{2+}$

d_{z^2}	$\sigma(O) >> \sigma(N_{ax}) > \sigma(N_{eq})$
$d_{x^2-y^2}$	$\sigma(N_{ax}) > \sigma(N_{eq})$
d_{xy}	$\pi_\perp(N)$, small
d_{xz}	$\pi_\perp(O) \approx \pi_\parallel(O)$, $\pi_\perp(N_{ax})$
d_{yz}	$\pi_\perp(O) \approx \pi_\parallel(O)$, $\pi_\perp(N_{eq})$

reasons are as follows. The hydrogen-bond O···O contact, referred to above, strongly indicates a structural description in terms of an sp^2 trigonal Cu–water interaction, and further, the plane of that water is calculated to make an angle of ca. 51° with respect to the TBP equatorial plane, as sketched in Figure 3. With respect to the coordinate frame of Figure 1, and in recognition of the approximate 45° inclination of the water plane to the TBP equatorial plane, we may construct Table II to indicate the main perturbations upon the various globally defined d orbitals. It is apparant that *each* of the d_{xz} and d_{yz} copper orbitals is expected to suffer essentially equal perturbation from *each* of $\pi_\perp(O)$ and $\pi_\parallel(O)$ influences. Therefore, while the mean value of $e_{\pi\perp}(O)$ and $e_{\pi\parallel}(O)$ can be expected to be of importance in the present system, the anisotropy—complete or otherwise—is not. Within the values to be quoted below, this conclusion was supported by various empirical checks. Accordingly, we refer to the (probably chemically more acceptable) scheme in which $e_{\pi\parallel}(O) = 0$.

Wide parameter variations were considered in the freely parameterized scheme: $e_\sigma(N_{ax})$ in the range 4000–8000 cm^{-1}; $e_\sigma(N_{eq})$, 2000–6000 cm^{-1}; $e_\sigma(O)$, 0–4000 cm^{-1}; $e_{\pi\perp}(N_{ax}$ or $N_{eq})$, -3000 to $+3000$ cm^{-1}; $e_{\pi\perp}(O)$, 0–2500 cm^{-1}. Many excellent fits to the observed spectrum were found. By "excellent" is meant that $A_1 \rightarrow A_1$, B_2, B_1 (C_{2v}) levels are calculated in that order and within ca. 300 cm^{-1} of the observed band maxima at 12 000, 13 000, and 15 000 cm^{-1} together with the $A_1 \rightarrow A_2$ transition (electric dipole forbidden in C_{2v} symmetry) lying within the observed envelope and at no more than 1500 cm^{-1} higher than the highest observed band maximum. Parameter values affording such agreement are strongly correlated, of course, but that does not prevent our making some *positive*, if qualitative, generalizations. In Table III are listed representative combinations of parameter values yielding good fits to the observed d–d spectrum, which serve as a focus for our observations.

The $e_\sigma(N_{ax})$ values are always considerably greater than the $e_\sigma(N_{eq})$ values, though the difference is a little less than in the bipyridyl system. There is again a large difference in $e_{\pi\perp}(N)$ values between axial and equatorial sites, the pattern closely resembling that in the bipyridyl complex. The average $e_{\pi\perp}(N)$ value correlates with, e.g., $e_\sigma(N_{ax})$ such that low $e_\sigma(N)$ values are associated with negative mean $e_{\pi\perp}(N)$, and high $e_\sigma(N)$ values with positive ones for nitrogen π bonding. For the "median" value $e_\sigma(N_{ax}) = 7000$ cm^{-1}, the axial end of the phenanthroline appears to function as a modest π donor while the equatorial end acts as a π acceptor. The AOM analyses for bpy and phen complexes thus give broadly similar results so far as the nitrogen chelates are concerned.

Table III. Correlation of "Best Fit" AOM Parameter Values (cm^{-1}) for $[Cu(phen)_2H_2O]^{+}$ [a]

$e_\sigma(N_{ax})$	$e_\sigma(N_{eq})$	$e_{\pi\perp}(N_{ax})$	$e_{\pi\perp}(N_{eq})$	$e_\sigma(O)$	$e_{\pi\perp}(O)$
6000	3000	−1000	−2000	500	1000
6000	3000	−1000	−2000	500	500
6000	3000	−500	−2000	500	0
7000	4000	500	−1000	1500	2000
7000	4000	500	−500	1000	1500
7000	4000	500	0	500	1000
8000	4000	2000	2000	1500	0
8000	5000	2500	2000	1500	0
8000	6000	3000	2000	2000	0

[a] $e_{\pi\parallel}(O)$ value set at zero.

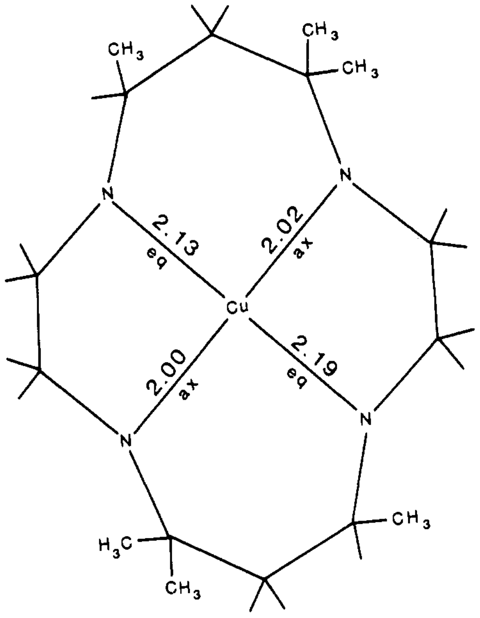

Figure 4. Coordination of the macrocyclic tetraamine tet-b to the copper atom in $Cu(tet\text{-}b)(o\text{-}SC_6H_4CO_2)$.

The ligand fields of the fifth ligands in the two systems appear to differ significantly, however. The low value of 1000–2000 cm^{-1} observed for $e_\sigma(O)$ is to be contrasted with one of 2000–3500 cm^{-1} for $e_\sigma(I)$ in the bpy complex, despite the higher position of oxygen in the spectrochemical series, and with one of 3700 cm^{-1} for $e_\sigma(N_{eq})$ in the following analysis for virtually equal M–L_{eq} bond lengths. On the other hand, the value of $e_{\pi\parallel}(O)$, equivalent to $2e_\pi(O)$ in the present analysis as discussed above, does not appear abnormally low. We emphasize that, despite the obvious correlations between the various parameter values in this study, the low $e_\sigma(O)$ value is certain. Calculations with $e_\sigma(O)$ values anywhere near the more expected values of, e.g., 3500–4500 cm^{-1} do not yield satisfactory agreement between observed and calculated transition energies, whatever values are chosen for the remaining parameters.

Finally, many calculations were performed, employing "best-fit" parameter sets within the space defined by Table III, to determine the magnitudes and orientations of the principal molecular g values as functions of spin–orbit coupling and Stevens' orbital reduction parameter. All such calculations yielded results like those illustrated in Figure 2. Thus, essentially perfect reproduction of the experimental[4] g^2 tensor is attainable without providing any further sharpening of the various parameter estimates. Again, this is disappointing but seems to be a common feature of the ESR experiment with copper(II) systems. The good agreement obtained by Bencini and Gatteschi,[4] therefore, is but one of a whole range of such fits and no especial weight should be placed upon it—indeed, rather the reverse as it corresponds to a parameter set that makes little chemical sense, as they observed.

Cu(tet-b)(*o*-$SC_6H_4CO_2$). This formally TBP structure involves the macrocyclic ligand *rac*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane or tet-b, for short, coordinated to two axial and two equatorial TBP sites in the copper(II) complex in a chemically symmetrical way. The cyclic tetraamine coordination is shown schematically in Figure 4. The Cu–N_{ax} bond lengths[10] average 2.01 Å, and the Cu–N_{eq} lengths, 2.16 Å. As in the bpy and phen structures, the TBP coordination geometry thus involves an axially compressed distortion. The N_{eq}–Cu–N'_{eq} angle is 103.5°. Hughey et al.[10] have claimed that the mercaptobenzoate is to be regarded as a mercaptide: there is "full Cu–S equatorial bonding" as evidenced by the bond length of 2.36 Å and a lengthening of the Cu–N_{eq} bonds. The Cu–S–C angle is 108.4° so that sp^3 hybridization for the S atom appears to be a reasonable guide. *We* consider the Cu–S bond to be neither especially long nor especially short. Further, the long Cu–N_{eq} bonds will be interpreted as reflecting a property of the copper atom rather more than the "fullness" of the Cu–S interaction. Altogether, therefore, we have conducted our fitting procedures with minimal prejudice on this issue, regarding the possibility of Cu–S bonding involving only σ contributions, on the one hand, or more than σ, on the other, as equally acceptable, a priori. We begin, however, with the simplest AOM schemes, incorporating only Cu–S σ bonding. In no case do we envisage a π-bonding role for the saturated amines comprising the nitrogen donor set in this system.

The analysis is based primarily upon the reported[10] d–d spectra, obtained from KBr pellets, mulls, and methanolic KOH solution experiments. A reasonably intense absorption at 13 700 cm^{-1} is accompanied by less intense, well-resolved shoulders at ca. 11 000 and ca. 17 000 cm^{-1}. Bands beyond 20 000 cm^{-1} are assigned to charge-transfer and other non-d–d transitions. No assignments are available for the three d–d bands observed.

No satisfactory reproduction of the spectrum is possible with use of an AOM parameterization scheme which constrains the axial and equatorial amine ligators to be equivalent, that is, with use of the two free parameters $e_\sigma(N) \neq e_\sigma(S)$. The calculated spectral pattern is characterized by too wide a spread of transitions for a satisfactory mean transition energy or, alternatively, an acceptable spectral width occurring at too low a mean energy. Recognition of the dissimilar axial and equatorial amine sites, involving the parameter set $e_\sigma(N_{ax})$, $e_\sigma(N_{eq})$, $e_\sigma(S)$, proved completely effective, however, defining an extended region of parameter space affording excellent reproduction of the observed spectrum. In all cases, the calculated eigenvalue spectrum falls into the pattern A_1 (ground) < B_2 (ca. 11 000 cm^{-1}) < A_1 (ca. 13 700 cm^{-1}) < B_1 (ca. 16 800 cm^{-1}) ≤ A_2 (ca. 17 300 cm^{-1}), where the (approximate) speciation corresponds with a C_{2v} point group using Cu–S as the principal rotation axis. In that same (idealized) point group, the $A_1 \rightarrow A_2$ transition is formally forbidden, so that some consistency with the overall observed spectrum is evident here also. The fitting region defines values for $e_\sigma(N_{ax})$ and $e_\sigma(N_{eq})$ fairly sharply, but not for $e_\sigma(S)$: the situation is illustrated in Figure 5. Excellent fits to the spectrum occur in the cylindrical region of this three-parameter space, the axis of which cylinder defines the relationships

$$\begin{aligned} e_\sigma(N_{ax}) &= -0.105[e_\sigma(S)] + 7585 \\ e_\sigma(N_{eq}) &= -0.31[e_\sigma(S)] + 5550 \end{aligned} \qquad (1)$$

when the AOM parameters are expressed in wavenumbers, as usual. Throughout the fitting region as a whole, while $e_\sigma(N_{ax})$ falls within 150 cm^{-1} of a mean value of 6900 cm^{-1} and $e_\sigma(N_{eq})$ within 300 cm^{-1} of a median 3700 cm^{-1}, values for $e_\sigma(S)$ range from 3000 to 8000 cm^{-1}. In any horizontal plane of the cube depicted in the diagram, acceptable $e_\sigma(N_{ax})$ values lie in the range ±100 cm^{-1} of the local mean, and similarly good $e_\sigma(N_{eq})$ values lie in a range of ±250 cm^{-1}.

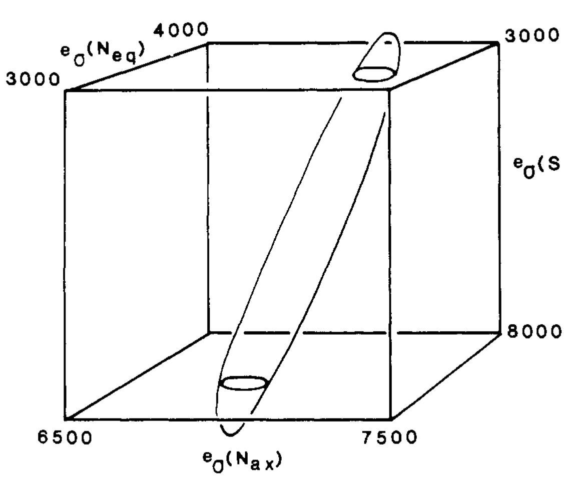

Figure 5. Region of good fit to the d–d spectrum of the tet-b complex.

Having obtained essentially perfect agreement with experiment using the three-parameter σ scheme, we can hardly justify extending the freedom of the model further. Nevertheless, it is obviously of interest to enquire, at least, if a model that includes any other form of Cu–S interaction could also reproduce the spectral data. As noted above, a description of the sulfur atom as sp^3 hybridized seems apposite, so we should consider any possible ligand field arising from the two lone pairs directed at roughly the tetrahedral angle away from the metal. These circumstances are appropriately dealt with by using local off-diagonal matrix elements of the form $e_{\pi\sigma} \equiv \langle d_{z^2}|v|d_{xz}\rangle$, as described elsewhere.[7-9] In the present case of two lone-pair interactions, calculations were performed by considering the ligand as a superposition of two "half-ligands" whose local *zx* planes are rotated with respect to one another about the local *z* axis, so as to include the (idealized) lone pairs. For each "half-ligand", inclusion of the off-diagonal parameter $e_{\pi\sigma}$ also logically requires inclusion of the diagonal element $e_{\pi x}$ ($\equiv e_{\pi\parallel}$) into the parameter set. Many calculations were performed, with $e_\sigma(N_{ax})$ = 7080 cm^{-1}, $e_\sigma(N_{eq})$ = 4000 cm^{-1} held as mean values, $e_\sigma(S)$ ranging from 4000 to 6000 cm^{-1}, and both sets of $e_{\pi\parallel}(S)$ and $e_{\pi\sigma}(S)$ parameters being varied independently from 0 to 150 cm^{-1}. Only small shifts in calculated energies were found, partly because the effects of $e_{\pi\sigma}$ and $e_{\pi\parallel}$ tend to oppose one another. The 11 000-cm^{-1} band was the most affected, and for this, calculated shifts were never more than 1000 cm^{-1} and usually around 300–400 cm^{-1}. Overall, we conclude that the present analysis neither supports nor denies the possibility of any multiple Cu–S interactions.

Hughey et al.[10] reported powder *g* values for Cu(tet-b) as 2.074, 2.086, and 2.117. Using various parameter combinations from the best-fit series, or even some rather less acceptable values with respect to optical spectrum reproduction, we could *not* reproduce these *g* values: typically, the best computed principal molecular *g* values we could achieve were 2.00, 2.12, and 2.14. Hughey et al.[10] regard their *g* values as "...appropriate for a magnetically dilute copper(II) chromophore having rhombic symmetry", which statement might be taken to imply a belief that their ESR spectrum pertained to a purely molecular experiment. However, it is common to find that an otherwise trivial degree of magnetic concentration in the solid can yield a spectrum of the *crystal* rather than of the molecule, while the spirit of the quotation above need not be broken. Using the known orientation of the molecules in the monoclinic lattice, we find that a tensorial addition of our calculated molecular *g* properties immediately yields principal *crystal g* values in excellent agreement with those reported by Hughey et al.[10] Once again, however, no sharpening of the AOM parameter values can be achieved, the situation being entirely similar to that represented in Figure 2 for the bpy and phen systems.

Discussion

The analyses of the bipyridyl and phenanthroline complexes demonstrate that the two ends of these otherwise symmetrical chelates behave markedly differently toward the copper atom in these systems. We consider this gross fact first, returning to more quantitative detail subsequently. We have described the analytical processes so fully in order that there be no doubt about the conclusions we now summarize and seek to interpret. The axial nitrogen coordinating atoms affect the metal d electrons so as to reflect a greater σ-donor function—roughly by a factor of 2 in terms of e_σ values—than for the equatorial nitrogen ligators. At the same time, the π donation by the axial ligators is also significantly greater than that by the equatorial ones: indeed, typical parameter sets suggest that, while the axial groups function as π donors, the equatorial ones act as π acceptors. As the free ligands are undoubtedly symmetric, this behavior is clearly caused by the complex environment.

The most obvious factor differentiating axial and equatorial sites of the TBP coordination shell arises from the metal electron configuration. While the distribution of electrons or holes in, e.g., high-spin d^7 systems will normally be relatively even over angular space, the single hole in the d^9 shell is frequently quite localized. In the TBP structure this is especially true, the hole being associated with the d_{z^2} orbital (with respect to the principal axis of a TBP description) and hence predominantly on or near the axial, *z*, direction. (Note that we have redefined *z*, e.g. by interchanging *x* and *z*, from that given in Figure 1. Our discussion here begins with a D_{3h} idealized symmetry as precursor.) Now, as argued extensively elsewhere,[7,9] the ligand-field formalism is apposite in transition-metal chemistry because the d electrons are largely uncoupled from the rest, rather like the way π electrons are "isolated" in the delocalized organic systems studied by "π-electron theory".[18] Accordingly, we regard the bonding electron density as predominantly established by overlap of ligand and *other* metal orbitals (s and p). Then the hole in the d shell concentrated near the TBP *z* axis repels the local bonding electrons less than the electrons in the filled d orbitals in the equatorial plane. This view closely parallels that first suggested by Gillespie,[19] and later by Ibers et al.,[20] at a time when metal d-orbital participation in transition-metal bonding was widely regarded as more important than it is now, at least by us. Anyway, as a consequence of the oblate ellipsoidal form of d-electron charge density on the copper ion in these structures, the axial ligands are expected to approach the metal more closely and to donate negative charge more strongly than those at the equatorial sites. It seems that a similar situation obtains for ligand–metal π donation. Of course, enhanced σ and π donation by the axial nitrogen ligators would notionally leave too high a positive charge on these atoms. Unlike the situation with normal σ and π donors, such as the halogens, our expectation is that enhanced σ donation by the axial nitrogen atoms might be associated with a lesser π donation or even a greater π acidity by familiar synergic processes. An approach to electrical balance can be achieved in the bpy and phen ligands, however, by another means. The electron deficit on the axial nitrogens can be made good by donation from the equatorial nitrogens via the chelate delocalized π-electron network. In turn, the consequent deficit on these nitrogen atoms is remedied by π donation from the metal which was electronically enriched initially by the axial nitrogen atoms. In short, we propose a synergic type of interaction that extends over the *whole* chelate, as illustrated schematically in Figure 6.

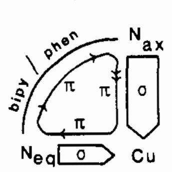

Figure 6. Synergic interaction in the bpy and phen complexes in which "back-bonding" involves the ligand π network.

Should it be argued that so large a difference in e_σ parameters for the two sites seems at odds with the near-equality of the Cu–N bond lengths, we observe that this geometry—a very slight axial compression—should be viewed against an elongation to be expected from the closed-shell considerations of simple Gillespie–Nyholm theory.[21] In rather similar vein, we argue that the greater TBP compression observed in the tet-b complex does not result from macrocycle ring strain: we provide evidence of the plasticity of this tetraamine ligand shortly. Instead, the lack of any Cu–N π interaction with the amines of tet-b implies that similar synergic processes do not operate. The axial nitrogens are notionally less positive initially than in the bpy or phen systems; in turn so are the equatorial nitrogens, and this is evidenced by their having found equilibrium at greater Cu–N distances than in the π-bonded systems. So the compression (or lateral expansion) of the Cu(tet-b) TBP structure, together with the marked dissimilarity of the nitrogen e_σ parameter values, reflects the seminal cause of all the "unusual" AOM parameter values we have discussed so far in this paper, namely, the hole in the d_{z^2} orbital.

It is interesting to contemplate the relationship between the proposed scheme and the familiar Jahn–Teller situation in "octahedral" copper(II) species. Octahedral d^9 systems commonly suffer tetragonal elongation to remove the orbital degeneracy in the e_g subshell that would otherwise obtain. In the TBP structures, the ground term is orbitally nondegenerate, of course, and is therefore not subjected to first-order Jahn–Teller distortion. But, despite this group-theoretical difference, both systems distort from otherwise "normal" geometries for essentially the *same* reason—the sterically active hole in the d shell.

Turning from the major qualitative feature of asymmetric chelation in these TBP structures, we now consider the quantitative differences between the AOM parameters for the phen and bpy complexes. They occur in two areas: one concerned with the different behaviors of the bpy and phen ligation, and the other with a comparison of the fifth ligands in each complex. We shall argue that these different features are related. First, we have noted that the difference between e_σ parameters for axial and equatorial nitrogens is rather less pronounced in the phenanthroline complex than in the bipyridyl one. We have also noted the small $e_\sigma(\mathrm{O})$ value for the copper–water interaction in the phen system: from Table III, values around 1000–1500 $\mathrm{cm^{-1}}$ are typical. By contrast, the $e_\sigma(\mathrm{I})$ values for the Cu–I ligation in the bipyridyl molecule lie in the more usual range, 2000–4000 $\mathrm{cm^{-1}}$, and yet water lies higher than iodine in the spectrochemical series. The low $e_\sigma(\mathrm{O})$ value seems to be in line with the relatively long Cu–O bond length of 2.18 Å. Compare this length with the Cu–N_{eq} distance of 2.03 Å and then note, for example, that the Cu–O bond length[22] in the equatorial octahedral coordination site

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[18] Lykos, P. G.; Parr, R. G.; *J. Chem. Phys.* **1956**, *24*, 1166.

[19] Gillespie, R. J. *J. Chem. Soc.* **1963**, 4679.

[20] Raymond, K. N.; Meek, D. W.; Ibers, J. A. *Inorg. Chem.* **1968**, *7*, 1111.

[21] Gillespie, R. J.; Nyholm, R. S. *Q. Rev., Chem. Soc.* **1957**, *7*, 339.

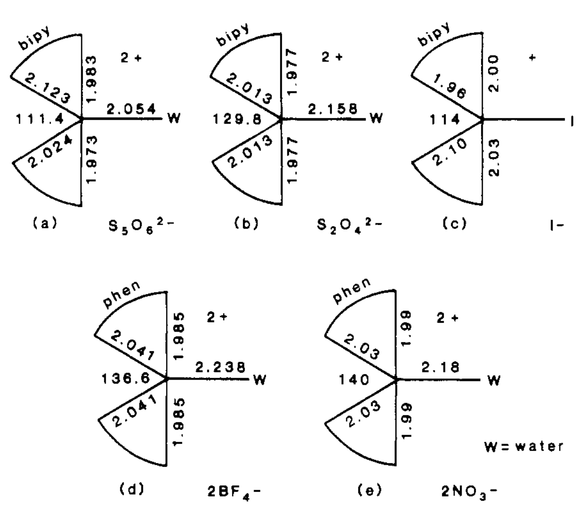

Figure 7. Comparative geometries for some formal TBP phen and bpy copper(II) complexes: (a) ref 24; (b) ref 25; (c) ref 12; (d) ref 26; (e) ref 5.

of bis(hexafluoroacetylacetonate)(bipyridine)copper is 1.93 Å while the Cu–$\mathrm{N_{eq}}$ bond length in the same complex is 1.98 Å. More persuasive still is the geometry pattern summarized in Figure 7 for a series of formal TBP systems. Each molecule presented possesses either exact (crystallographic) or approximate twofold symmetry with respect to the copper–water (or copper–iodine) bonds. The series illustrates a trend from near-TBP geometry (Figure 7a, c) toward square pyramidal (SPY)—Figure 7d, e, especially—as evidenced most particularly by the $\mathrm{N_{eq}}$–Cu–$\mathrm{N_{eq}}$ bond angles. The geometry adopted in each case appears to be a function of the counterion, so that crystal-packing forces are once again important in copper(II) structural chemistry. It seems that the strong spatial asymmetry of the one-hole electronic structure is the root cause of this evident plasticity of the TBY–SPY transition. Those structures of Figure 7 that begin to approximate SPY geometry—the present phenanthroline complex, in particular—involve a large coordinationally void region opposite the fifth ligand. The ligand-field form of the AOM requires such "empty cells" to be parameterized with a substantial and negative e_σ value, as discussed and experimentally verified in the preceding paper. So the "e_σ(O)" value determined in the present analysis is the mean of the true e_σ(O) value and that for the coordination void opposite: a mean, because of the usual consequences of the holohedral symmetry.[9,23] We emphasize that this diminution of the e_σ(O) value in the present phen complex is additional to any such arising out of the longer Cu–O bond length.

A simultaneous consequence of the trend from TBP to SPY (bpy and phen and complexes) is some lessening distinction between axial and equatorial sites (TBP description) for the nitrogen ligators. From Tables II and III, we observe typical values for $e_\sigma(\mathrm{N_{ax}})$ and $e_\sigma(\mathrm{N_{eq}})$ of 7000 and 3000 cm^{-1} for the bipyridyl complex or of 7000 and 4000 cm^{-1} for the phenanthroline complex. This trend, taken together with the low e_σ(O) value, persuades us of the reality of the ligand-field activity of an empty cell subtending an $\mathrm{N_{eq}}$–Cu–$\mathrm{N_{eq}}$ angle of 140°: it has already been demonstrated for planar (180°) and regular SPY (164°) geometries in the preceding paper.

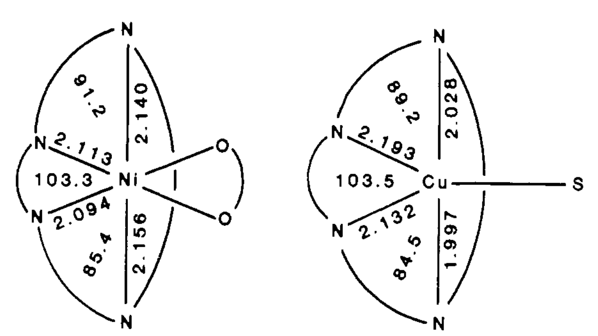

Figure 8. Coordination geometry of tet-b in [Ni(tet-b)(OAc)]$^{+}$[27] compared with that in the present copper(II) complex.

Considering a trend from TBP toward SPY geometry in these d^9 systems, the hole in the d shell becomes associated less uniquely with the d_{z^2} orbital (TBP description again) and so the facility of TBP ↔ SPY conversion is enhanced. Thus a change of geometry along this structural pathway is accompanied by the ligand-field changes just described—the contribution from the coordination void and the changing roles of the axial and equatorial TBP sites—which lead in turn to a different location of the d hole. Altogether, the hole in d_{z^2} confers stability on the TBP geometry but moves on distortion, conferring stability on the new geometry: the electronic equivalent of neutral mechanical equilibrium. Against this electronic background, the sensitivity of these structures to crystal-packing forces seems readily acceptable.

We have mostly discussed the various copper–nitrogen interactions so far, but we recall that the main interest of Hughey et al.[10] in the tet-b complex lay with the sulfur ligand. Those authors argued for "full Cu–S bonding" as evidenced by (a) the "short" Cu–S bond length of 2.36 Å and (b) and "long" Cu–$\mathrm{N_{eq}}$ bonds. We have argued that the long equatorial Cu–N contacts and "compressed" TBP geometry, violating the simple Gillespie–Nyholm prediction, is a direct consequence of the single hole in the copper d^9 configuration. We further contend that the more marked elongation of the equatorial Cu–N bonds in the tet-b structure results from the lack of the π bonding with this cyclic amine. So we do not believe that the long Cu–$\mathrm{N_{eq}}$ bonds owe much to the Cu–S interaction. In support of this, compare the geometries of the present tet-b complex and an octahedral complex of nickel(II), as shown in Figure 8. It is interesting to observe how, despite the different coordination numbers and gross geometries, the angular details of the macrocyclic coordination are so similar in the two systems. At the same time, however, we note that the tet-b ligand is sufficiently flexible to accommodate the reversed sense of axial vs. equatorial bond lengths. Altogether then, we consider that these various geometrical features fail to support Hughey et al.'s[10] contention that full Cu–S bonding is evidenced by the Cu–$\mathrm{N_{eq}}$ bond lengths. It is then especially disappointing that our AOM analysis fails to establish directly, either way, whether any form of Cu–S multiple bonding is indicated by the electronic spectrum. This neutral result is, of course, no indictment of the AOM ligand-field approach itself.

The notable achievement of the present study is the demonstration of marked asymmetric chelation by the bipyridyl and phenanthroline ligands. This result is interesting not only for the intrinsic chemical bonding views it engenders but also for its implicit comment upon the angular-overlap method itself. Bencini and Gatteschi[4] obtained fits to their hard-won spectra involving dissimilar e_σ(N) values but considered them "not to be meaningful since...the $e_\sigma(\mathrm{N_{ax}})$ and $e_\sigma(\mathrm{N_{eq}})$ values are too different from each other". Clearly, the thinking behind this statement stems from a view of the AOM as a molecular orbital approach and that e_λ parameters are pro-

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(22) Veidis, M. V.; Schreiber, G. H.; Grugh, T. E.; Palenik, G. T. *J. Am. Chem. Soc* **1969**, *91*, 1859.

(23) Jørgensen, C. K. "Modern Aspects of Ligand Field Theory"; North-Holland: Amsterdam: 1971.

(24) Harrison, W. D.; Hathaway, B. J.; Kennedy, D. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *35B*, 2301.

(25) Harrison, W. D.; Hathaway, B. J. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *36B*, 295.

(26) Nakai, H.; Noda, Y. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1386.

(27) Wimp, P. O.; Bailey, N. A.; Curtis, N. F. *J. Chem. Soc. A* **1970**, 1956.

portional to the squares of metal-ligand overlap integrals. We have urged, many times, both empirically and theoretically, that the AOM *as used* in ligand-field analysis is *not* a molecular orbital scheme and does not suffer the whole range of deficiencies normally associated with semiempirical and approximate MO models applied to transition-metal systems. We argue, therefore, for a realignment of our prejudices based on well-founded ligand-field theory rather than on more common but inappropriate molecular orbital theory.

Acknowledgment. We record our appreciation of useful discussions with Dr. R. G. Woolley.

Registry No. [Cu(bpy)$_2$I]$^+$I$^-$, 15679-48-8; [Cu(phen)$_2$H$_2$O]$^{2+}$(NO$_3$)$^-_2$, 57572-96-0; Cu(tet-b)(*o*-SC$_6$H$_4$CO$_2$), 92471-16-4.

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Dynamics of Spin-State Interconversion and Cooperativity for Ferric Spin-Crossover Complexes in the Solid State. 1. The Unperturbed Fast Spin-Flipping N$_4$O$_2$ Complex [Fe(SalAPA)$_2$]ClO$_4$

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Samples of the ferric spin-crossover complex [Fe(SalAPA)$_2$]ClO$_4$, where SalAPA is the monoanionic Schiff base derived from salicylaldehyde and *N*-(3-aminopropyl)aziridine, prepared by two different methods, are shown to have different properties. In the more crystalline samples, [Fe(SalAPA)$_2$]ClO$_4$ is one of the relatively rare N$_4$O$_2$ ferric spin-crossover complexes that flip spins between the low-spin and high-spin states at a rate faster than the ^{57}Fe Mössbauer time scale. On the other hand, the less crystalline sample of [Fe(SalAPA)$_2$]ClO$_4$ shows two quadrupole-split doublets in the Mössbauer spectrum from ~150 to 205 K. Differences are also seen in the magnetic susceptibility and EPR characteristics for these two types of samples, in spite of the fact that both sample types have the same chemical analyses and IR spectra and similar (lines are sharper in more crystalline samples) powder X-ray diffraction patterns. It is concluded that the less crystalline sample type has a greater concentration of defect structure than the crystalline samples that give one (average) quadrupole-split doublet. The increased defect structure results in a certain fraction of the ferric complexes either persisting totally in the high-spin state across the temperature range or more slowly interconverting between low- and high-spin states. Both types of samples of [Fe(SalAPA)$_2$]ClO$_4$ are found to flip spins faster than a sample of the related N$_4$O$_2$ complex, [Fe(SalAEA)$_2$]ClO$_4$, which contains the monoanionic ligand derived from salicylaldehyde and *N*-(2-aminoethyl)aziridine. The factors that lead to certain N$_4$O$_2$ ferric spin-crossover complexes flipping spins faster by at least 1 order of magnitude than other N$_4$O$_2$ complexes are discussed.

Introduction

Spin-crossover behavior has been observed for complexes of Mn^{3+} (d^4),[2] Mn^{2+} (d^5),[3] Co^{3+} (d^6),[4] Co^{2+} (d^7),[5] and Ni^{2+} (d^8),[6] for inorganic solids containing Mn^{3+},[7] Fe^{2+},[8] or Co^{3+},[9] and for cluster compounds of niobium.[10] The results for ferrous spin-crossover complexes, which have received by far the greatest attention, are summarized in a comprehensive and recent review by Gütlich.[11] Spin-crossover ferric complexes, also quite prominent in the literature since the initial work by Cambi et al.[12] on the tris(dithiocarbamates), were last reviewed by Martin and White;[13] a more current account by Sinn is forthcoming.[14]

In the last few years attention has been directed to understanding the kinetics and mechanisms of the spin-crossover transformation. A given complex interconverts between low-spin and high-spin electronic states in what amounts to an intramolecular electron-transfer reaction. In the *solution state* it appears that there is a dynamic equilibrium present with a Boltzmann distribution of spin-crossover complexes in low-spin ground and high-spin excited states, as indicated by variable-temperature magnetic susceptibility data (Evans technique). Relaxation techniques have been used to measure spin-crossover interconversion rates for complexes in *solution*.[15-24] Buhks et al.[25] have applied the theory of radiationless nonadiabatic multiphonon processes in order to estimate the rate of spin-state interconversion of complexes in *solution*.

Most investigations of the physical properties of spin-crossover complexes have been conducted exclusively on samples in the *solid state*. Spin-crossover transformations come

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(1) 3M Fellowship, 1979-1980. Owens-Corning Fellowship, 1980-1981. Present address: Magnetic Audio/Video Products Division, 3M, St. Paul, MN 55144.

(2) Sim, P. G.; Sinn, E. *J. Am. Chem. Soc.* **1981**, *103*, 241.

(3) Ammeter, J. H.; Zoller, L.; Bachmann, J.; Baltzer, E.; Gamp, E.; Bucher, R.; Deiss, E. *Helv. Chim. Acta* **1981**, *64*, 1063.

(4) Klaui, W. *J. Chem. Soc., Chem. Commun.* **1979**, 700.

(5) Barefield, E. K.; Busch, D. H.; Nelson, S. M. *Q. Rev., Chem. Soc.* **1968**, *22*, 457.

(6) Sacconi, L. *Pure Appl. Chem.* **1971**, *27*, 161.

(7) Haneda, S.; Noriaki, K.; Yamaguchi, Y.; Watanabe, H. *J. Phys. Soc. Jpn.* **1977**, *42*, 31.

(8) Eibschütz, M.; Lines, M. E. *Phys. Rev. Lett.* **1977**, *39*, 726.

(9) Ramasesha, S.; Ramakrishnan, T. V.; Rao, C. N. R. *J. Phys. C* **1979**, *12*, 1307.

(10) Imoto, H.; Simon, A. *Inorg. Chem.* **1982**, *21*, 308.

(11) Gütlich, P. *Struct. Bonding (Berlin)* **1981**, *44*, 83.

(12) (a) Cambi, L.; Cagnasso, A. *Atti. Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1931**, *13*, 809. (b) Cambi, L.; Szego, L. *Ber. Dtsch. Chem. Ges.* **1931**, *64*, 2591.

(13) Martin, R. H.; White, A. H. *Transition Met. Chem. (N.Y.)* **1968**, *4*, 113.

(14) Sinn, E., private communication.

(15) Binstead, R. A.; Beattie, J. K.; Dewey, T. G.; Turner, D. H. *J. Am. Chem. Soc.* **1980**, *102*, 6442.

(16) Binstead, R. A.; Beattie, J. K.; Dose, E. V.; Tweedle, M. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 5609.

(17) Beattie, J. K.; Binstead, R. A.; West, R. J. *J. Am. Chem. Soc.* **1978**, *100*, 3044.

(18) Reeder, K. A.; Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 1071.

(19) Petty, R. H.; Dose, E. V.; Tweedle, M. F.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 1064.

(20) Dose, E. V.; Hoselton, M. A.; Sutin, N.; Tweedle, M. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 1141.

(21) Simmons, M. G.; Wilson, L. J. *Inorg. Chem.* **1977**, *16*, 126.

(22) Dose, E. V.; Murphy, K. M. M.; Wilson, L. J. *Inorg. Chem.* **1976**, *15*, 2622.

(23) Hoselton, M. A.; Drago, R. S.; Wilson, L. J.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6967.

(24) Beattie, J. K.; Sutin, N.; Turner, D. H.; Flynn, G. W. *J. Am. Chem. Soc.* **1973**, *95*, 2052.

(25) Buhks, E.; Navon, G.; Bixon, M.; Jortner, J. *J. Am. Chem. Soc.* **1980**, *102*, 2918.

0020-1669/84/1323-3861$01.50/0