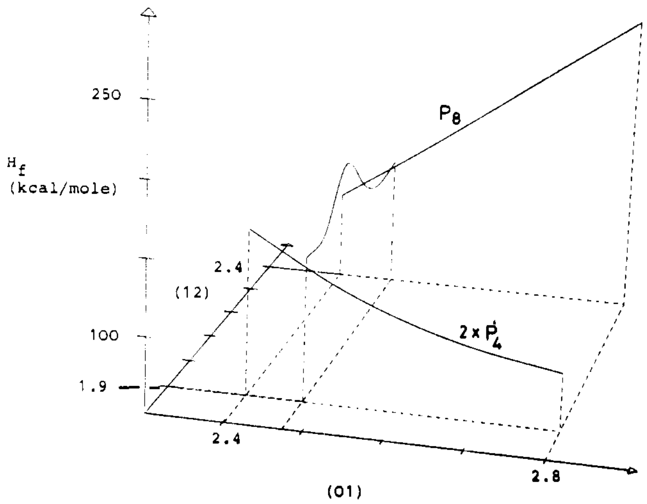

Figure 4. Crossing from A to B in $D_{3d}$ at (01) = 2.475 Å.

## Conclusions

The presence of a barrier some 100 kcal high to the dimerization of tetrahedral $P_4$ to cubic $P_8$ has been established computationally. The calculations confirm the results of the orbital symmetry analysis, which predicts the presence of such a barrier, ascribing it to the incompatibility of one doubly occupied LCBO of the two $P_4$ ($a_{2u}$) with one of $P_8$ ($a_{1u}$), which cannot be overcome by any reduction of symmetry below $D_{3d}$, which is both geometrically feasible and energetically convenient.

An energy barrier of this magnitude should be sufficient to prevent the formation of cubic $P_8$ at temperatures below that at which $P_4$ is fully dissociated to $P_2$, particularly if routes to more stable species such as red $(P_4)_n$ are available. The possible formation of noncubic $P_8$ species, which can serve as possible intermediates in the polymerization process, is presently being explored.[11]

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**Registry No.** Phosphorus, 7723-14-0.

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(11) Bock, H.; Roth, B.; Halevi, E. A. unpublished results.

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# EPR of Copper(II) Complexes with Tripodal Ligands: Dynamical Properties

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A major theme in bioinorganic chemistry is the understanding of the role played by metal ions in metalloenzymes with particular focus on their unique characteristics. Many of the iron proteins can be successfully modeled because they contain extrinsic active sites which may be reasonably reproduced outside of the actual protein. By contrast, copper proteins possess intrinsic active sites which are uniquely defined by the interactions of the ligating protein residues with the copper ions.[2] Thus, much of the activity in generating model systems for copper proteins has focused on small, well-defined structural or spectroscopic analogues that allow a particular feature(s) to be examined in detail. Many of the studies heretofore have examined the static spectral characteristics because these aspects may (or even must) be understood before additional dynamical features can be explored. Nevertheless, it is clear that a detailed understanding of the motional adjustments of the metalloprotein are needed to provide information on reaction rates and other dynamical properties.[3] Indeed, since changing structural properties are believed to be important in influencing the chemistry of real copper-containing enzymatic systems,[4-7] a further step in modeling enzyme active sites and reactivity should be to examine the possible roles of dynamical distortions in physcially realistic model systems.

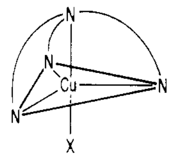

Figure 1.

This paper provides a vehicle for examining dynamical behavior by EPR spectroscopy on trigonal-bipyramidal (TBP) systems of the type $[Cu(TMPA)X]PF_6$, TMPA = tris(2-pyridylmethyl)amine and X = $Cl^-$ and $N_3^-$, in frozen solutions and as a single crystal for X = $Cl^-$. The latter material has been characterized by X-ray crystallography[8] and has in-plane bonding very close to the 120° expected in the ideal TBP geometry.[8] A schematic drawing is shown in Figure 1. The usefulness of some tripod ligands in studying and modeling certain aspects of the coordination chemistry and structural properties of five-coordinate copper(I) and copper(II) complexes is well established.[8-13] Furthermore, the general features of many EPR spectra of five-coordinate Cu(II) covering the full range from TBP to square pyramidal are also now reasonably well understood within the framework of the $C_{2v}$ model.[14] Of course, the well-known tendency of the Cu(II) ion to prefer a square-pyramidal geometry has greatly limited the number of examples that approach the trigonal-bipyramidal limit. Thus Cu(II) complexes near this limit might be expected to exhibit a rhombic EPR pattern and some do. On

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(2) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding (Berlin)* **1983**, *53*, 1–57 and references cited therein.

(3) Gurd, F. R. N.; Rothgeb, T. M. *Adv. Protein Chem.* **1979**, *33*, 77–166.

(4) An example of this kind is the dramatic structural changes expected and observed at Cu(I)–Cu(II) centers in redox-active copper metalloproteins.

(5) Gray, H. B.; Solomon, E. I. In "Copper Proteins"; Spiro, T. G., Ed.; Wiley: New York, 1981; pp 1–40. Solomon, E. I. *Ibid.* pp 41–108.

(6) Bacci, M. *Struct. Bonding (Berlin)* **1983**, *55*, 67.

(7) Karlin, K. D.; Zubieta, J., Eds. "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Adenine Press: Guilderland, NY, 1983.

(8) Karlin, D. D.; Hayes, J. C.; Juen, S.; Hutchinson, J.; Zubieta, J. *Inorg. Chem.* **1982**, *21*, 4106 and references cited therein.

(9) Padula, F.; Goldstein, C.; Orsini, J.; Kokoszka, G.; Karlin, K. D. *Inorg. Chim. Acta* **1983**, *79*, 198–199.

(10) Zubieta, J.; Karlin, K. D.; Hayes, J. C. In ref 5, pp 97–108.

(11) Sorrell, T. N.; Jameson, D. L. *Inorg. Chem.* **1982**, *21*, 1014.

(12) Addison, A. W.; Hendriks, H. M. J.; Reedijk, J.; Thompson, L. K. *Inorg. Chem.* **1981**, *20*, 103.

(13) Thompson, L. K.; Ball, R. G.; Trotter, J. *Can. J. Chem.* **1980**, *58*, 1566–1576.

(14) Bencini, A.; Bertini, I.; Gatteschi, D.; Scozzafava, A. *Inorg. Chem.* **1978**, *17*, 3194.

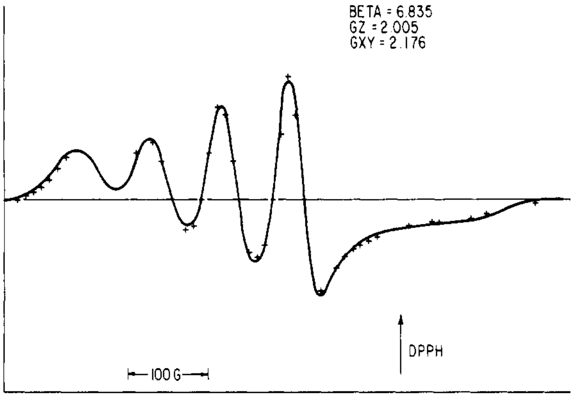

**Figure 2.**

the other hand, a reasonable number exhibit an apparent axial spectrum. One purpose of this paper is to propose that the axial appearance of many of the EPR spectra of TBP Cu(II) complexes may be due to vibronic effects that average the in-plane $g$ and $A$ values.

## Experimental Section

The EPR spectra of frozen solutions of several Cu(TMPA) complexes in various solvents as well as single crystals of the chloride complex were obtained with a Varian E-4 spectrometer equipped with a liquid-nitrogen Dewar insert and variable-temperature device. The solutions that produced well-resolved spectra included DMF–$CHCl_3$ (1:1 ratio), acetone–ethanol–methanol (1:1:1 ratio), and DMF–ethanol–methanol (1:1:1 ratio). Occasionally, a rhombic spectrum could be observed in the lower temperature range. However, most of the time good glassy spectra were obtained and exhibited the major features shown in Figure 2: (1) a "reversed Cu(II) pattern", (2) the four low-field hyperfine components increasing in peak-to-peak height and narrowing in width with increasing magnetic field, (3) no structure in the broad parallel region above the well-resolved hyperfine components, and (4) no ligand hyperfine structure. Most spectra were observed at 77 K, but several glassy samples were studied as a function of temperature over the limited range in which the glass exhibited high viscosity. In addition, some of our earlier spectra on single crystals and polycrystalline samples of [Cu(TMPA)Cl]$PF_6$ were remeasured[8,9] and the line shape of the pure material showed deviation from the Lorentzian shape in the region around $g = 2$ in both the single-crystal and polycrystalline samples of the pure material. The latter was inferred from computer simulation of the spectrum.

## Discussion

The tendency for Cu(II) ions to form square-pyramidal or elongated-octahedral complexes with a $x^2 - y^2$ ground state is well-known. Even in tetrahedral complexes, greatly distorted TBP samples, or seemingly compressed octahedral complexes, the ground state is or contains usually some metal $x^2 - y^2$ orbital character.[7,15,16] For many nearly TBP complexes there is a temptation to assert that the metal $x^2 - y^2$ contribution to the ground state has been effectively countered and that the metal $z^2$ orbital contribution has been achieved because of the reversed axial appearance of the EPR spectrum. Experimentally, in terms of the $C_{2v}$ model[14] it would seem that the $\alpha = 120°$ limit (equatorial angle) is the usual case rather than the exception. However, we believe that a closer examination of the data suggests that a small but important $x^2 - y^2$ contribution remains in the ground state and that the apparent axial appearance of the reversed spectra is due to vibronic effects. These effects are not associated with the usual Jahn–Teller effects[6,15] nor can they be associated with purely strain effects although the latter may play a role in some cases.[17] Some background information on the pure material is presented next.

A more detailed treatment of our initial attempts to interpret the EPR spectrum of the single crystal in terms of a weak intermolecular exchange[9] ($J\bar{S}_1 \cdot \bar{S}_2$) required a good understanding of the magnetic behavior of the isolated complex.[18,19] This was especially important because the observation of the half-field lines in the pure material suggested the presence of mainly dipolar intermolecular forces or quite strong exchange (the upper end of the 10/3 effect curve). The former seems reasonable while the latter seemed unlikely on the basis of the X-ray data and the very light blue color of the crystal—the usual signature of very weak exchange. Therefore, we began to examine the glassy spectra in detail in several frozen solutions and made the four observations outlined above.

In order to extract the magnetic parameters from these spectra, a simple computer program that provided a "best fit" using the $g$ and $A$ values as parameters was developed, but it did not product a very good fit.[18] Further computer simulations of the frozen spectra with a wide range of line shapes and line widths could not satisfactorily reproduce the experimental results. However, it was possible to significantly improve the agreement of the experiment and the theoretical glassy spectrum by invoking a dependence of line width (and later line shape) on $M_I$. Furthermore, by relaxation of the condition $g_\parallel = g_e$ (required for the $\alpha = 120°$ limit in the $C_{2v}$ model[14]), a quite good fit could be obtained (Figure 2). For our computer simulation the line width was assumed to be of the form

$$\Delta H(\theta) = \alpha(\theta) + \beta M_I + \gamma M_I^2$$

while the line shape was

$$S(M_I) = CG + (C - 1)L$$

where $G$ and $L$ are the Gaussian and Lorentzian line shape functions and $C$ varies from 0 to 1. This approximation is similar to that presented by Menzel and Wasson,[20] but they used the squared Lorentzian and Gaussian functions. Comparison with the Anderson mixed line function[21] showed that our simple approximation does not exceed 2% error in the peak-to-peak line width distance from the center. In the "wings" the distortion is somewhat larger, but there is a fortuitous cancellation in errors when the lines centered on nearby points are added together in a glassy spectrum. Because of the simple geometry in the single crystal it was convenient to assume[22]

$$\alpha^2(\theta) = \alpha_\parallel{}^2 \cos^2 \theta + \alpha_\perp{}^2 \sin^2 \theta$$

and this functional form was used to simulate the frozen spectra as well.

The results of a typical spectral fit are shown in Figure 2, where the crosses indicate the maximum deviation of the experimental points from the line width. Where no crosses are shown, the experimental points lie within the calculated curve. Over the limited temperature range that could be studied in the glassy state, it was found that the values of the line shape parameters were similar to those found in solutions[23] but that

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(15) Kokoszka, G. F.; Baranowski, J.; Goldstein, C.; Orsini, J.; Mighell, A. D.; Himes, V. L.; Siedle, A. R. *J. Am. Chem. Soc.* **1983**, *105*, 5627 and references cited therein.

(16) Bencini, A.; Gatteschi, D. *Transition Met. Chem.* (*N.Y.*) **1983**, *8*, 127–142.

(17) Froncisz, W.; Hyde, J. S. *J. Chem. Phys.* **1980**, *73*, 3123.

(18) Presented at the 6th International EPR Conference, Denver, CO, Aug 1982. More details of the program will be published by J. Baranowski et al. in a paper dealing with the temperature dependence of the complex of ref 15.

(19) Barbucci, R.; Bencini, A.; Gatteschi, D. *Inorg. Chem.* **1977**, *16*, 2117.

(20) Menzel, R. E.; Wasson, J. R. *J. Phys. Chem.* **1975**, *79*, 366.

(21) Gaura, R.; Adams, R.; D'Avignon, D.; Kokoszka, G.; Szydlik, P. *J. Magn. Reson.* **1977**, *25*, 299.

(22) Servant, Y.; Bissey, J. C.; Gharbage, S. *J. Magn. Reson.* **1976**, *24*, 335.

(23) Wilson, R.; Kivelson, O. *J. Chem. Phys.* **1966**, *44*, 4440, 4445.

the averaging was mainly in the equatorial plane. These dynamical effects manifested by changes in the M–L distances and the L–M–L angles result in deviation from the idealized 120° TBP geometry. As a consequence, (1) $g_1$ and $g_2$ and (2) $A_1$ and $A_2$ are averaged into an effective $g_\perp$ and $A_\perp$ (see Figure 4 in ref 14). In other words, temperature-dependent metal–ligand vibrations are operative and they (1) average the $g_1$ and $g_2$ values due to a modulation of the $\alpha$ angular parameter and/or (2) produce a jumping of the effective $C_{2v}$ axis between the three equatorial positions. This results in the observed axial spectrum. This vibrational averaging of the $C_{2v}$ model accounts for the lack of a strong temperature dependence of $g_\perp$ and $A_\perp$ because they average two lines which depend on $T$ but (to a first approximation) this average is independent of $T$. In addition, the vibronic effects would be expected to produce a smearing of $A_\parallel$ and a value of $g_\parallel$ that increases with increasing temperature (vibronic activity). This has been observed here and was first measured by Barbucci et al.[19] in a single-crystal study of a TBP complex. Moreover, this proposal of dynamical averaging is consistent with earlier experimental observations.[12,13]

## Conclusion

The results of our experiments and computer simulations suggest that a vibrational effect may be producing the apparent axial appearance of the EPR spectra in five-coordinate complexes of Cu(II) containing tetradentate tripod ligands.[8–12] This result is a natural extension of our chemical intuitive feeling that the Cu(II) ion prefers a metal $x^2 - y^2$ ground state,[10,23] which is also supported by structural data on Cu(II) complexes containing systematically varied tripod ligands.[10] Thus, as in the usual Jahn–Teller effect, it appears that appropriate vibrational modes may be admitted allowing deviation from the $z^2$ ground state that has been forced upon Cu(II) by a constraining tripod ligand. Finally, it may be noted that both intra- and intermolecular effects may be present and play a role in the dynamical processes.[18,24,25]

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**Registry No.** [Cu(TMPA)Cl]$PF_6$, 82865-79-0; [Cu(TMPA)$N_3$]$PF_6$, 92788-05-1.

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(24) For several discussions of related problems, see: *Faraday Discuss. Chem. Soc.* **1980**, *No. 69*.

(25) Abragam, A.; Bleaney, B. "Electron Paramagnetic Resonance of Transition Ions"; Clarendon Press: Oxford, 1970; pp 465–466.

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# Mixed-Ligand Iron(II) Complexes Containing 2,2′-Bipyrimidine. Spectroscopic, Electrochemical, and Coulombic Modification of Highly Absorbing Metal Complexes by Ligand Substitution

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There have been several recent articles concerning the synthesis and characterization of M$(bpym)_{3-n}L_{2n}$ (where M = Cr,[1] Co,[2] Mo,[3] W,[1] Ru,[4–8] Fe[9–11] or Ni[12] and bpym = 2,2′-bipyrimidine) systems and their possible use as precursor complexes for the formation of polymetallic systems. The 2,2′-bipyrimidine ligand serves as an effective bidentate ligand in either mono- or polymetallic systems, and results from previous studies indicate that this bidentate ligand is more effective at electronically communicating two metal centers than most of the monodentate bridges.[13–16]

We report here the synthesis, electronic absorption spectroscopy, magnetic susceptibility, and electrochemistry of a series of $Fe(bpym)_{3-n}(CN)_{2n}^{(2-2n)+}$ complexes that, in addition to serving as possible backbones for polymetallic complexes, might also serve as effective visible-light-absorbing, energy-transfer antenna fragments in intramolecular sensitization processes.[6]

## Experimental Section

Procedures for the preparation of mixed-ligand complexes of Fe(II) with $CN^-$ and 2,2′-bipyridine have been previously described.[17–19] The preparation of mixed-ligand complexes of Fe(II) with $CN^-$ and 2,2′-bipyrimidine was achieved by modification of those procedures. Complete procedural details are described here for the preparation of the newly characterized mixed-ligand complexes of Fe(II), as well as for the tris(2,2′-bipyrimidine)iron(II) complex.

**Materials.** Analytical reagent grade compounds were used for all preparations described in this work. Water, which was used as the solvent for synthesis and electrochemistry, was redistilled from alkaline permanganate in an all-glass apparatus. Elemental analyses were performed by Atlantic Microlab, Atlanta, GA, with satisfactory results obtained for all complexes. The bpym was purchased from Alfa Inorganics and had a proton-decoupled, $^{13}C$ NMR spectrum in $D_2O$ corresponding to $C_\alpha$ and $C_\gamma$ (159.0 ppm) and $C_\beta$ (123.4 ppm) vs. $Me_4Si$.

**Instrumentation.** Cyclic voltammograms were recorded on an IBM Instruments Inc. Model EC/225 voltammetric analyzer using a glassy-carbon working electrode (IBM). Voltammograms in nonaqueous solution were recorded in DMF (Fisher Scientific Co.) with 0.1 M TEAP (Fisher Scientific Co.) as a supporting electrolyte. Voltammograms in water were recorded in pH 7.00 buffer solution (Fisher Scientific Co.) for comparison with the pH-dependent hexacyanoferrate(III/II) reduction potential. The supporting electrolyte was 0.1 M KCl for aqueous voltammograms, and they were recorded at 10–100 mV/s vs. SCE.

Magnetic susceptibility measurements were made on solid samples with use of the Faraday method. A Cahn Model RG automatic electrobalance and Alfa Scientific 7500 M electromagnet were used. $HgCo(SCN)_4$ was used as a calibrant.[20] Diamagnetic corrections for molar susceptibilities were made with use of Pascal's constants.[21]

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(1) Moore, K. J.; Petersen, J. D. *Polyhedron* **1983**, *2*, 279.

(2) Ruminski, R. R.; Petersen, J. D. *Inorg. Chim. Acta*, in press.

(3) Overton, C.; Connor, J. A. *Polyhedron* **1982**, *1*, 53.

(4) Dose, E. V.; Wilson, L. J. *Inorg. Chem.* **1978**, *17*, 2660.

(5) Hunziker, M.; Ludi, A. *J. Am. Chem. Soc.* **1977**, *99*, 7370.

(6) Ruminski, R. R.; Petersen, J. D. *Inorg. Chem.* **1982**, *21*, 3706.

(7) Rillema, D. P.; Callahan, R. W.; Mack, K. B. *Inorg. Chem.* **1982**, *21*, 2589.

(8) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1614.

(9) Bly, D. D.; Mellon, M. G. *Anal. Chem.* **1963**, *35*, 1386.

(10) Watanabe, J.; Saji, T.; Aoyagui, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 327.

(11) Burstall, F. H.; Nyholm, R. S. *J. Chem. Soc.* **1952**, 3570.

(12) Ruminski, R. R.; Petersen, J. D. *Inorg. Chim. Acta*, in press.

(13) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(14) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

(15) Powers, M. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 1289.

(16) Felix, F.; Ludi, A. *Inorg. Chem.* **1978**, *17*, 1782.

(17) Schilt, A. A. *J. Am. Chem. Soc.* **1960**, *82*, 3000.

(18) Barbieri, G. A. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1934**, *20*, 273.

(19) Parry, R. W. *Inorg. Synth.* **1970**, *12*, 247.

(20) Sullivan, S.; Thorpe, A. N.; Hambright, P. *J. Chem. Educ.* **1971**, *48*, 345.

0020-1669/84/1323-4380$01.50/0