Magnetic Studies of Substituted Pyridine *N*-Oxide Complexes of Copper(II) Nitrate[1]

Kenneth T. McGregor, James A. Barnes, and William E. Hatfield*

Contribution from the Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27514. *Received March 24, 1973*

Abstract: Magnetic measurements and electron paramagnetic resonance studies on the pyridine *N*-oxide bridged, dimeric complexes $[Cu(R\text{-}pyO)_2(NO_3)_2]_2$, where R = H, CH_3, and OCH_3, have demonstrated that the copper(II) ions are coupled by a spin–spin interaction. The substituents have a profound effect on the nature of this interaction since the unsubstituted pyridine *N*-oxide and 4-picoline *N*-oxide complexes have triplet ground states while the 4-methoxypyridine *N*-oxide complex has a singlet ground state; the $2J$ values are 10, 2, and -2 cm^{-1}, respectively.

Electronic spin–spin coupling in dimeric and multimetallic cluster compounds has been the subject of much research in recent years.[2] Of the magnetically condensed systems which have been studied, great numbers of dimeric copper(II) complexes have been found to exhibit reduced magnetic moments due to spin–spin interactions which lead to singlet ground states.[3] Prior to the preliminary report[1] from our laboratory, there was a notable absence from the literature of examples of dimeric copper(II) complexes with triplet ground states. Although the theory of spin–spin coupling *via* a superexchange mechanism, which was first advanced by Anderson,[4] encompasses ferromagnetic interactions, only a limited number of triplet ground-state copper(II) dimers have been found.[5]

There are two major reasons why only a very few dimeric copper(II) complexes with triplet ground states have been reported. First, only a superexchange mechanism is likely to permit a spin–spin interaction which results in ferromagnetic coupling since a copper(II)–copper(II) through-space interaction necessarily produces a singlet ground state according to the Pauli principle. In addition, due to the irregularities in the structures of copper(II) complexes, few adjacent copper(II) ions have their unpaired electrons in orthogonal interacting orbitals, a requirement for ferromagnetic spin–spin coupling *via* superexchange. The negative terms in the exchange integral, J, are weighted by the overlap,[6] S, while the positive terms are not multiplied by S. Thus, the negative terms will disappear when there is no overlap. Secondly, of the potentially fewer numbers of copper(II) dimers with positive values of J, the probability of finding examples is diminished by experimental difficulties. Spin–spin coupling which leads to a singlet ground state is readily apparent from the temperature dependence of the magnetic susceptibility, but interactions which lead to a triplet ground state are much more difficult to detect. Usually copper(II) complexes with low moments due to $-J$ values lead to X-ray crystal structure investigations. On the other hand, complexes which exhibit "normal" moments, as do triplet ground-state dimers, attract very little attention, and consequently crystallographers have not provided much structural information on such complexes. While electron paramagnetic resonance can detect population of the triplet state, only low-temperature magnetic measurements can verify the multiplicity of the ground state.

Among the few examples of triplet ground-state copper(II) dimers, the complex di-μ-(pyridine *N*-oxide)-bis[bisnitrato(pyridine *N*-oxide)copper(II)] is of particular interest. The crystal structure of $[Cu(pyO)_2(NO_3)_2]_2$ was solved by Šcavnicar and Matković[7] by X-ray diffraction techniques and the complex was found to be dimeric. Because of the difficulty in detecting triplet ground states, the complex was first thought to be magnetically dilute. A spin–spin interaction in $[Cu(pyO)_2(NO_3)_2]_2$ has now been detected by epr measurements and the triplet multiplicity has been verified by low-temperature magnetic measurements. In order to further evaluate the factors which lead to a positive J, complexes of the type $[Cu(R\text{-}pyO)_2(NO_3)_2]_2$ where R = CH_3 and CH_3O (substituted in the 4-position) have been prepared and their magnetic properties studied. The results of these studies and computer simulations of the epr spectra are presented herein. The computer simulations are thought to provide the most accurate description of the magnetic parameters of these systems while the magnetization studies validate the ground-state multiplicity.

Experimental Section

Preparation of Complexes. Samples of $Cu(R\text{-}pyO)_2(NO_3)_2]_2$ (R = H, CH_3, CH_3O) were prepared by mixing 2,2-dimethoxypropane solutions of copper(II) nitrate and R-pyridine *N*-oxide in 1:2 molar ratios. The ligands used in the preparations were purified by vacuum distillation. The complexes were stored in a desiccator since they have a tendency to adsorb water. In addition, samples of magnetically dilute $[Zn(Cu)(R\text{-}pyO)_2(NO_3)_2]_2$[8] were prepared by the reported method in order to obtain well-resolved

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[1] A preliminary account of portions of this work has been published: W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and E. R. Jones, Jr., *J. Amer. Chem. Soc.*, **92**, 4982 (1970). See also K. T. McGregor, T. Lund, and W. E. Hatfield, *Spectrosc. Lett.*, **6**, 309 (1973).

[2] For some reviews, see P. W. Ball, *Coord. Chem. Rev.*, **4**, 361 (1969); A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, **5**, 45 (1971); W. E. Hatfield in "Theoretical Principles and Applications of Magnetochemistry," E. A. Boudreaux and L. N. Mulay, Ed., Marcel Dekker, New York, N. Y., in press.

[3] M. Kato, H. B. Jonassen, and J. C. Fanning, *Chem. Rev.*, **64**, 99 (1964).

[4] P. W. Anderson, *Phys. Rev.*, **115**, 2 (1959).

[5] K. T. McGregor, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, **12**, 731 (1973).

[6] R. L. Martin, "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, New York, N. Y., 1968.

[7] S. Šcavnicar and Matković, *Chem. Commun.*, 297 (1967); *Acta Crystallogr., Sect. B*, **25**, 2046 (1969).

[8] The X-ray powder patterns of $[Zn(Cu)(pyO)_2(NO_3)_2]_2$ and $[Cu(pyO)_2(NO_3)_2]_2$ are nearly identical.

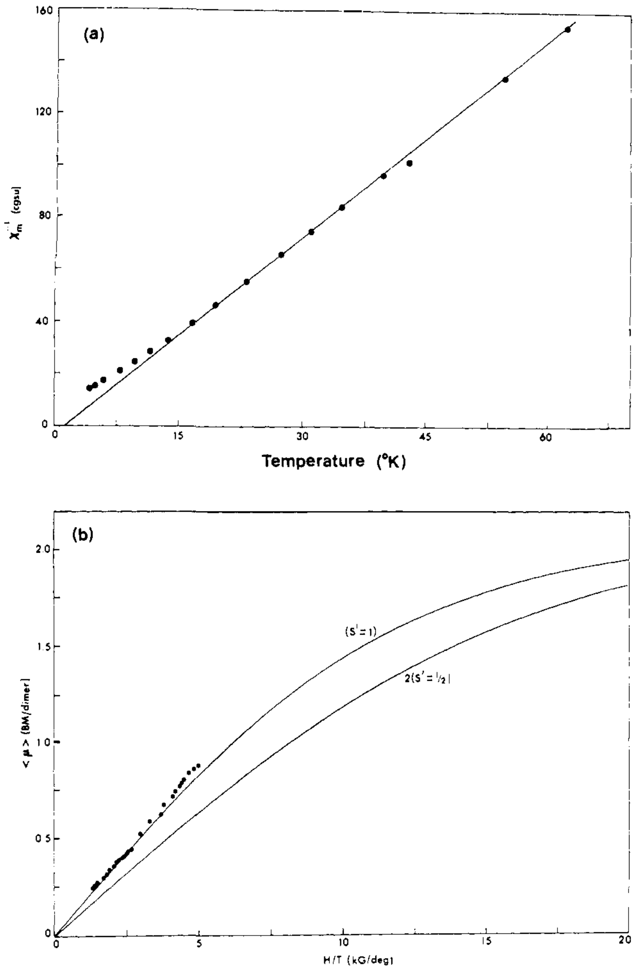

Figure 1. Magnetic data for $[Cu(pyO)_2(NO_3)_2]_2$: (a) the temperature variation of the inverse susceptibility, the solid line shows the Curie–Weiss behavior at high temperatures; (b) the magnetization data, the full curves are plots of the magnetization of the triplet state and of two uncoupled doublet states.

epr spectra. The copper(II) ions were doped into the isomorphous zinc complex by using zinc nitrate and copper nitrate in a 9:1 ratio. The analytical data for all the complexes are shown in Table I.

Table I. Analytical Data for $[Cu(4\text{-}R\text{-}pyO)_2(NO_3)_2]_2$ and $[Zn(Cu)(4\text{-}R\text{-}(pyO)_2(NO_3)_2]_2$

R	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
			For 100% Cu			
H	31.80	31.86	2.67	2.67	14.83	14.73
CH_3	35.52	35.68	3.48	3.43	13.81	13.87
CH_3O	32.92	32.96	3.22	3.21	12.80	12.98
			For 10% Cu			
H	31.65	31.57	2.65	2.57	14.77	14.70
CH_3	35.37	35.38	3.46	3.43	13.75	13.53
CH_3O	32.80	32.80	3.21	3.11	12.75	12.83

Magnetic Measurements. The magnetic susceptibilities of a powdered sample of each complex were determined using a Foner-type vibrating-sample magnetometer.[9] Measurements were made from 1.7 to 70°K and at 300°K using a field strength of 10 kG. Magnetization data for $[Cu(pyO)_2(NO_3)_2]_2$[5] and for $[Cu(4\text{-picoline } N\text{-oxide})_2(NO_3)_2]_2$ were taken at temperatures of 1.7, 4.2, and 7°K and field strengths of 2.5, 10, and 12.5 kG. The field strengths were calibrated by nuclear (Li) resonance techniques. The temperatures were measured with a calibrated gallium arsenide diode and by a calibrated germanium resistance thermometer. Susceptibilities were also measured at 77, 195, and 300°K on a Faraday balance.[10] Mercury tetrathiocyanatocobaltate(II) was used as a susceptibility standard.[11] All susceptibilities were corrected for the diamagnetism of the substituent atoms using Pascal's constants[12] and for the TIP of copper(II) (estimated to be 60×10^{-6} cgsu/Cu).

Epr Measurements. The epr spectra of powdered samples of the magnetically diluted complexes were obtained using a Varian E-3 X-band spectrometer. A spectrometer frequency of 9.372 GHz and a modulation frequency of 100 KHz were used. All spectra were recorded at 77°K.

Results

Bulk Magnetic Susceptibility Measurements. The temperature variation of the inverse magnetic susceptibility of $[Cu(pyO)_2(NO_3)_2]_2$ is shown in Figure 1a. The data obey a Curie–Weiss law above 11° with a room temperature magnetic moment of 1.90 BM per copper(II) ion. The intercept of the temperature axis at $\chi^{-1} = 0$ is +2°K. The magnetic data can be described by the modified Van Vleck equation[13] (1) for exchange coupled

$$\chi = \frac{Ng^2\beta^2}{3k(T-\theta)}\{1 + {}^1/_3 \exp(-2J/kT)\}^{-1} + N\alpha \qquad (1)$$

copper(II) ions with a singlet–triplet splitting $2J$ of $+10$ cm^{-1}, $\theta = -2.7°$, and $\langle g\rangle = 2.11$. The best estimate of the standard deviation is 0.00153. Using the best fit magnetic parameters the experimental values fit eq 1 with an average difference between experimental and calculated susceptibilities being less than 2%. In eq 1, θ accounts for interdimer interactions (*vide post*). The estimated precision of the magnetic parameters are ±10% for $2J$, ±0.01 for g, and ±0.1° for θ. Figure 1b is a plot of the magnetization $\langle\mu\rangle$ *vs.* H/T for the unsubstituted complex.[5] The solid curves are calculated from the relation

$$\langle\mu\rangle = gS'B_{S'}(X) \qquad (2)$$

In eq 2 $B_{S'}(X)$ is the Brillioun function[14]

$$B_{S'}(X) = \frac{2S'+1}{2S'}\coth\left(\frac{(2S'+1)}{2S'}X\right) + \frac{1}{2S'}\coth\frac{X}{2S'}$$

where $X = (H/T)(S'g\beta/k)$ and S' is the effective spin of the dimeric molecule. The magnetic field H is taken to be the sum of the applied field and the molecular field,[5,14,15] *i.e.*, $H = H_{ex} + H_m$. The molecular field is assumed to be proportional to the magnetization M as in eq 3.

$$H_m = N_wM = N_wN\beta\langle\mu\rangle \qquad (3)$$

The value of H_m was estimated using the relation

$$N_w = \frac{3k\theta}{Ng^2\beta^2S'(S'+1)} \qquad (4)$$

The solid curves of Figure 1b were calculated with $g = 2.11$ and $\theta = -0.50$. Figure 2a shows the temperature

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(9) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).

(10) W. E. Hatfield, C. S. Fountain, and R. Whyman, *Inorg. Chem.*, **5**, 1855 (1966).

(11) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

(12) E. Konig, "Magnetic Properties of Transition Metal Compounds," Springer-Verlag, Berlin, 1966.

(13) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, Chapters IX and XII, 1932.

(14) J. S. Smart, "Effective Field Theories of Magnetism," W. B. Saunders, Philadelphia, Pa., 1966.

(15) J. A. Bertrand, A. P. Ginsberg, R. I. Kaplan, C. E. Kirkwood, R. L. Martin, and R. C. Sherwood, *Inorg. Chem.*, **10**, 240 (1971).

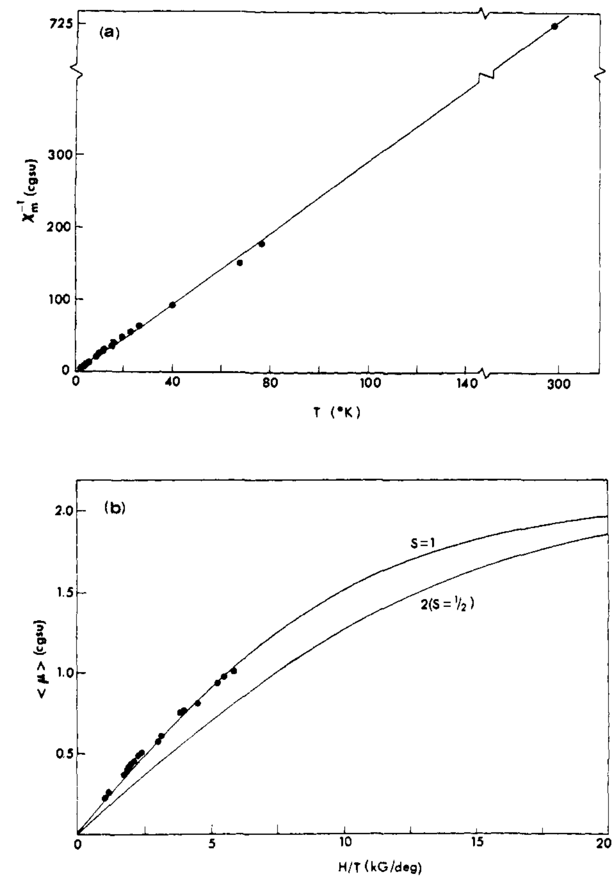

Figure 2. Magnetic data for $[Cu(4\text{-}CH_3\text{-}pyO)_2(NO_3)_2]_2$: (a) the temperature variation of the inverse susceptibility, the solid line is a plot of eq 1 with the best fit parameters; (b) the magnetization data, the full curves are plots of the magnetization of the triplet state and of two uncoupled doublet states.

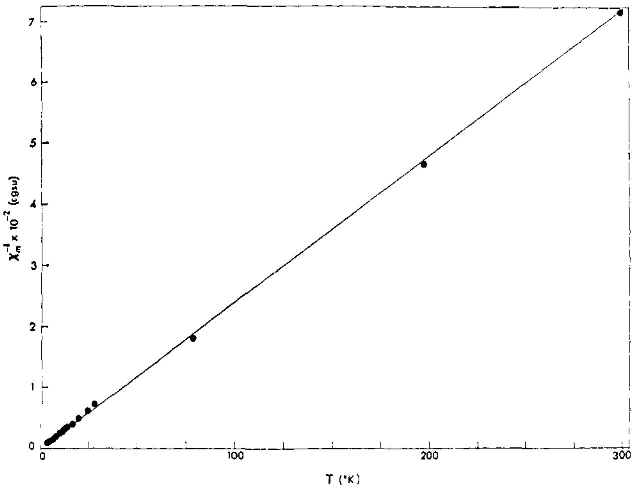

Figure 3. The temperature variation of the inverse susceptibility for $[Cu(4\text{-}CH_3OpyO)_2(NO_3)_2]_2$; the solid line is a plot of eq 1 using the best fit parameters (see text).

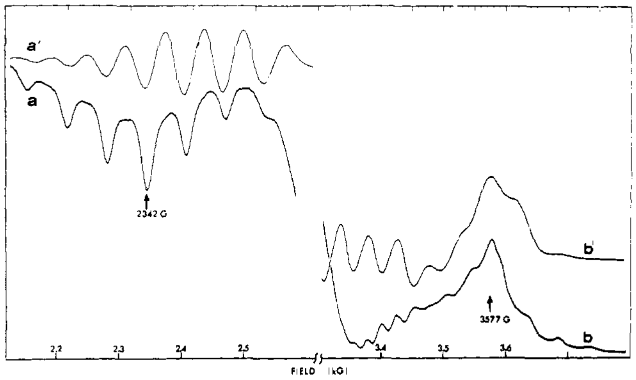

Figure 4. Epr spectra and computer simulations for the unsubstituted complex: (a) the low field spectrum; (b) the high field spectrum. The computer simulations are denoted by primes. The simulated spectra were generated using the parameters given in Table II.

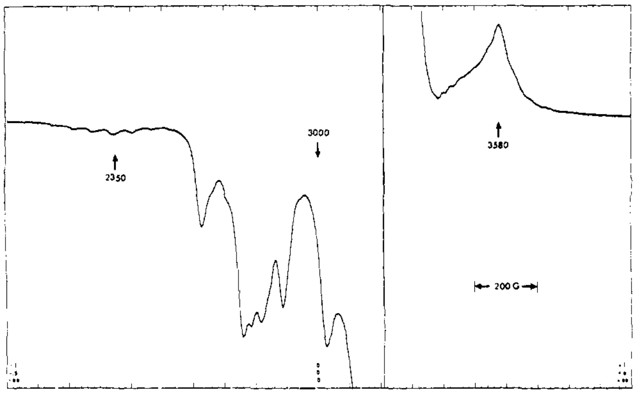

Figure 5. A view of the epr spectra of the 4-picoline *N*-oxide complex in the range 2–4 kG. The triplet-state spectra are seen on either side of the intense doublet-state resonance.

dependence of the inverse susceptibility of the 4-methyl substituted complex, while Figure 2b shows the magnetization plot for this compound. The best fit parameters are $\langle g \rangle = 2.11$ and a singlet–triplet splitting of 2 cm^{-1}. A θ value of -0.15 resulted from the best fit of the inverse susceptibility data. Here the best estimate of the standard deviation is 0.00431, and the average difference between calculated and experimental susceptibilities is less than 4%. The room temperature magnetic moment is 1.83 BM. Since some population of the singlet state is expected even at the very low temperatures used in the experiment, the points in the magnetization data were normalized to a total population of the triplet state according to the Boltzmann distribution law. The inverse magnetic susceptibility *vs.* temperature plot for the 4-methoxy substituted complex is shown in Figure 3. The room temperature magnetic moment is 1.82 BM for the complex. The data for the methoxy complex can be fitted to eq 1 with a singlet–triplet energy separation of 2 cm^{-1} with the singlet state lying lowest in energy. Here the best estimate of the standard deviation is 0.00407, and the average difference between calculated and experimental susceptibilities is less than 4%.

Epr Measurements. The epr spectrum of a powdered sample of $[Cu(pyO)_2(NO_3)_2]_2$ diluted in the corresponding zinc matrix is shown in Figure 4. The seven well-resolved resonance lines centered at 2312 G are assigned to the low field transitions (Figure 4a) of the z direction. Some of the high field transitions (Figure 4b) of the parallel and perpendicular directions are centered about the 3550 G marker. The low field spectra, due to orientations in the x and y directions, are not resolved due to the strong resonance at 3100 G. This absorption is due to transitions in the doublet-state copper(II) ions which have zinc ions as their nearest neighbors. The

Table II. Epr Parameters for $[Cu(4\text{-}R\text{-}pyO)_2(NO_3)_2]_2$ in a $[Zn(4\text{-}R\text{-}pyO)_2(NO_3)_2]_2$ Matrix

R	$g_{\parallel}$	$g_{\perp}$	$\lvert D\rvert$, cm^{-1}	$A \times 10^4$, cm^{-1}	$B \times 10^4$, cm^{-1}
H	2.275 ± 0.005	2.07 ± 0.01	0.073 ± 0.001	130 ± 2	40 ± 4
CH_3	2.275 ± 0.005	2.07 ± 0.01	0.069 ± 0.001	133 ± 2	40 ± 4
CH_3O^a	2.28	2.07	0.05		

[a] The g values are assumed to be consistent with the other complexes of the series; the D value was calculated from the $\Delta M_s = 2$ transition.

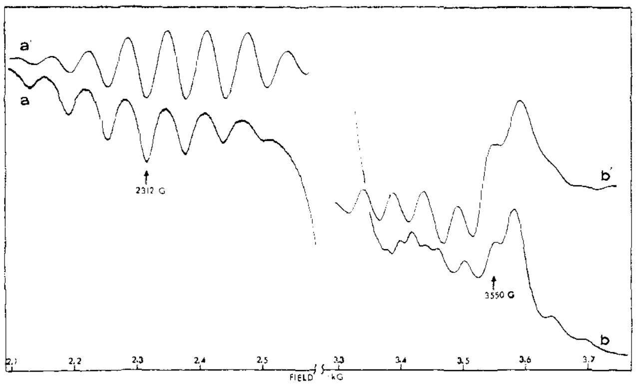

Figure 6. A view of the epr spectrum and computer simulations for the 4-picoline N-oxide complex: (a) the low field spectrum, (b) the high field spectrum. The computer simulations are denoted by primes. The simulated spectra were generated using the parameters given in Table II.

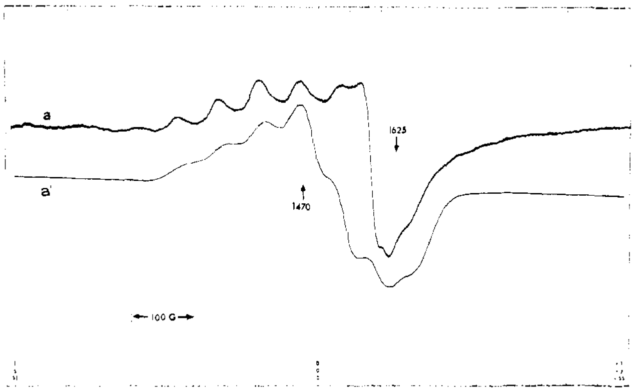

Figure 7. The half-field resonances of the unsubstituted complex: (a) the experimental spectra, (a') the computer simulation. The simulated spectra were generated using the parameters given in Table II.

spectra of $[Cu(4\text{-}picO)_2(NO_3)_2]_2$ provides a better overall view of the resonance spectrum from 2000 to 4000 G of this series and is shown in Figure 5. The much weaker (*vide post*) triplet-state spectra are seen below and above the intense doublet-state resonance fields. Figure 6 shows the triplet-state spectra of the 4-picoline complex at much higher spectrometer gains. The spectra shown in Figure 4a',b' and the spectra denoted with primes in Figure 6 are computer simulations of the spectra to be described shortly. In Figure 7a are the half-field lines due to the $\Delta M_S = 2$ transitions of the unsubstituted complex; these lines are somewhat better resolved than the forbidden transitions of the 4-picoline complex. Figure 7a' is the corresponding computer simulation. The epr spectra observed for the 4-methoxy complex is shown in Figure 8. Notable features which are assigned to triplet-state transitions are the half-field line at ≃1600 G and the shoulder on the doublet resonance at 3500 G. All attempts at better resolution of the spectra using various spectrometer gains and modulation amplitudes were unsuccessful.

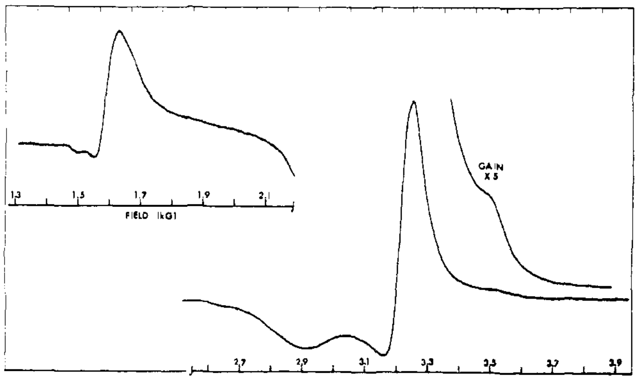

Figure 8. A view of the epr spectrum of the 4-methoxypyridine N-oxide complex. The half-field line at ≃1600 G and the shoulder at ≃3500 G are assigned to triplet state resonances.

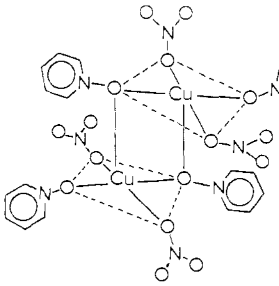

Figure 9. A schematic diagram of the structure of $[Cu(pyO)_2(NO_3)_2]_2$ as determined by Šcavincař and Matković.

Simulation of the Epr Spectra. The simulated epr spectra shown in Figures 4, 6, and 7 were generated by computer programs written by Lund and have been described elsewhere.[16] The spin Hamiltonian (5) used

$$\mathcal{H}_{S'} = g_{\parallel}\beta H_z S_z' + g_{\perp}\beta(S_x'H_x + S_y'H_y) + D(S_z'^2 - 2/3) + A(S_{1z}I_{1z} + S_{2z}I_{2z}) + B(S_{1x}I_{1x} + S_{1y}I_{1y} + S_{2x}I_{2x} + S_{2y}I_{2y}) \quad (5)$$

to calculate the resonance fields in the computer program was solved by the perturbation approach. The program considers only systems of axial symmetry.

Discussion

The structure of $[Cu(pyO)_2(NO_3)_2]_2$ as determined by Šcavnicař and Matković[7] is shown schematically in Figure 9. Each copper(II) ion of the dimeric molecule is in a distorted tetragonal pyramidal environment. The basal plane is composed of trans pyridine N-oxide and nitrate groups with the fifth position being occupied by an oxygen atom of a pyridine N-oxide group which is

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[16] T. Lund and W. E. Hatfield, *J. Chem. Phys.*, **59**, 885 (1973).

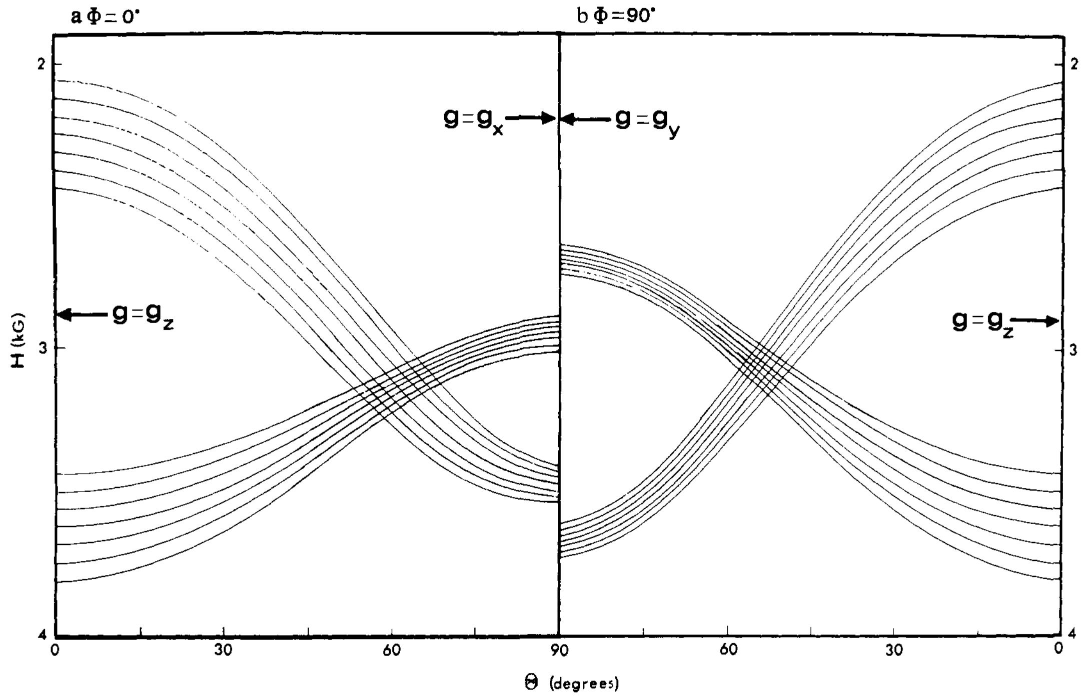

Figure 10. The angular dependence of triplet-state resonance fields for the $\Delta M_S = 1$ transitions: (a) Φ is maintained at 0° while θ varies from 0 to 90°, (b) Φ is maintained at 90° while θ varies from 0 to 90°.

part of the basal plane of the other copper(II) ion. The axial Cu–O distance is 2.439 Å. The copper(II)–copper(II) separation is 3.448 Å and the Cu–O–Cu bond angle is 102.9°. The local symmetry of each copper(II) in the dimer is not axial.

As pointed out by Stevens,[17] a system need not necessarily possess axial symmetry to be described by eq 5. In view of this, our initial values of the magnetic parameters were determined using the equations (6) of Wasserman, *et al.*,[18] where the axial case is assumed and no hyperfine terms are included.

$$\begin{aligned} H_1(z) &= (g_\parallel\beta)^{-1}|h\nu - D| \\ H_2(z) &= (g_\parallel\beta)^{-1}(h\nu + D) \\ H_1(x,y) &= (g_\perp\beta)^{-1}[h\nu(h\nu - D)]^{1/2} \\ H_2(x,y) &= (g_\perp\beta)^{-1}[h\nu(h\nu + D)]^{1/2} \\ H_1(\mathrm{forb}) &= (2g_\parallel\beta)^{-1}h\nu \\ H_2(\mathrm{forb}) &= (2g_\perp\beta)^{-1}(h^2\nu^2 - D^2)^{1/2} \end{aligned} \tag{6}$$

Here the subscript 1 indicates the low field line while subscript 2 indicates the high field transition field. The $\Delta M_S = 2$ transitions are labeled forbidden.

The parameters obtained from the application of Wasserman's equations were used as starting values in the computer program which does include the hyperfine interaction. These values were allowed to vary in the simulations with the best fit values given in Table II. As seen from Figures 4, 5, and 7, the low field portions of the simulations agree very well with the experimental spectra while the high field portions of the experimental spectra show additional lines not included in the simulation. The additional resonances are probably due to the magnetic inequivalence of orientations in the x and y directions. This fact is illustrated by the plots of the angular dependence of the resonance fields shown in Figure 10. The computer program EPR, written by M. Gladney and available from the Quantum Chemistry Program Exchange, was used to calculate the curves shown in Figure 10. Parameters very near those shown in Table II were used except that $g_x = 2.06$ and $g_y = 2.08$ replaced $g_\perp = 2.07$ and a value of $E = 0.1$ D was included. The angle θ was allowed to vary from 0 to 90° for $\Phi = 0$ and $\Phi = 90°$. As seen from Figure 10, when $\theta = 0°$ then $g = g_z$. However, when $\theta = 90°$, $g = g_x$ in one case and $g = g_y$ in the other, *i.e.*, for $\Phi = 0$ and 90°. Analysis of the transition probabilities shows that sufficient intensity is given to these orientations to account for the observed resonances. Alternately, the lines may arise from resonances in a small percentage of magnetically nonequivalent dimers with slightly different g values which are present in the diluted material.

In the case of the 4-picoline complex the possibility of "singlet–triplet" transitions was considered since the singlet–triplet splitting is only 2 cm^{-1}. The resulting simulated spectrum was identical with those shown and produced no additional lines at X band when the singlet–triplet energy separation was 2 cm^{-1} or more.

Although the programs used to simulate the spectra are restricted to cases of axial symmetry, they allow complete simulation in relatively small amounts of computer time. While the program EPR is more general and would allow a more complete description of the spectra, the computer time required for the simulations is not available to us.

It is not possible to make an analysis of the zero field splitting in terms of exchange and dipolar contributions since structural details are unavailable for the zinc host crystal, and it is probably inadvisable to assume the same copper–copper separation in the pure and diluted materials. Also, there is no structural information for

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[17] K. W. H. Stevens, *Proc. Roy. Soc., Ser. A*, **214**, 237 (1952).

[18] E. Wasserman, L. C. Snyder, and W. A. Yager, *J. Chem. Phys.*, **41**, 1763 (1964).

the 4-picoline and 4-methoxypyridine *N*-oxide complexes, but, since both give triplet state spectra, it seems clear that these complexes are dimeric also.

In analysis of the magnetization studies as well as the inverse susceptibility plots, some interdimer interactions were detected. These interactions are accounted for by the θ value used in the estimation of the molecular field. Some idea of the interdimer exchange may be calculated using the relation[14]

$$J' = \frac{3k\theta}{2zS'(S' + 1)}$$

where J' is the interdimer exchange coupling constant for the z nearest neighbors of a given dimer. Using the effective dimer spin S' of 1 and the two nearest neighbors,[7] values of $-J'$ are found to be $\simeq$0.15 or 0.8 cm^{-1} for $[Cu(pyO)_2(NO_3)_2]_2$ and 0.30 or 0.04 cm^{-1} for $[Cu(4\text{-}CH_3\text{-}pyO)_2(NO_3)_2]_2$ where the first value was calculated from the magnetization data and the second from the inverse susceptibility data. In any case, a small antiferromagnetic interdimer exchange interaction is apparent.

Conclusions

Three complexes of the form $[Cu(R\text{-}pyO)_2(NO_3)_2]_2$ have been characterized by low-temperature magnetic susceptibility and epr studies. In addition, magnetization studies have been carried out on the unsubstituted and the 4-methyl substituted complexes. Each of the complexes is found to exhibit electronic spin–spin coupling; the interaction leads to a triplet ground state for the unsubstituted and picoline complexes while a singlet state is found to be the ground state for the 4-methoxy complex.

Since the copper(II)–copper(II) separation of 3.458 Å is considered to be too great for any metal–metal bond formation and since a dipole–dipole interaction could not produce singlet–triplet splittings of the observed magnitude, it is not probable that a through space interaction dominates the exchange coupling in any of the complexes studied. Moreover, any direct metal–metal interaction would necessarily be antiferromagnetic according to the Pauli principle; this is not consistent with the two triplet ground-state cases. The copper(II) centers in the complexes studied must be coupled by a superexchange mechanism which is subject to changes in Cu–O–Cu bridge angle in the same way as previously reported[5,19] for oxygen-bridged copper(II) dimers. Further evidence for the superexchange mechanism is manifested by the substituent effects on the exchange energy.

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[19] K. T. McGregor, N. T. Watkins, D. L. Lewis, R. F. Drake, D. J. Hodgson, and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, **9**, 423 (1973).

Photochemical Reaction of the Azidopentaammineiridium(III) Ion. Coordinated Nitrene Intermediate

Harry D. Gafney, James L. Reed, and Fred Basolo*

Contribution from the Department of Chemistry, Northwestern University, Evanston, Illinois 60201. Received April 27, 1973

Abstract: Photolysis of aqueous solutions of $Ir(NH_3)_5N_3^{2+}$ results in the evolution of nitrogen and the formation of a coordinated nitrene intermediate as the only reaction products. For solutions containing hydrochloric acid, the photolysis reaction yields exclusively $Ir(NH_3)_5NH_2Cl^{3+}$. The quantum yields are wavelength dependent and are appreciable for excitation in the ligand-field region of the spectrum. The data are interpreted in terms of a model where a lower energy azido group excited state is the reactive level. An intermediate is observed when $Ir(NH_3)_5N_3^{2+}$ is irradiated in a glass at 77°K or flashed in aqueous solution. The intermediate is attributed to the product of a reaction of the coordinated nitrene and the solvent. A mechanism for the photochemical reaction is proposed.

Metal coordinated nitrene intermediates, M–NH, have been reported for the thermal reactions of azidopentaammine complexes of ruthenium[1] and iridium.[2] Nitrene intermediates also form during the photolysis of hydrazoic acid[3,4] and organic azides.[5,6] However, prior to a recent communication from this laboratory,[7] metal coordinated nitrene intermediates had not been studied nor postulated in the photochemistry of azido metal complexes. Previous investigations on the photodecomposition of azido metal complexes were largely limited to the first-row transition

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[1] L. A. P. Kane-Maguire, P. S. Sheridan, F. Basolo, and R. G. Pearson, *J. Amer. Chem. Soc.*, **92**, 5865 (1970).

[2] B. C. Lane, J. W. McDonald, F. Basolo, and R. G. Pearson, *ibid.*, **94**, 3786 (1972).

[3] I. Burak and A. Treinin, *ibid.*, **87**, 4031 (1965).

[4] K. H. Welge, *J. Chem. Phys.*, **45**, 4373 (1966).

[5] E. Wasserman, G. Smolinsky, and W. A. Yager, *J. Amer. Chem. Soc.*, 86, 3166 (1964).

[6] E. Koch, *Tetrahedron*, 23, 1747 (1967).

[7] J. L. Reed, F. Wang, and F. Basolo, *J. Amer. Chem. Soc.*, **94**, 7173 (1972).