the decays of these emissions are not single exponentials nor can they be adequately described by any three-state equilibrium model, which would yield double-exponential decays. Furthermore, the time behavior of the emissions as well as the quantum efficiencies for luminescence and certain features of the emission spectra are all dependent upon the concentration of the complexes in the solvent matrix. These two complexes appear to provide the best opportunities for examining the photophysical interactions between excited electronic states in chromium(III) systems.

Acknowledgment. We gratefully acknowledge the support of the National Science Foundation under Grants DMR-7203026 and GP-37661X. J.T.Y. has benefited greatly in this work from a Teacher-Scholar Award from the Henry and Camille Dreyfus Foundation.

Registry No. $[Cr(ur)_6]Cl_3$, 14023-01-9; $[Cr(antip)_6](NO_3)_3$, 55660-57-6; $K_3[Cr(CN)_6]$, 13601-11-1; $[Cr(acac)_3]$, 13681-82-8.

References and Notes

(1) Alfred P. Sloan Fellow, 1972–1974.

(2) (a) W. M. Watson, Ph.D. Thesis, University of Illinois, 1973; (b) W. M. Watson, R. P. Zerger, J. T. Yardley, and G. D. Stucky, *Inorg. Chem.*, in press.

(3) (a) P. D. Fleischauer and P. Fleischauer, *Chem. Rev.*, **70**, 199 (1970); (b) L. S. Forster, *Transition Met. Chem.*, **5**, 1 (1969); (c) S. N. Chen, and G. B. Porter, *J. Am. Chem. Soc.*, **92**, 2189 (1970).

(4) (a) J. T. Yardley and J. K. Beattie, *J. Am. Chem. Soc.*, **94**, 8925 (1972); (b) F. Castelli and L. S. Forster, *ibid.*, **95**, 7223 (1973); (c) L. S. Forster, *Phys. Rev. B*, in press.

(5) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, **36**, 3330 (1962).

(6) (a) C. A. Thayer and J. T. Yardley, *J. Chem. Phys.*, **57**, 3992 (1972); (b) A. Z. Moss, Ph.D. Thesis, University of Illinois, 1973.

(7) (a) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1393 (1963); (b) H. L. Schläfer, H. Gausmann, and W. Witzke, *J. Chem. Phys.*, **46**, 1423 (1967); (c) H. L. Schläfer, H. Gausmann, and H. Witzke, *Z. Phys. Chem. (Frankfurt am Main)*, **56**, 55 (1967); (d) K. K. Chatterjee and L. S. Forster, *Spectrochim. Acta*, **20**, 1603 (1964).

(8) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1403 (1963).

(9) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **19**, 1687 (1963).

(10) N. Sabbatini and V. Balzani, *J. Am. Chem. Soc.*, **94**, 7587 (1972).

(11) H. L. Schläfer, H. Gausmann, and H. U. Zander, *Inorg. Chem.*, **6**, 1528 (1967).

(12) G. B. Porter and H. L. Schläfer, *Z. Phys. Chem. (Frankfurt am Main)*, **37**, 109 (1963).

(13) (a) J. L. Laver and P. W. Smith, *Aust. J. Chem.*, **24**, 1807 (1971); (b) D. M. Klassen and H. L. Schläfer, *Ber. Bunsenges. Phys. Chem.*, **72**, 663 (1968).

(14) (a) R. Dingle, *J. Chem. Phys.*, **50**, 1952 (1969); (b) G. Gliemann and H. Yersin, *Ber. Bunsenges. Phys. Chem.*, **75**, 1257 (1971).

Contribution from the Departments of Chemistry, University of Kentucky, Lexington, Kentucky 40506, and
University of North Carolina, Chapel Hill, North Carolina 27514

Magnetic Properties and Bonding of the Pyrido[2,3-*b*]pyrazine and the 1,5-Naphthyridine Complexes of Copper(II) Nitrate

HENRY J. STOKLOSA,[1a] JOHN R. WASSON,*[1a] ELLIS V. BROWN,[1a] H. WAYNE RICHARDSON,[1b]
and WILLIAM E. HATFIELD[1b]

Received January 23, 1975 AIC500608

The 1:1 pyrido[2,3-*b*]pyrazine adduct of copper(II) nitrate has been prepared and characterized using magnetic susceptibility measurements and electronic and infrared spectroscopy. Semiempirical molecular orbital calculations have been employed to characterize ligands of the pyrazine type as well as the pyrazine adduct of copper(II) nitrate. The latter calculations provide a basis for the interpretation of the properties of several heterocyclic amine adducts of copper(II) nitrate. The 1,5-naphthyridine complex of copper(II) nitrate has also been prepared, and the structure which was deduced from low-temperature magnetic susceptibility and spectroscopic studies supports the novel structure assigned to the pyrido-[2,3-*b*]pyrazine complex.

Introduction

A number of polymeric complexes of the general type $CuLX_2$ (L = heterocyclic amine, X = halide, NO_3^-) have been prepared and characterized.[2–9] In an effort to assess the change in bonding by a different arrangement of nitrogen atoms in the heterocyclic amine ligand the pyrido[2,3-*b*]pyrazine adduct of copper(II) nitrate has been prepared and compared with the pyrazine,[7,8] quinoxaline,[9] and 1,5-naphthyridine adducts of copper(II) nitrate. The results of the present study indicate that the nitrate ions are bidentate ligands as found in the structure[6] of the 1:1 pyrazine–copper(II) nitrate complex and the proposed structure of the pyrido[2,3-*b*]pyrazine (PP) complex is given in Figure 1. Earlier studies of copper(II) complexes of this type have indicated the presence of antiferromagnetic exchange interactions.[5] Billing et al.[5] postulated that exchange coupling between copper(II) ions occurred via the bidentate heterocyclic ligand even though the room-temperature magnetic moment was normal. Such an exchange interaction was found[7,8] for the 1:1 pyrazine–copper(II) nitrate compound and is probably present in the polymeric adducts of copper(II) halides with pyridazine, phthalazine, and 3,4-benzocinnoline.[10]

In the present work the magnetic susceptibility of $(PP)Cu(NO_3)_2$ and $(nap)Cu(NO_3)_2$ is reported. The infrared and electronic spectrum of $(PP)Cu(NO_3)_2$ is also included. The results of simple Hückel molecular orbital calculations for the ligands and extended Hückel MO calculations for pyrazinecopper(II) nitrate have been utilized to elucidate the electronic structure of polymeric complexes of the type $[CuL(NO_3)_2]_n$ where L is a bridging heterocyclic amine.

Experimental Section

Pyrido[2,3-*b*]pyrazine was obtained from Aldrich Chemical Co., Milwaukee, Wis., and used as received. The 1,5-naphthyridine was prepared by the method of Hamada and Takeuchi.[11] All other chemicals were of the best available reagent grades. Elemental analyses were performed by Chemalytics, Inc., Tempe, Ariz.

Preparation of Pyrido[2,3-*b*]pyrazinecopper(II) Nitrate, $(PP)Cu(NO_3)_2$, and (1,5-Naphthyridine)copper(II) Nitrate, $(nap)Cu(NO_3)_2$. The complexes were obtained by adding a 1 *M* solution of copper(II) nitrate trihydrate in methanol (which also contained sufficient 2,2-dimethoxypropane for removal of water) dropwise with vigorous stirring to a 1 *M* solution of the ligand in methanol. The blue complex which precipitated was isolated by filtration, washed with several small portions of methanol followed by ether, and then air-dried.

Anal. Calcd for $Cu(C_7H_5N_3)(NO_3)_2$: C, 26.38; H, 1.58; N, 21.09.

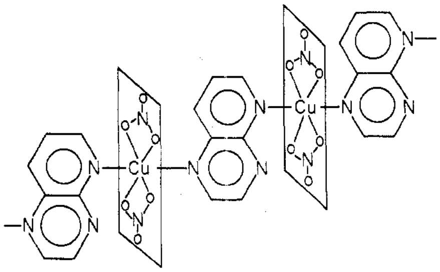

Figure 1. Proposed structure for the pyrido[2,3-*b*]pyrazine adduct of copper(II) nitrate.

Table I. Extended Hückel Parameters

Atom	Orbital	Exponent	−VOIP, eV
Cu	3d	3.080	$1.76q^2 + 11.84q + 5.901$
	4s	1.482	$0.911q^2 + 8.561q + 7.538$
	4p	1.482	$0.986q^2 + 6.552q + 3.893$
C	2s	1.588	19.464
	2p	1.588	10.662
N	2s	1.920	25.539
	2p	1.920	13.142
O	2s	2.236	32.358
	2p	2.236	15.869
H	1s	1.200	13.60

Found: C, 26.47; H, 1.46; N, 21.47; mp (uncor) 285° dec. Calcd for $Cu(C_8H_6N_2)(NO_3)_2$: C, 30.2; H, 1.90; N, 17.6; Found: C, 30.4; H, 2.01; N, 17.4.

The infrared spectrum (4000–200 cm^{-1}) was measured with a Perkin-Elmer 621 recording spectrophotometer using Nujol Mulls on cesium iodine plates as well as potassium bromide pellets. Mull (transmission) electronic spectra were obtained with a Cary Model 14 recording spectrophotometer. The magnetic susceptibilities were taken with a Foner-type vibrating-sample magnetomer[12] operating at a field strength of 10 kG which was calibrated with mercury(II) tetrathiocyanatocobaltate(II).[13,14] A value of 60×10^{-6} cgsu was taken for the temperature-independent paramagnetism of the copper(II) ion.

Extended Hückel molecular orbital (EHMO) calculations were performed using the method described by Hoffmann[15] in which all overlap is included. The off-diagonal matrix elements are given by[16]

$$H_{ij} = -KS_{ij}(H_{ii}H_{jj})^{1/2}$$

where $K = 1.75$. The valence orbital ionization potentials (VOIP's) taken from Basch et al.[17] were for nickel since those for copper are somewhat controversial and this has been found satisfactory in calculations for other copper complexes.[18] Ligand VOIP's were taken from the tabulation of Ballhausen and Gray.[19] The charge dependence of the metal VOIP's followed the approximation employed by Schachtschneider et al.[20] in their calculations for vanadocene. The metal VOIP's are expressed as

$$H_{ii} = -(Aq^2 + Bq + C)$$

where A, B, and C are parameters obtained from spectroscopic data on the free atom and ions and q is the net charge on the metal. The initial charge on the copper atom was obtained from Sanderson's electronegativity method,[21] the secular equations were solved for eigenvalues and eigenvectors, and the metal charge was evaluated using a Mulliken[22] population analysis. The calculations were repeated until the computed charge agreed to within less than 0.01 unit with the input charge. The copper atom Slater orbital exponents were those employed by Zerner and Gouterman[23] in their calculations on copper(II) porphyrins. Ligand atom Slater orbital exponents were simple averages of energy-optimized valence-shell orbital exponents listed by Clementi and Raimondi.[24] The parameters utilized in the calculations are summarized in Table I. The structural data employed were taken from the crystal structure[6] of $Cu(pyr)(NO_3)_2$ as well as an average of the bond angles and bond distances so as to have D_{2h} symmetry for this molecule. The calculations employed a version[18] of Hoffmann's program,[15] obtained from the Indiana University Quantum Chemistry Program Exchange, modified to permit inclusion of a first-row transition metal atom. Calculations were performed using the IBM 360-65 digital computer at the University of Kentucky Computing Center.

Table II. Infrared Spectrum[a] of $(PP)Cu(NO_3)_2$

Ligand	Complex	Assignment
	283 s	ν(Cu–N)
	338 m, br	ν(Cu–O)
400 s		
425 s	431 s	
	464 s	
490 s		
	527 s	
593 w		
641	641 s	
	652 s	
	708 w	$\nu(NO_3^-)$
755 w	749 m	
	770 sh	
775 m, br	775 m, br	
	799 s	$\nu(NO_3^-)$
830 vw	830 m	
850 w	855 m	
	870 m	
875 m, br	875 m	
945 m	955 vw	
	972 sh	$\nu(NO_3^-)$
1010 s, br	1013 s, br	
1038 w	1030 sh	
	1068 w	
1110 w, br	1104 m	
	1148 s	
1175 m, br		
	1195 m	
1205 m	1209 m	
	1272 s, br	$\nu(NO_3^-)$
1285 vw	1292 sh	
1350 sh		
1380 s, br	1372 m, br	
1410 br		
	1450 br	
1560 w	1565 w	
1595 m, br	1585 s	
	1605 br	

[a] All values in cm^{-1}.

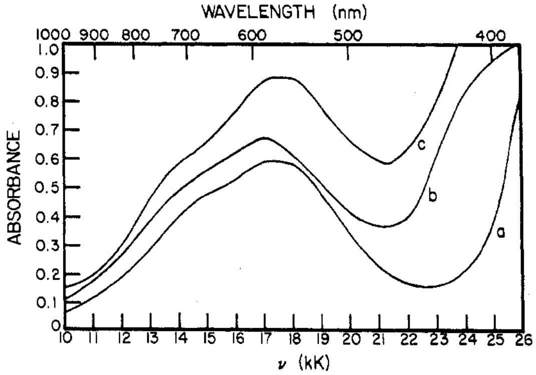

Figure 2. Electronic spectra of several adducts of copper(II) nitrate as Nujol mulls: a, pyrazine adduct; b, pyrido[2,3-*b*]-pyrazine adduct; c, quinoxaline adduct.

Results and Discussion

Spectroscopic Data. The infrared spectrum of $(PP)Cu(NO_3)_2$ exhibits no bands above 1600 cm^{-1}. Tentative assignments of nitrate and metal–ligand stretching frequencies are proposed in Table II. In general, metal–oxygen stretching frequencies are larger than metal–nitrogen stretching frequencies.[25] The 338- and 283-cm^{-1} bands of $(PP)Cu(NO_3)_2$ have been assigned to ν(Cu–O) and ν(Cu–N), respectively. These assignments are in accord with those for a variety of oxygen and nitrogen donor ligands. Bands at 344 and 290 cm^{-1} have been similarly assigned[9] for $(quinox)Cu(NO_3)_2$ (quinox = quinoxaline).

Table III. Electronic Spectral Parameters

Complex	ν_1, kK	ν_2, kK
Nujol Mulls		
$Cu(pyr)(NO_3)_2$	14.7 sh	17.5[a]
$Cu(quinox)(NO_3)_2$	14.4 sh	17.6[a]
$Cu(PP)(NO_3)_2$	14.5 sh	17.0[a]
$Cu(nap)(NO_3)_2$	14.1	17.8[a]
Diffuse Reflectance		
$Cu(quinox)(NO_3)_2$		18.02[b]
$Cu(2\text{-}Me(quinox)(NO_3)_2$	13.8 sh	17.2[c]
$Cu(2,3\text{-}Me_2quinox)(NO_3)_2$	13.9 sh	17.5[c]

[a] This work. [b] Reference 2. [c] Reference 5.

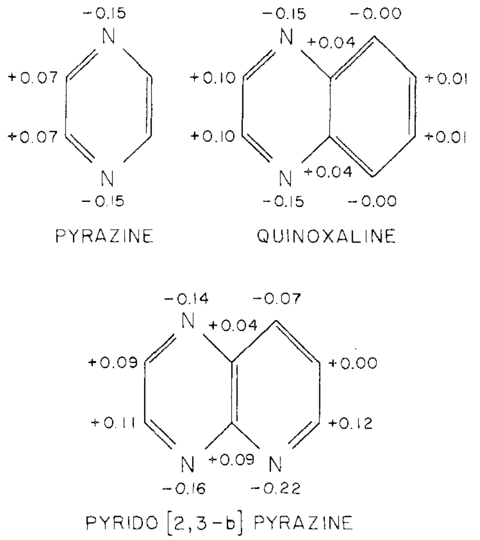

Figure 3. Simple Hückel π-electron charge distributions calculated for the various molecules.

The electronic spectra of several related copper(II) nitrate adducts are shown in Figure 2. The band positions and shapes differ from those reported by Billing et al.[5] for polymeric copper(II) halide complexes of quinoxaline and substituted derivatives. Within the pyrazinecopper(II) nitrate family of complexes the compounds apparently have very similar electronic structures. Electronic spectral data are summarized in Table III. The spectrum of the quinoxaline complex, which is suspected[9] of having a greater cant of the planar copper(II) nitrate groups with respect to the copper–nitrogen bond axis, differs a bit from the spectra of the pyrazine and pyrido[2,3-*b*]pyrazine compounds and this difference is in accord with other properties reported[9] for the complex. The similarity of the electronic spectrum of the $(PP)Cu(NO_3)_2$ compound with that of the pyrazine analog supports the structure proposed in Figure 1. Additional support for the proposed structure of $(PP)Cu(NO_3)_2$ comes from simple Hückel molecular orbital (using $\alpha_N = 0.5$ and $\beta_{CN} = 1.0$) calculations for pyrazine, quinoxaline, and pyrido[2,3-*b*]pyrazine. Taking the π-electron charges of nitrogen atoms as a measure of basicity Figure 3 shows that, except for steric effects, pyrazine and quinoxaline are expected to give rise to similar complexes whereas π-electron charges definitely favor the use of pyrido[2,3-*b*]pyrazine as a "stepped" bridging ligand. The nitrogen atom with a −0.16 charge could possibly be involved in "semicoordination" with the copper(II) ion. The diffuse-reflectance spectral data[5] for the analogous 2-methyl- and 2,3-dimethylquinoxaline complexes suggest that all of these compounds belong to the same structural class.

Magnetic Susceptibility Data. The reciprocal susceptibility from 4.2 to 254° K for the $(PP)Cu(NO_3)_2$ complex is shown in Figure 4. The experimental data obey the Curie–Weiss law, $\chi = C/(T + \Theta)$, in the temperature region 30–254° giving a Θ of 24° and $\mu_{eff} = 1.74$ BM. The minimum in the $1/\chi$ vs. T plot near 17° indicates an antiferromagnetic interaction. The data were interpreted using the Heisenberg[26] and Ising[27] models for a linear chain of interacting spins using the Hamiltonian (1) where a negative J is indicative of an antiferromagnetic interaction. The anisotropic Ising model obtains with $\gamma = 0$ in the Hamiltonian and expressions for the susceptibility are

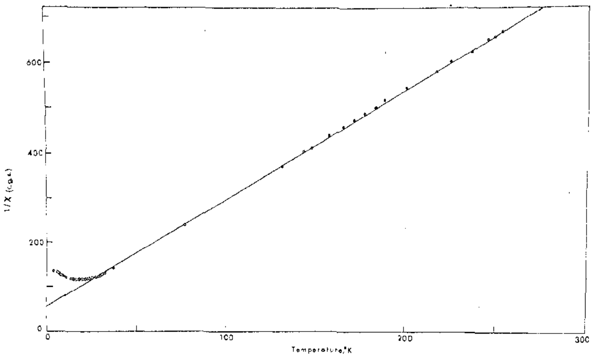

Figure 4. Plot of reciprocal susceptibility against temperature from 4.2 to 254°K for $(PP)Cu(NO_3)_2$.

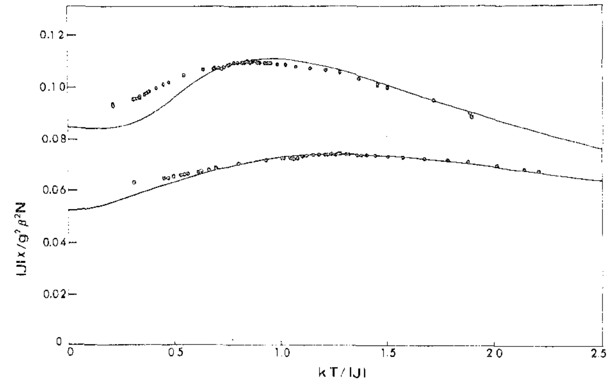

Figure 5. Proportionate susceptibility vs. temperature expressed in terms of Ising (upper) and Heisenberg (lower) models for $(PP)Cu(NO_3)_2$.

$$\mathcal{H} = -2J\sum_{i=1}^{N}[S_{iz}S_{(i+1)z} + \gamma(S_{ix}S_{(i+1)x} + S_{iy}S_{(i+1)y})] - g\beta\sum_{i=1}^{N} HS_i \qquad (1)$$

$$\chi_{\parallel} = (Ng^2\beta^2/4kT)\exp(2J/kT)$$

and

$$\chi_{\perp} = (Ng^2\beta^2/8J)[\tanh(J/kT) + (J/kT)\operatorname{sech}^2(J/kT)]$$

with respect to the isolated chain. However, only approximate solutions are available for the Heisenberg model; they are $kT_{max}/|J| \simeq 1.282$ and $|J|\chi_{max}/g^2\beta^2N \simeq 0.07346$. The magnetic data were fit to the Ising model using a least-squares program whereby J and g were varied. Because no closed form expressions are available for the Heisenberg model, estimated standard deviations were calculated relative to Bonner and Fisher's approximated curve.[26] The estimated standard deviations of the Ising and Heisenberg models using unweighted data sets are 7.5×10^{-6} and 3.7×10^{-8}, respectively. Agreement clearly favors the Heisenberg model over the Ising model as compared in Figure 5. Recent results on chain complexes by Takeda et al.,[28] Matsuura,[29] Jeter and Hatfield,[30] and Richardson et al.[8] also indicate a definite preference for the Heisenberg model. The divergence of the data from the theoretical prediction in the lowest temperature region may be due to interchain coupling or may arise from the effects

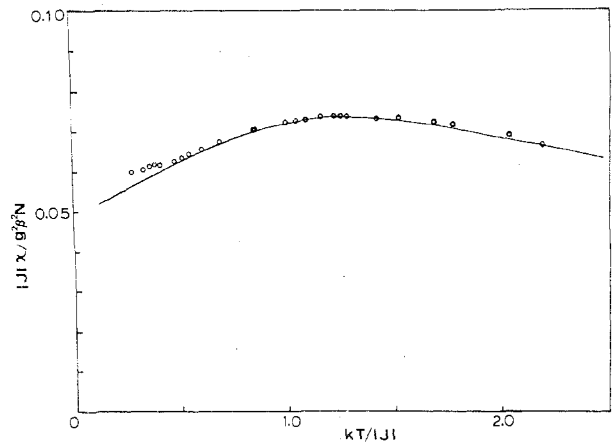

Figure 6. Proportionate susceptibility vs. temperature expressed in terms of the Heisenberg model for $(nap)Cu(NO_3)_2$.

Table IV. Magnetic Data

Complex	g_{Heis}	J_{Heis}, cm^{-1}	T_{max}, °K
$(pyr)Cu(NO_3)_2$	2.08 ± 0.01	−3.6	6.8
$(quinox)Cu(NO_3)_2$	2.13 ± 0.04	−4.5	8.3
$(PP)Cu(NO_3)_2$	2.07 ± 0.04	−9.6	17
$(nap)Cu(NO_3)_2$	2.10 ± 0.04	−10.8	18

of small amounts of monomeric impurities.

An explanation not to be discounted for the low-temperature variance of the data is that the results of the Heisenberg model[26] are based on calculations for an infinite chain. A finite chain of varying lengths will obey the model in all but the lowest temperatures where a positive divergence in χ is expected.

Perhaps the most convincing evidence for a "stepped" bridging structure in the $(PP)Cu(NO_3)_2$ complex comes from the low-temperature magnetism of the $(nap)Cu(NO_3)_2$ complex. The naphthyridine complex exhibits an enhanced spin exchange relative to the pyrazine complex much like the pyrido[2,3-*b*]pyrazine complex. The maximum in susceptibility occurs at 18°K. The 1,5-naphthyridine ligand offers the advantage of only two binding sites restricting the possible conformations of the complex. (See Figure 6.)

In Table IV the *g* and *J* values of the pyrido[2,3-*b*]pyrazine and 1,5-naphthyridine complexes are compared with those obtained from magnetic data for the pyrazine and quinoxaline complexes. The structures of the pyrazine and quinoxaline complexes were proposed to be analogous on the basis of infrared and magnetic data and any differences in exchange were assumed to be due to changes in covalency or steric factors. For a linear structure a fused pyridine ring in the case of the pyrido[2,3-*b*]pyrazine would not be expected to alter the *J* values relative to the pyrazine complex much more than the fused phenyl ring in the case of the quinoxaline complex, assuming bonding in both is analogous to the pyrazine. However, the $(PP)Cu(NO_3)_2$ and $(nap)Cu(NO_3)_2$ complexes are found to have an exchange value more than twice as great as the pyrazine and quinoxaline complexes. The comparison of magnetic data seem to indicate that the pyrido[2,3-*b*]-pyrazine ligand bonds in an analogous manner as the naphthyridine complex and gives support to the "stepped" bridging as hypothesized from Huckel molecular orbital calculations.

We prepared and characterized the naphthyridine complex for proof of structure after completing the work with the pyridopyrazine compound.

Molecular Orbital Calculations. Figure 7 summarizes the results of the EHMO calculations for $(pyr)Cu(NO_3)_2$. Since calculations for the infinite polymer are not tractable, calculations for a trans "octahedral" $Cu(pyr)_2(NO_3)_2$ unit were undertaken. Since spin-exchange coupling is reasonably small ($J < -5.0$ cm^{-1})[8] in $(pyr)Cu(NO_3)_2$, it was believed that EHMO calculations would be of assistance in understanding the electronic structure of complexes of this type; i.e., it was assumed that consideration of calculated one-electron energies ($>>>|J|$) could provide an adequate picture of the bonding and properties of the complexes. Although extended Hückel calculations are not the best which can be performed for transition metal complexes, EHMO calculations can be performed for large molecules of the type of interest here comparatively economically. The results of the calculations for the actual structure[6] indicate that the ground state is made up of 26.8% d_{z^2}, 16.1% $d_{x^2-y^2}$, and 11.9% 4s metal orbital character with $2p_z$ orbitals of pyrazine nitrogen and carbon atoms being the other major contributors. Since the effective coordination geometry can be considered as being D_{2h}, calculations were also performed for the molecule possessing this somewhat idealized geometry. The results of the calculation are also presented in Figure 7. An additional advantage associated with calculations employing D_{2h} microsymmetry is that various metal–ligand orbital interactions can be more clearly classified. The coordinate system used for the orbital transformation scheme is given in Figure 8. The symmetry orbitals, normalized neglecting ligand–ligand orbital overlap, were generated by standard projection operator techniques. The coefficients of all the metal orbitals in the ^2A_g ground state in D_{2h} symmetry (22.7% d_{z^2}, 14.2% $d_{x^2-y^2}$, and 12.9% 4s) and

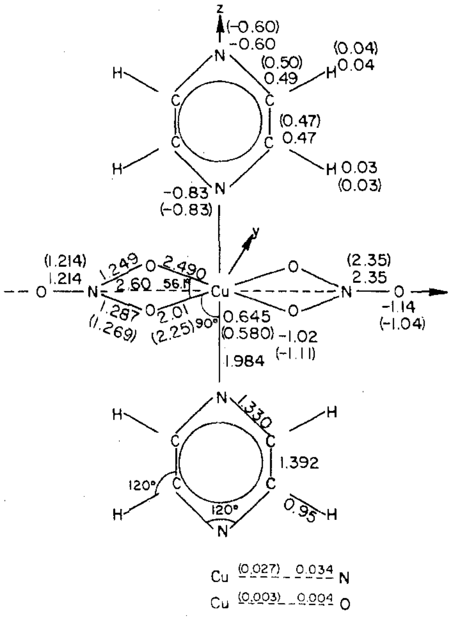

Figure 7. Left-hand side: bond angles and distances used; the values in parentheses are values used for the symmetric case. Right-hand side: resultant charge on the atoms. The Mulliken reduced overlap populations (ROP) for the transannular interaction of Cu–N and Cu–O are given at the bottom.

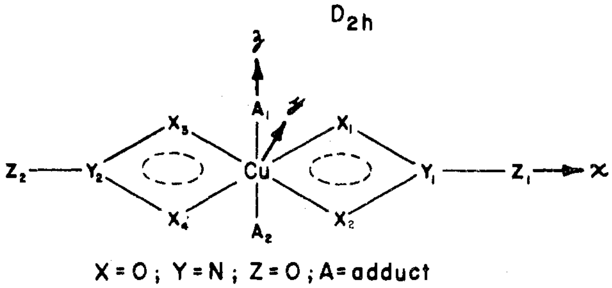

Figure 8. Coordinate system employed in calculations and generation of symmetry orbitals.

the coefficients for the atoms in the ligands are very close to those found in the calculations involving the actual structure. The coefficients derived from the MO calculations must be viewed with caution; they reflect the low symmetry and extensive mixing of orbitals which is expected in such cases. The coefficients are not adequate for the calculations of molecular properties, but they do provide a guideline for the classification of the properties of these interesting systems.

Electronic transition energies were evaluated from the molecular orbital energy level diagram using the hole concept,[32] and assignments were guided by the evaluation of electric dipole transition moment integrals.[33] The calculated energies of the largely metal-based transitions were in reasonable agreement with the experimental results; that is, transitions were predicted to occur in the 11,000–17,000-cm^{-1} region. In order to check the calculated transition energies and assignments, we also performed crystal field calculations[34] for $Cu(pyr)_2(NO_3)_2$. The α_4 parameter[34] for the oxygen atoms of the bidentate nitrate ion and the nitrogen atoms of pyrazine was chosen to be -8000 cm^{-1}, and D_{2h} symmetry with a O–Cu–O bond angle of 56° was assumed. There was crude agreement between the transition energies calculated by the crystal field and MO methods, and it is clear that single-crystal optical spectral studies are needed to determine the exact nature of the transitions in these complexes. However, both methods do agree that there is an ^2A_g ground state which involves considerable admixture of metal $d_{x^2-y^2}$ and d_{z^2} orbitals. This agrees with the results of the EPR study of $Cu(pyr)(NO_3)_2$ by Kokoszka and Reimann.[35] Hathaway and coworkers have shown[36] that the description of the ground state is not as unusual as originally thought. Metal–ligand π bonding which is related to the superexchange spin-coupling mechanism, as indicated by the EHMO results, plays an important role in determining the ordering of the energy levels.

Acknowledgment. This work was supported by the University of Kentucky Research Foundation, the National Science Foundation through Grants GP-22887 and GP-42487X, and the Materials Research Center of the University of North Carolina under Grant No. G-33632 from the National Science Foundation. The Magnion EPR spectrometer was purchased with the assistance of NSF Grant No. GP-19307. We wish to thank Mr. K. T. McGregor and Mr. R. P. Eckberg for experimental assistance.

Registry No. $(pyr)Cu(NO_3)_2$, 28209-64-5; $(quinox)Cu(NO_3)_2$, 40187-03-9; $(PP)Cu(NO_3)_2$, 56210-53-8; $(nap)Cu(NO_3)_2$, 56030-13-8.

References and Notes

(1) (a) University of Kentucky. (b) University of North Carolina.
(2) A. E. Underhill, *J. Chem. Soc.*, 4336 (1956).
(3) M. J. M. Campbell, R. Grzeskowiak, and F. B. Taylor, *J. Chem. Soc. A*, 19 (1970).
(4) G. W. Inman, Jr., J. A. Barnes, and W. E. Hatfield, *Inorg. Chem.*, **11**, 764 (1972).
(5) D. E. Billing, A. E. Underhill, D. M. Adams, and D. M. Morris, *J. Chem. Soc. A*, 902 (1966).
(6) A. Santoro, A. D. Mighell, and C. W. Reimann, *Acta Crystallogr., Sect. B*, **26**, 979 (1970).
(7) J. F. Villa and W. E. Hatfield, *J. Am. Chem. Soc.*, **93**, 4081 (1971).
(8) D. B. Losee, Jr., H. W. Richardson, and W. E. Hatfield, *J. Chem. Phys.*, **59**, 3600 (1973).
(9) H. W. Richardson, W. E. Hatfield, H. J. Stoklosa, and J. R. Wasson, *Inorg. Chem.*, **12**, 2051 (1973).
(10) J. R. Allan, G. A. Barnes, and D. H. Brown, *J. Inorg. Nucl. Chem.*, **33**, 3765 (1971).
(11) Y. Hamada and I. Takeuchi, *Chem. Pharm. Bull.*, **19**, 1857 (1971).
(12) S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).
(13) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958); H.-St. Rade, *J. Phys. Chem.*, **77**, 424 (1973).
(14) E. Konig, "Magnetic Properties of Transition Metal Compounds", Springer-Verlag, Berlin, 1966.
(15) R. A. Hoffmann, *J. Chem. Phys.*, **39**, 1397 (1963).
(16) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).
(17) H. Basch, A. Viste, and H. B. Gray, *J. Chem. Phys.*, **44**, 10 (1966).
(18) H. E. Montgomery, H. J. Stoklosa, and J. R. Wasson, unpublished results.
(19) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory", W. A. Benjamin, Reading, Mass., 1964, p 122.
(20) J. H. Schachtschneider, R. Prins, and P. Ros, *Inorg. Chim. Acta*, **1**, 462 (1967).
(21) R. T. Sanderson, "Inorganic Chemistry", Reinhold, New York, N.Y., 1967, Chapter 3; H. J. Stoklosa, *J. Chem. Educ.*, **50**, 290 (1973).
(22) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).
(23) M. Zerner and M. Gouterman, *Theor. Chim. Acta*, **4**, 44 (1966).
(24) E. Clementi and D. L. Raimondi, *J. Chem. Phys.*, **38**, 2686 (1963).
(25) D. M. Adams, "Metal-Ligand and Related Vibrations", Edward Arnold, London, 1967; K. Nakamoto, *Angew. Chem., Int. Ed. Engl.*, **11**, 666 (1972).
(26) J. Bonner and M. Fisher, *Phys. Rev. A*, **135**, 640 (1964).
(27) M. E. Fisher, *J. Math. Phys.*, (*N.Y.*), **4**, 124 (1963).
(28) K. Takeda, S. Matsukwa, and T. Haseda, *J. Phys. Soc. Jpn.*, **30**, 1330 (1971).
(29) M. Matsuura, *Phys. Lett. A*, **34**, 274 (1971).
(30) D. Y. Jeter and W. E. Hatfield, *J. Inorg. Nucl. Chem.*, **34**, 3055 (1972).
(31) D. A. Brown, W. J. Chambers, and N. J. Fitzpatrick, *Inorg. Chim. Acta, Rev.*, **6**, 7 (1972), and references therein.
(32) A. B. P. Lever, "Inorganic Electronic Spectroscopy", American Elsevier, New York, N.Y., 1968.
(33) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **6**, 917 (1967).
(34) A. L. Companion and M. A. Komaryusky, *J. Chem. Educ.*, **41**, 257 (1964); J. R. Wasson and H. J. Stoklosa, *ibid.*, **50**, 186 (1973); H. J. Stoklosa and J. R. Wasson, *J. Inorg. Nucl. Chem.*, in press.
(35) G. F. Kokoszka and C. W. Reimann, *J. Inorg. Nucl. Chem.*, **32**, 3229 (1970).
(36) B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970); B. J. Hathaway and D. E. Billing, *ibid.*, **5**, 143 (1970).