Contribution from the Department of Chemistry University of Nevada, Reno, Reno, Nevada 89507, U.S.A.

An Investigation of the Influence of *trans*-Axial Ligation on Metal-Metal Bond Formation in Copper(II) Acetate Complexes with 4-Substituted Pyridine N-Oxides

D. Hibdon[1] and J.H. Nelson*

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A series of 4-substituted pyridine N-oxides (4-ZPyNO) have been found to react with copper(II) acetate to form the dimeric complexes $[Cu(CH_3COO)_2\cdot 4ZPyNO]_2$*, where Z is* CH_3O, CH_3, *H, Cl or* NO_2. *The complexes were characterized by elemental analyses, electronic and infrared spectra and magnetic measurements. The magnetic data, electronic spectra and the infrared spectra are all consistent with the δ-bond model. Several correlations of these data are found and discussed. It is concluded that pyridine N-oxides with relatively low basicities and high π-acceptor abilities enhance copper-copper bonding. In this respect high π-acceptor ability seems to be significantly more effective than weak σ-donation in promoting copper-copper bonding for pyridine N-oxides as well as other ligands capable of π-back bonding.*

Introduction

The dimeric transition metal carboxylates $[M(RCO_2)_2L]_2$ having the general structure depicted in Figure 1 have been extensively studied for a number of reasons.[2] Paramount among these are the interest in metal-metal bonds;[3-5] and the fact that three independent factors are subject to variation within these series of complexees. The resultant changes in the metal-metal interaction may be assessed as these are changed.[3,4] One of the factors, the metal, M, has been the subject of numerous investigations by Cotton[5,6] to determine the metal-metal bond lengths. While these studies have focused primarily on the metal, the ligands, L, and the substituents, R, have been varied as well. Others[2,7,8] have focused primarily upon R or L with the metal generally being copper. Prior to this study, no one had studied a series of complexes where the basicity of L varies greatly while steric effects are held constant.

Copper complexes have been studied in detail because their magnetic moments reflect the magnitude of the metal-metal interaction.[9-12] Since copper(II) has a d^9 electron configuration, a monomeric complex of this metal, regardless of geometry, will possess one unpaired electron and hence exhibit a magnetic moment in the vicinity of 1.73 Bohr Magnetons. If, however, a normal strong metal-metal bond were to form between two of these monomers, then the two formerly unpaired electrons could pair, leading to a diamagnetic dimer. The intermediate situation should also conceptually be possible wherein the magnetic moment of the complexes could vary between zero and 1.73 Bohr Magnetons as the strength of the metal-metal interaction varies. The strength of the metal-metal interaction should be critically dependent upon L and R.[2,15]

In copper(II) carboxylates (Fig. 1), whose structures are ideally suited for a direct metal-metal interaction, a weak covalent bond exists[2-8] and the ground state is a diamagnetic singlet. However, the paramagnetic triplet state is thermally accessible re-

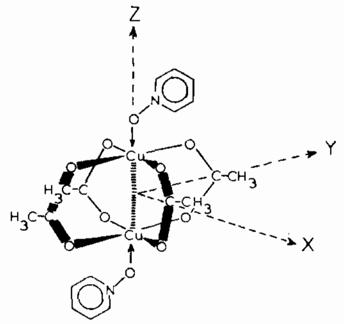

Figure 1. Assumed structure of the complexes, $[Cu(CH_3\text{-}COO)_2.4ZPyNO]_2$ illustrating the symmetry properties of the molecule and the symmetry of overlap between the N-O π and π* orbitals with the Cu d_{xy}. d_{xz}, d_{yz} and/or $d_{x^2-y^2}$ orbitals. The dihedral angle between the plane of the pyridine ring and the O_4 plane is assumed to be ca. 90°C.

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sulting in temperature dependent magnetic moments and antiferromagnetic behavior.

Beginning with the early studies on copper(II) acetate[13,14] itself, the questions of the existence and nature of the metal-metal bond have become rather controversial.[15] Three types of metal-metal interaction are formally possible: a σ-bond formed *via* overlap of the d_{z^2} orbitals on each metal center, a π-bond formed by overlap of the d_{xz} or d_{yz} orbitals on each metal center or a δ-bond formed by overlap of the d_{xy} or $d_{x^2-y^2}$ orbitals on each metal center. The σ and δ bonding models have received the greatest support, with most authors currently favoring the δ-bond model. The exact nature of the bond depends critically upon the relative energies of the atomic orbitals involved and their respective electron densities.

In the present study we have chosen to investigate the effect of the ligands on the electron density along the z-axis and the consequences on the strength of the metal-metal bond. The 4-substituted pyridine N-oxides (4Z-PyNO) were selected because they are an ideal series of ligands whose basicities span 4-orders of magnitude[16] while maintaining constant steric effects at the donor site.

The interactions of pyridine N-oxides with copper (II) have been extensively studied and are exceedingly interesting in their own right.[16-30] They form complexes with copper(II) halides possessing subnormal magnetic moments and a copper-copper interaction arising through a superexchange mechanism. In these complexes no direct copper-copper bond is believed to exist.

Three questions could then potentially be answered by investigating complexes of copper(II) acetate with pyridine N-oxides: (1) Is the dimeric copper carboxylate structure preserved with these ligands; i.e., is the structure thermodynamically more stable than one involving pyridine N-oxide bridges? (2) If the dimeric carboxylate structure is preserved, how do changes in the basicity of L affect the strength of the copper-copper interaction? (3) Since pyridine N-oxides have been shown to be good π-acceptors,[16] what is the relative importance of σ-donation and π-acceptance towards the magnitude of this metal-metal interaction?

Experimental

Synthesis. Preparations of the 4-substituted pyridine N-oxides have been previously described.[31,32] All of the amine oxides were purified either by vacuum sublimation or by recrystallization from acetone immediately prior to preparing the complexes. The complexes were all prepared by the same general method as illustrated by the following example.

$[Cu(CH_3COO)_2 \cdot C_5H_5NO]_2$. Twenty-five ml of 2,2-dimethoxypropane was added to a solution containing 0.732 g (3.68×10^{-3} moles, twice recrystallized from dilute acetic acid[33]) copper acetate in 250 ml boiling methanol and the heating continued for several minutes. To this blue solution was added, with stirring, a solution containing 1.40 g (1.47×10^{-2} moles) freshly purified pyridine N-oxide in 25 ml methanol plus 10 ml 2,2-dimethoxypropane. The resultant green solution was concentrated by heating to a volume of approximately 150 ml and allowed to cool to room temperature. The cool solution was filtered and the minor quantity of blue precipitate (unreacted copper acetate) was isolated and discarded. The filtrate was then reduced in volume to approximately 50 ml by heating, cooled to room temperature, and anhydrous ethyl ether added to incipient precipitation. The resultant green precipitate was filtered, washed with anhydrous diethyl ether and vacuum dried over phosphorus pentoxide at ambient temperature to yield 0.85 g (85% based on copper acetate) of $[Cu(CH_3COO)_2 \cdot C_5H_5NO]_2$. The decomposition points, yields and analytical data for the complexes are listed in Table I. The complexes are hydroscopic and the elemental analyses for the 4-methylpyridine N-oxide complex reflect this. They decompose slowly in air to yield hydrated copper acetate and the free N-oxide, but are stable in a desiccator for periods of at least one year. Repeated attempts to prepare the analogous complex of 4-cyano pyridine N-oxide met with failure owing primarily to solubility difficulties with the ligand. Carbon, hydrogen and nitrogen analyses were performed by Galbraith Laboratories, Knoxville, Tennessee and copper analyses were obtained by titration with EDTA according to Welcher.[34]

Magnetic Moments. Magnetic susceptibilities were determined by the Gouy technique at 8 K Gauss. The compound $Hg[Co(SCN)_4]$ was used as a calibrant.[35] The diamagnetic corrections were calculated from Pascal's constants.[36] The effective magnetic

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Table I. Elemental Analyses and Physical Constant Data.

Complex $[Cu(OAc)_2L]_2$	Color	(°C)^{mp}	%C Calc.	 Found	%H Calc.	 Found	%N Calc.	 Found	%Cu Calc.	 Found	% Yield
$L4CH_3OC_5H_4NO$	green	190-195	39.17	38.99	4.24	4.19	4.57	4.80	20.72	20.3	81%
$4CH_3C_5H_4NO \cdot H_2O$	green	190-193	38.99	39.37	4·87	4.70	4.55	4.77	20.63	20.9	74%
C_5H_5NO	green	199-204	39.06	39.03	3.91	4.07	5.06	5.22	22.97	23.3	85%
$4ClC_5H_4NO$	green	205-208	34.75	34.72	3.21	3.23	4.50	4.76	20.42	20.6	80%
$4NO_2C_5H_4NO$	green	165-170	33.61	33.84	3.11	3.24	8.71	8.93	19.76	19·6	69%

Table II. Magnetic Data for the Complexes $[Cu(CH_3COO))_2 \cdot 4ZPyNO]_2$.

Z	$10^6\chi_g$ [a] (cqesu)	$10^6\chi_{m'}$ cgesu)	μ_{eff} B.M.
CH_3O	2.63±0.15	950±10	1.46±0.02
CH_3	2.42±0.13	782±40	1.37±0.03
H	2.61±0·13	790±50	1.37±0.03
Cl	2.37±0.15	829±50	1.41±0.01
NO_2	0.88±0.09	360±35	0.92±0.02
H_2O [b]	4.10±0.03	891±7	1.408±0.007
H_2O [c]	4.03	889	1.40

[a] Measured at 295.3°K. Uncertainties are standard deviations of five independent determinations on samples from at least two separate preparations. [b] This work measured at 295.03° K. [c] Data taken from reference 13 measured at 294.2°K.

Table III. Electronic Spectral Data for the Complexes $[Cu(CH_3COO)_2 \cdot 4ZPyNO]_2$.

Z	Band I (kK)	Band II (kK)	$\pi\rightarrow\pi^*$ [a] complex	$\pi\rightarrow\pi^*$ [b] ligand	$\Delta\nu\pi\rightarrow\pi^*$ [c]
NO_2	14.69 [d]	29.85 sh	42.55	44.25	—1.70
Cl	13.91	26.32 sh	37.45	39.22	—1.77
H	13.93	26·04 sh	37·59	39.37	—1.78
CH_3	13.61	32.79 sh	37.04	39.06	—2.02
CH_3O	13.59	32.79 sh	36.36	37.04	—0.68

[a] Essentially an intraligand transition. [b] The $\pi\rightarrow\pi^*$ transition in the free ligand data taken from reference 51, pages 140 ff. [c] $\Delta\nu\pi\rightarrow\pi^* = \nu_{\pi\rightarrow\pi^*}$ free ligand $- \nu_{\pi\rightarrow\pi^*}$ complex. [d] Bands are in kilo kaysers, sh = shoulder.

moments were calculated using the expression $\mu_{eff} = 2.839[(\chi_{m'} - N\alpha)T]^{1/2}$, where $N\alpha$ represents the temperature–independent paramagnetism associated with the copper ion; a value of $N\alpha = 60 \times 10^{-6}$ cgesu was used.[37] The accuracy of the results was checked by measuring the susceptibility of copper acetate monohydrate and comparing it with that reported in the literature.[13] The results listed in Table II are the averages of five independent measurements on different samples from at least two separate preparations with a maximum variance of ±0.03 Bohr Magnetons in the derived magnetic moments.

Electronic Spectra. Electronic spectra were obtained using a Cary 14 recording spectrophotometer using dispersions in Nujol suspended on filter paper for solid state results. The reference was a Nujol saturated piece of filter paper. Solution spectra were recorded using 1 and 10 cm quartz cells with ethanol, methanol or nitromethane as solvents with and without excess ligand present. In the absence of excess ligand, the spectra were essentially those of solvated copper acetate even in the presence of 2,2-dimethoxypropane. With excess ligand the complexes precipitated from solution. Continuous variation studies were attempted, but the spectra of the complexes and that of copper acetate monohydrate are too similar to make these of any value. In addition, in the presence of a large excess of ligand and 2,2-dimethoxypropane, the complexes precipitated from solution making it impossible to determine concentrations. For these reasons, only solid state spectral results are reported in Table III. Typical spectra are illustrated in Figure 2.

Infrared Spectra. Infrared spectra were recorded on both the free ligands and the complexes as nujol mulls between sodium chloride disks and as KBr wafers in the sodium chloride region (650-4000 cm^{-1}) on a Beckman IR-8 recording spectrophotometer. The

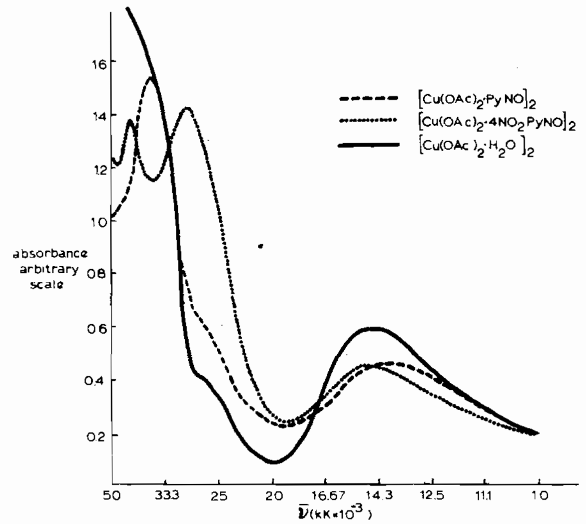

Figure 2. Solid state electronic spectra taken as nujol mulls for $[Cu(CH_3COO)_2 \cdot H_2O]_2$(—), $[Cu(CH_3COO)_2 \cdot PyNO]_2$(- - -), and $[Cu(CH_3COO)_2 \cdot 4NO_2PyNO]_2$(. . . .).

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Table IV. Infrared Spectral Data for the Complexes $[Cu(CH_3COO)_2 \cdot 4ZPyNO]_2$.

Z	State	ν_{NO} [a]	$\Delta\nu_{NO}$ [a]	$\nu_{COO^-(assym)}$ [a]	$\nu_{COO^-(sym)}$ [a]	δ_{NO} [a]	$\Delta\delta_{NO}$ [a]
CH_3O	KBr	1210	30	1619	1420	850	0
	Nujol mull	1213	27	1619	1433	855	+5
CH_3	KBr	1228	32	1620	1425	855	0
	Nujol mull	1234	26	1626	1429	859	+4
H	KBr	1235	30	1609,1624	1429	839	0
	Nujol mull	1233,1246	25	1613,1625	1433	843	+4
Cl	KBr	1235,1245	29	1626,1608	1436	851	+3
	Nujol mull	1239,1249	25	1610,1626	1439	850	+2
NO_2	KBr	1274	29	1604	1429	869	—5
	Nujol mull	1254	49	1603,1623	1433	873	—1
H_2O	KBr	—	—	1605	1425	—	

[a] Frequencies and frequency shifts are in cm^{-1}. For the free N-oxide ν_{NO} frequencies, see H. Shindo, *Chem. Pharm. Bull.* (Tokyo), 6, 117 (1958) or ref. 51, page 119. The carboxylate symmetric and assymetric stretching frequencies were assigned according to ref. 45. $\Delta\nu_{NO} = \nu_{NO}$ free ligand $- \nu_{NO}$ complex, $\Delta\delta_{NO} = \delta_{NO}$ free ligand $- \delta_{NO}$ complex.

spectra were calibrated with known frequency bands of polystyrene. The data obtained are listed in Table IV.

Results

The elemental analyses indicate that the compounds may be formulated as $[Cu(CH_3COO)_2 \cdot 4ZPyNO]$. The complexes are all somewhat hydroscopic and decompose in water and alcoholic solvents to yield solvated copper acetate and the free N-oxide. This occurs even in the solid state under atmospheric moisture over a period of days to weeks, the rate depending on the particular ligand (see experimental section). This behavior is typical of amine oxide complexes.[38-43]

The structure of these complexes is established as that of the parent dimeric copper acetate monohydrate (Figure 1) from the following observations. In each case ν_{NO}, the nitrogen-oxygen stretching frequency, is shifted to lower energy upon complexation by about 30 cm^{-1} (Table IV) and a linear correlation is observed between ν_{NO} and σ_{PyNO}[44] (Figure 3). In each case the N-O bending frequency δ_{NO} shifts to higher energy or remains unshifted as well. These observations indicate that the amine oxide is in fact coordinated.[16]

The retention of the dimeric carboxylate structure as opposed to a structure involving bridging N-oxides is supported by the following observations. Each complex exhibits the carboxylate stretching frequencies, ν_{COO}-(sym) and ν_{COO}-(assym), at very similar energies to those reported for copper acetate monhydrate (Table IV).[45] The electronic spectra of the complexes and that of copper acetate monohydrate also strongly resemble one another (Table III and Figure 2) as they should since the ligational properties of the pyridine N-oxides and water are very similar.[16] Of particular importance in this regard is the presence of band(II) in all complexes, a band which is peculiar to the dimeric carboxylates and their adducts.[7,15]

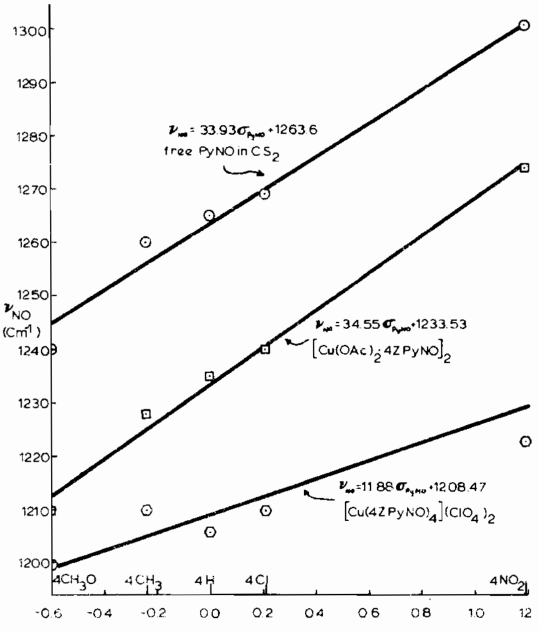

Figure 3. Correlations of ν_{NO} with σ_{PyNO} for the free ligand,[51](⊙) $[Cu(CH_3COO)_2 \cdot 4ZPyNO]_2$(⊡) and $[Cu(4ZPyNO)_4](ClO_4)_2$.[25](⊙)

In addition, ν_{NO} for bridging amine-oxide complexes is always shifted to lower energy and varies over a more limited range than observed for these complexes: $\nu_{N\text{-}O}$ = 1199-1208 cm^{-1} [20,26] for bridging amine-oxides as compared to $\nu_{N\text{-}O}$ = 1210-1274 cm^{-1} for the complexes reported herein.

The magnetic moments, however, cannot be used to differentiate between the two likely structures since complexes having either bridging carboxylates or bridging amine oxides would be expected to exhi-

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bit antiferromagnetism and subnormal magnetic moments.[2]

There remain two points of the structure as illustrated in Figure 1 yet to be established, namely the N-O-Cu bond angle the dihedral angle between the plane of the pyridine ring and the O_4 plane. The N-O-Cu angle can be taken with fair certainty to lie in the range of 114 to 125° as all the complexes containing terminal amine-oxides whose structures have been determined by X-ray crystallography have M-O-N angles in this region.[24,46-49]

The dihedral angle between the plane of the pyridine ring and the O_4 plane should lie fairly close to 90° as similar complexes, namely $Cu_3Cl_6(H_2O)_2(C_6H_7NO)_2$[50] and $SnCl_2(CH_3)_2(C_5H_5NO)_2$[49] have dihedral angles of 89° and 83°, respectively. Thus, the structure of these complexes seems reasonably well established as being that shown in Figure 1.

Discussion

Infrared Spectra. The nitrogen oxygen stretching frequency, ν_{NO}, has been found to be extremely sensitive to both substituents on the aromatic ring and to interactions wih various acids.[51,52] Linear correlations of ν_{NO} with σ_{PyNO} have been obtained for the free ligands and a large number of complexes.[16,31,44,51,52] In almost every case, ν_{NO} shifted upon coordination to lower energy by a non-uniform amount as one varies the 4-substituent on the pyridine N-oxide. Thus, when one compares plots of ν_{NO} *versus* σ_{PyNO} for various transition metal complexes, the slopes of these lines vary from nearly zero to maximum of about 17. Explanations have been offered for the differences, in terms of π-bonding, mass, and charge effects.[52] In no case, except that reported here, have slopes as high or greater than that for the free ligand (33.93) been observed. The observation of a decrease in energy for ν_{NO} as well as the nearly parallel correlation of ν_{NO} with σ_{PyNO} for both the free ligand and the complexes $[Cu(OAc)_2 \cdot 4ZPyNO]_2$ suggests two things: First, that the pyridine N-oxides are indeed coordinated to copper and second, that those substituent effects which are found in the free ligands are also manifested in the copper carboxylate complexes. This is definitely not the case for other copper pyridine N-oxide complexes such as $[Cu(4ZPyNO)_4](ClO_4)_2$ (Figure 3) whose slope is 11.88 and $[Cu(4ZPyNO)X_2]_2$[16] (where X = Cl or Br) whose slope is essentially zero. These results suggests that the double bond character of the pyridine N-oxide N-O bond in complexes with copper acetate is weakened relative to the free ligand but still very susceptible to variance as the para-substituent varies. Since both σ-donation and π-acceptance by the N-oxide would serve to weaken the N-O bond there must be a very subtle balance of these two effects in these complexes. Thus, for the 4-methoxy and 4-methyl complexes, σ-donation is probably predominant whereas for the 4-nitro complex π-acceptance is probably predominant. This means that the metal-oxygen bond strength is most likely fairly constant and weak within this series of complexes. Attempts to measure the relative bond strengths by differential thermal analyses and differential scanning calorimetry met with failure as the complexes underwent massive decomposition at the melting point to ultimately produce copper oxide. This differs from he behavior of copper(II) acetate monohydrate which undergoes loss of water at 180°C followed, at higher temperature, by rapid decomposition to CuO.[56,57] The weakness of the M-O bond is exemplified by the facile replacement of the amine oxide by atmospheric moisture (see experimental section). In at least two cases, replacement by nujol probably occurred as well since the infrared spectra taken on the nujol mulls of the complexes with pyridine N-oxide and 4-chloropyridine N-oxide both exhibit two bands for ν_{NO}, one of which occurs at the same frequency as the free ligand in nujol.[52] The near constancy of the metal-oxygen bond strength is likewise reflected in the electronic spectral and magnetic data (Vide infra).

The weakness and constancy of the M-O bonds are also shown in the small changes of δ_{NO}, a vibration which varies less than ν_{NO} upon coordination,[16] but which also usually shifts to higher energy by a greater amount than exhibited for these complexes.

Magnetic Results. The magnetic moments of the complexes are all less than 1.73 Bohr Magnetons suggesting that some coupling of the two copper atoms occurs as is the case for copper acetate monhydrate. In fact, for all of the complexes except that with 4-nitropyridine N-oxide, they are remarkably close to the value for copper acetate monohydrate This reflects the comparable donor abilities of water and pyridine N-oxides (Table II). For the 4-nitropyridine N-oxide complex, the magnetic moment is considerably reduced to a value of 0.92 B.M. at 295.3°K. This is the lowest value yet reported for a copper carboxylate other than the formates.[2] In fact, it has previously been stated[2] that "it is significant that the magnetic moments of addition compounds of copper (II) acetate or its higher homologs are not very different from those of the parent compounds."

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(52) L.C. Nathan, Ph.D. Thesis, The University of Utah, Salt Lake City, Utah, 1971. It has been argued by a referee that the fact that the slopes of ν_{NO} *vs* σPyNO (Fig. 3) are the same for both the free ligand and the complexes studied here implies that no Cu-O-π-bonding is present in these complexes. While on the surface this seems plausible, it would imply that the extent of σ-interaction in each of the complexes studied here was very nearly the same. This is totally inconsistent with the magnetic data and so some other explanation must result.

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We have concluded above that the predominant interaction in the 4-nitropyridine N-oxide complex is one involving π-acceptance. This conclusion is further supported by the lowering in the magnetic moment for this complex relative to the others. Other workers have found that the magnetic moment of copper carboxylate adducts decreases slightly as the basicity of the ligands L decreases,[7,8] but that within a given series of complexes with analogous ligands such as the para-substituted pyridines[7] or the para-substituted anilines[7] the susceptibility was essentially invariant. The greatest decrease in the magnetic susceptibility has previously been found with ligands capable of π-back bonding such as triphenylphosphine or pyrazine, and the decrease in μ for these complexes has been attributed to π-bonding.[8] Where complete temperature studies of the magnetic susceptibilities have been conducted,[7,13] it has been found that the complexes obey the equation $\chi_m = \frac{g^2N\beta^2}{3kT}[1 + 1/3\exp J/kT]^{-1} + N\alpha$. For all the complexes studied thus far, g varies over the limited range 2.13-2.25, such that at a given temperature the lead term and Nα are essentially constants in the above expression. Consequently, χ_m is roughly proportional to exp(–J/kT). Thus, as J increases the singlet triplet energy separation increases and χ_m should decrease. For complexes of copper(II) the lowest energy electronic transition is generally related to the spectrochemical parameter 10Dq and therefore related to the strength of the metal ligand interaction.[53,54] Therefore, the energy of this transition should be related to χ_m. This is nicely illustrated in Figure 4 where a correlation between Band I in the electronic spectra and χ_m' is shown. This is the first example of such a correlation. It should be noted that for the complexes undergoing predominantly σ-interactions (4-methyl and 4-methoxypyridine N-oxide) Band I remains essentially the same but χ decreases as the ligand basicity decreases. Other investigators have found that Band I varies over a much more limited range--a range of 0.26kK being found for complexes with 4-substituted pyridines[7,15] and a range of 0.45kK being found for complexes of 4-substituted anilines. Similarly $10^6\chi_m'$ only varies over a range of 32 Cgesu for 4-substituted pyridine[7] complexes and 152 Cgesu for 4-substituted aniline[7] complexes. For the 4-substituted pyridine N-oxide complexes, the ranges are much larger (Band I, 1.1kK and $10^6\chi_m'$ 530 Cgesu). If the 4-nitropyridine N-oxide complex were not included in the above data, then a range of 0.34 kK in Band I and a range of 108 Cgesu in $10^6\chi_m'$ would be found for these complexes. Thus, without the 4-nitropyridine N-oxide data we would reach the same conclusions that previous investigators have.

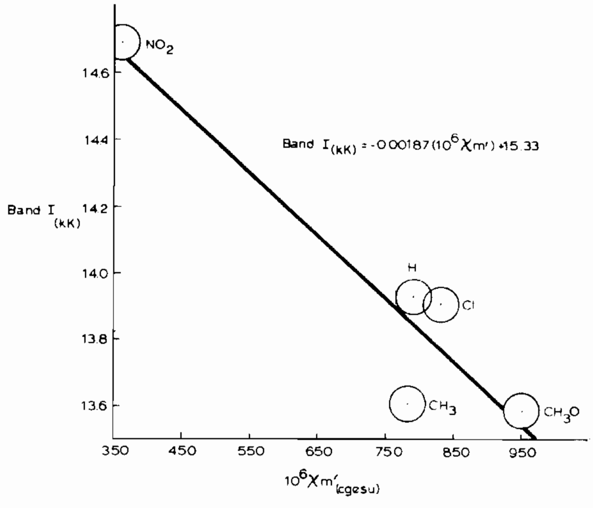

Figure 4. Correlation of the corrected molar magnetic susceptibility, $\chi_{m'}$ with the energy of the first electronic absorption band (d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$) for the complexes $[Cu(CH_3COO)_2 \cdot 4Z\text{-}PyNO]_2$.

Since 4-nitropyridine N-oxide is the best π-acceptor in the series and pyridine N-oxides are believed to be better π-acceptors than pyridines[16,38] we are led to conclude that the greater the π-accpetor ability of the ligand L, the stronger is the metal-metal interaction.

I was also found that the complexes with 4-substituted anilines exhibited lower energies for Band I and higher magnetic susceptibilities than complexes with pyridines. These differences have been attributed to differences in the π-acceptor abilities of the two series of ligands.[7]

The existence of the copper pyridine N-oxide π-bonding in these complexes is further indicated by the data shown in Figure 5. Here a linear correlation between the energy of the N-oxide π – π* transition, for both the free ligand and the complexes, and the magnetic susceptibility, $\chi_{m'}$, is found. A smaller decrease in the energy of this transition for the 4-methoxypyridine N-oxide complex compared to the other complexes indicates that π-bonding is probably less important here. If no π-interaction were present, this transition should be nearly unaffected by coordination.

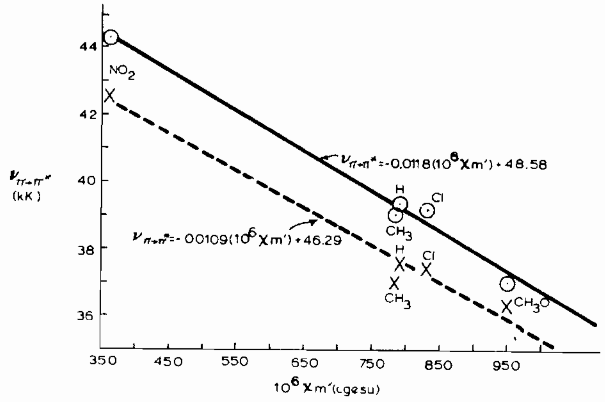

Figure 5. Correlation of the corrected molar magnetic susceptibility, χ_m', with the energy of the π→π* transitions for the free ligand (o,—) and the complexes $[Cu(CH_3COO)_2 \cdot 4ZPy\text{-}NO]_2$· (x, - - -).

Electronic Spectra. The electronic spectra of copper carboxylates have been extensively investigated.[7,8,13-15,53-55] It has been found that these complexes possess three absorption bands (I, II and III) in the regions

13.5-15 kK, 26-27 kK, and 38-40 kK, respectively. The assignments which have received the most convincing support are band I, d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$; band II, d_{xy}—$d_{x^2-y^2}$; and band III, a charge transfer transition (O → Cu).[53] These assignments are based upon the δ bond model and are consistent[10,53] with polarization measurements,[7,55] epr measurements,[7] magnetic data[13] and solvent sensitivities.[8] Figure 6 illustrates the variation in orbital energies for the complexes [Cu(OAc)$_2$4–ZPyNO]$_2$ in terms of the δ-bonding model.

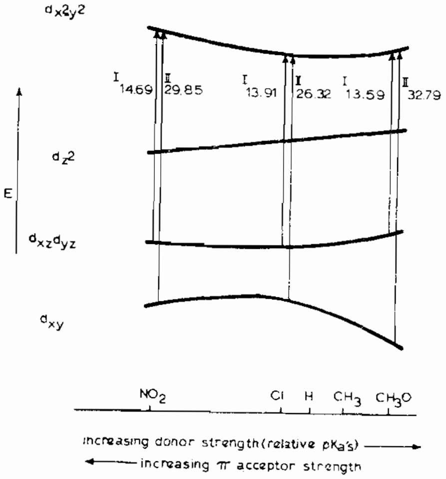

Figure 6. Variation of the d-orbital energies and the respective d-d transitions as a function of the 4-substituent for the complexes [Cu(CH$_3$COO)$_2$·4ZPyNO]$_2$. The magnitude of the electronic transitions are given in kilokaysers (see Table III).

These results can be rationalized in the following manner. As the basicity of the pyridine N-oxide increases, it should undergo a stronger interaction with the d_{z^2}, d_{xz} and d_{yz} orbitals. Hence, the d_{z^2} orbital should increase in energy regularly as the ligand basicity increases. Since the d_{xz} and d_{yz} orbitals are not directly involved in the M-O sigma bond, they will increase in energy probably through an antibonding interaction which will increase as the M-O bond length decreases, but most likely not in a linear fashion. The $d_{x^2-y^2}$, d_{xz}, d_{yz} and d_{xy} orbitals would undergo interactions with the N-O π and π* orbitals. The energies of the amine oxide π and π* orbitals vary in the following way: The π orbital is at lowest energy and the π* orbital at highest energy for 4-nitropyridine N-oxide, and the π-orbital at highest energy and π* orbital at lowest energy for 4-methoxypyridine N-oxide as illustrated in Figure 7. For 4-nitropyridine N-oxide the N-O π-orbital is probably lower in energy than the copper d_{xz} orbital and the N-O π* orbital lower in energy than the copper $d_{x^2-y^2}$ orbital. Thus, metal to amine oxide back donation will destabilize both the $d_{x^2-y^2}$ and d_{xy} orbitals while stabilizing both the amine oxide π and π* orbitals. The effects on $d_{x^2-y^2}$ and π* will most likely be greater than be effects on the d_{xy} and π orbitals.

At the other extreme, 4-methoxypyridine N-oxide, the amine oxide π-orbital is probably higher in energy than the copper d_{xy} orbital and the π* orbital lower in energy than the $d_{x^2-y^2}$ orbital. This would result in destabilization of both the $d_{x^2-y^2}$ and π-orbitals and stabilization of the π* and d_{xy} orbitals. The observation of a decrease in both band I, d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$, and band III, amine oxide π → π*, as one transcends the series from 4-nitropyridine N-oxide to 4-methoxypyridine N-oxide is in agreement with this interpretation. The observation that band II also varies, something which other authors have not found,[53] is also explained by the above interpretation.

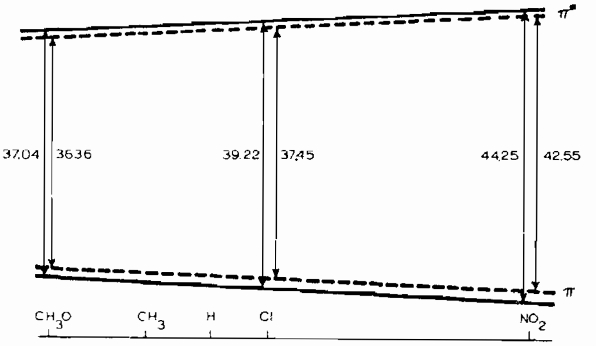

Figure 7. Variation of the π and π* orbital energies for the 4-substituted pyridine N-oxides (—) and the complexes, [Cu(CH$_3$COO)$_2$·4ZPyNO]$_2$ (- - -). The numbers represent the energy differences in kilokaysers between the orbitals (see Table III).

Conclusions

The following correlations have been found among the data obtained on the dimeric complexes [Cu(OAc)$_2$·4-ZPyNO]$_2$:

1) ν_{NO}, the nitrogen oxygen stretching frequency decreases in energy upon coordination by a uniform amount (ca. 30 cm^{-1}) and folows the same trend as the free ligand when plotted *versus* σ_{PYNO}. (Figure 3)

2) The magnetic moments of the complexes decrease as the basicity decreases and the π-acceptor ability of the ligand, L, increases.

3) The magnetic susceptibilities of the complexes decrease as the energy of the- ligand π→π* transition increases for both the free and coordinated ligand. (Figure 5).

4) The energy of band I increases as the magnetic susceptibility decreases and as the basicity of the ligand L decreases. (Figure 4)

5) The π → π* ligand transition decreases in energy by a nearly uniform amount upon coordination except for the 4-methoxypyridine N-oxide complex. (Figure 7)

6) Band II generally decreases in energy as ligand basicity decreases.

All of these correlations have been explained in terms of the δ-bonding model including metal-ligand π-bonding. From these data it can be argued that ligands with very low basicity promote copper-copper interaction (the greater the metal ligand π-back donation and the less the ligand-metal sigma donation, the greater is the metal-metal interaction). This leads one to conclude that the metal-metal bond is strengthened by removing electron density from the copper atoms (probably from copper-copper non-bonding orbitals). The above arguments, save perhaps for the electronic spectral data, could also be made in terms of the σ-bonding model or by invoking the presence of low lying singlet excited states[58] so that these data do not specifically allow a differentiation between the σ and δ bonding models. However, all the data are consistent with the δ-bonding model and appear to be most easily rationalized in terms of that model.

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Helpful discussion with Dr. H. E. LeMay, Jr. Professor H. B. Jonassen, and Professr R. O. Ragsdale are also gratefully acknowledged.

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