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Magnetic Exchange Interactions in Transition Metal Dimers. II. Copper and Nickel Di-μ-azido and μ-Oxalato Complexes

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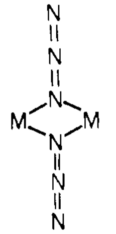
Variable-temperature (4.2–283°K) magnetic susceptibilities were measured for $[M_2(\text{tren})_2(N_3)_2][B(C_6H_5)_4]_2$, where M = Ni(II) and Cu(II). A relatively strong antiferromagnetic interaction ($J = -35$ cm^{-1}) was noted for the nickel dimer, whereas the magnetic susceptibility curve of the copper complex exhibits no indications of interaction. The observation of a $\Delta m_s = \pm 2$ transition in the esr spectrum of the copper compound indicates it to be dimeric in the solid state. Magnetic susceptibilities (4.2–283°K) were also determined for two μ-oxalato–copper dimers. No exchange interactions were detected, in contrast to that ($J = -17$ cm^{-1}) observed for the μ-oxalato-bridged nickel complexes discussed in part I of this series. A discussion of the differences in magnetic exchange between the copper and nickel systems is given.

Introduction

In comparison to copper(II) there have been relatively few variable-temperature magnetic susceptibility studies[2] of nickel(II) dimers. Most of the dimeric nickel(II) systems that have been studied are complexes of planar binucleating ligands with solvent molecules coordinated above and below the plane. There are relatively few investigations of octahedrally coordinated nickel(II) dimers with simple bridging moieties (small anions), whereas these have proved to be the most interesting in terms of exchange effects. Ferromagnetic exchange coupling has been found for nickel(II) dimers with the bridging provided by bromide,[3a] chloride,[3a] and thiocyanate.[3,4] Antiferromagnetic coupling has been detected in oxalate-,[2,5] squarate-,[5] and cyanate-bridged[6] octahedrally coordinated nickel(II) dimers. The paucity of variable-temperature magnetic susceptibility data on such nickel dimers is due to a shortage of characterized nickel systems. A program has been initiated in these laboratories to synthesize a series of nickel(II) dimers, incorporating various polyatomic bridges, in order to study the mechanism of magnetic exchange between nickel(II) centers. Where possible, the substitution of other metal ions (in particular copper) into the same dimer structures will be effected; comparisons of the susceptibility data for such systems with that for the nickel(II) dimers will provide additional information about the exchange mechanism.

The azide group (N_3^-) is known to bridge metals in various polymeric metal azides. Two bridging modes are available for the azide anion (modes A and B). The crystal structure[7] of polymeric $Cu(N_3)_2$ has shown that both bridging modes are present in this system. Several dimeric metal complexes have been reported to contain azido bridges on the basis of physical data: $[Au(CH_3)_2N_3]_2$,[8] $[Pd(N_3)_2P(C_6H_5)_3]_2$,[8] $[Pd_2(N_3)_6{}^{2-}]$,[9] and $[Ni(\text{dtet})N_3]_2(ClO_4)_2$.[10] Very recently Ziolo, *et al.*,[11] determined the first X-ray crystal structure of an azido-bridged metal dimer, $[Cu(N_3)P(C_6H_5)_3]_2$. They found this Cu(I) complex to have mode B type bridging. We have synthesized di-μ-azido-bis[4-(2-aminoethyl)diethylenetriamine]dinickel(II) tetraphenylborate, $[Ni_2(\text{tren})_2(N_3)_2](BPh_4)_2$. We have also prepared the analogous Cu(II) complex, as well as the diethylenetriaminecopper complex $[Cu_2(\text{dien})_2(N_3)_2](BPh_4)_2$. In this paper the results of a characterization and variable-temperature (4.2-283°K) magnetic susceptibility study of the Ni(II) and Cu(II) systems will be presented.



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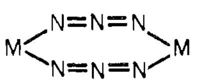

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The pursuit of a comparison of magnetic susceptibilities of related Cu(II) and Ni(II) dimers has led us to synthesize and study $[Cu_2(\text{tren})_2(C_2O_4)](BPh_4)_2$ and to prepare and study samples of the complex $[Cu_2(\text{dien})_2(C_2O_4)](ClO_4)_2$ reported by Curtis.[12] We have already reported a thorough magnetic susceptibility study of various μ-oxalato-nickel(II) complexes. The effect of metal substitution on magnetic exchange interaction in a given dimer has received far from adequate coverage in the literature. This work represents part of a sequence of studies intended to fill this gap.

Experimental Section

Compound Preparation. Analytical work was carried out by the University of Illinois School of Chemical Sciences microanalytical laboratory. The ligands 4-(2-aminoethyl)diethylenetriamine (Ames Laboratories, Inc.) and diethylenetriamine (Union Carbide) were used as received.

A sample of the oxalate-bridged $[Cu_2(\text{dien})_2(C_2O_4)](ClO_4)_2$ was prepared as described by Curtis.[12] *Anal.* Calcd for $[Cu_2(C_4H_{13}N_4)_2(C_2O_4)](ClO_4)_2$: C, 19.36; H, 4.22; N, 13.55; Cu, 20.48. Found: C, 19.61; H, 4.36; N, 13.57; Cu, 20.56.

The compound $[Cu_2(\text{tren})_2(C_2O_4)](BPh_4)_2$ was prepared by slowly adding an aqueous solution containing ~1 g of $NaB(C_6H_5)_4$ to a filtered aqueous solution of 2.50 g (10 mmol) of $CuSO_4 \cdot 5H_2O$, 0.67 g (5 mmol) of $Na_2C_2O_4$, and 1.5 ml of tren. The resulting blue precipitate was washed with water followed by diethyl ether and then dried *in vacuo* over P_2O_5. *Anal.* Calcd for $[Cu_2(C_6H_{18}N_4)_2(C_2O_4)]$-

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Table I. Analytical Data

	% C		% H		% N		% M	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
Ni(II) Prepn 1	63.64	63.72	6.77	6.95	17.32	17.05	10.37	10.18
Prepn 2		63.66		6.81		17.25		10.35
Cu(II)	63.10	63.00	6.71	6.81	17.17	17.20	11.13	11.02

$[B(C_6H_5)_4]_2$: C, 64.98; H, 6.68; N, 9.78; Cu, 11.09. Found: C, 65.60; H, 6.55; N, 9.81; Cu, 10.85.

$[M_2(tren)_2(N_3)_2](BPh_4)_2$, Where M = Ni(II) and Cu(II). These compounds were prepared similarly to the oxalate described above, with the exception that when making a solution of Cu^{2+}, tren, and N_3^- it is advisable to add the azide last in order to avoid formation of polymeric $Cu(N_3)_2$, which is exceedingly *explosive* when dry. Two preparations of the Ni(II) compound were made for the magnetic susceptibility measurements (see Results and Discussion). The analytical data for the di-μ-azido complexes are given in Table I.

$[Cu_2(dien)_2(N_3)_2](BPh_4)_2$. This compound was prepared in a manner similar to that for the other complexes. However, less than a stoichiometric amount of dien must be used as well as ~75% of the theoretical amount of NaN_3. *Anal.* Calcd for $[Cu_2(C_4H_{13}N_4)_2(N_3)_2]$-$[B(C_6H_5)_4]_2$: C, 63.70; H, 6.30; N, 15.92; Cu, 12.03. Found: C, 63.55; H, 6.44; N, 16.05; Cu, 12.09.

Physical Measurements. Variable-temperature (4.2–283°K) magnetic susceptibility measurements were made using a Princeton Applied Research Model 150A magnetometer as described in a previous paper.[5] Molecular weights were determined using a Mechrolab Model 301A vapor pressure osmometer. Infrared spectra were obtained with a Perkin-Elmer Model 457 spectrophotometer using KBr pellets of the various compounds. All esr measurements were made using a Varian E-9 spectrometer at X-band frequencies. Electronic absorption spectra were measured using a Cary 14 spectrophotometer. Solid samples were prepared as 13-mm KBr pellets, and reference KBr pellets of transparent $NaBPh_4$ were used to balance the dispersion effects of this sampling technique. Powder patterns were measured on a Norelco (Philips Electronics Co.) diffractometer, using Cu Kα radiation. Samples were prepared by evaporation of a benzene slurry onto a glass slide.

Molecular Orbital Calculations. Calculations were performed on an IBM 360/75 computer using an extended Huckel program developed as stated in the literature.[13,14] Off-diagonal matrix elements were calculated using the expression $H_{ij} = (k/2)S_{ij}(H_{ii} + H_{jj})$, where $k = 1.75$, S_{ij}'s are overlap integrals, and the H_{ii}'s are valence orbital ionization potentials (VOIP's). The Mulliken population analysis[15] was used for charge iteration. At convergence atomic charges were self-consistent to within 0.002 charge unit. Calculations were also carried out using the Lowdin population analysis,[14,16] however, for both copper and nickel complexes the metal atom charge was calculated to be negative. The molecular orbital coefficients were qualitatively similar for both the Lowden and Mulliken analyses. Results for only the Mulliken calculations will be presented.

VIOP's and charge correction terms for nickel were used as reported by Basch, Viste, and Gray,[17], whereas for copper, values were obtained by graphical extrapolation of such data[17] for the elements Ti through Ni. The metal orbital basis for both Cu and Ni was formed from 4s, 3d, and 4p functions. The 4p orbitals used were developed by Strange, White, and Drago[18] as were the 4s orbitals used for copper. Clementi[19] orbitals were used for the Cu 3d, Ni 3d, and Ni 4s functions, Clementi's "double-ζ" functions were used for C, N, and O. (The nickel 4s function included only 2s, 3s, and 4s contributions.) An orbital exponent of 1.2 was used for hydrogen.

Results and Discussion

Nickel Azide Dimer. A compound with the empirical formula $[Ni(tren)N_3]BPh_4$ was found to precipitate from a solution containing Ni(II), tren, and N_3^- upon addition of BPh_4^-. The magnetic susceptibility of this compound was determined from 4.2 to 283°K (see Figure 1 and Table II). The susceptibility increases with decreasing temperature until a maximum is reached at 103°K. At temperatures below 103°K the susceptibility decreases with temperature until a minimum is reached at ~20°K, where the susceptibility increases with decreasing temperature (20–4.2°K). The overall appearance of the χ *vs.* T curve is indicative of a moderately strong antiferromagnetic interaction between nickel(II) centers and thus we conclude that the compound is a dimer. The low-temperature (4.2–20°K) "tail" on the susceptibility curve is due to the presence of a small (<3%) amount of monomeric paramagnetic impurity. Paramagnetic monomer "tails" have been found for copper dimer preparations.[4] Of the two preparations of $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$, Table I indicates preparation 2 to be analytically more pure. This is also reflected in the susceptibility curves for the two materials (see Figure 1). The smaller "tail" and better fit to the theoretical line for preparation 2 confirm that these low-temperature effects are indeed due to impurities.

The χ *vs.* temperature curve for preparation 2 of $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ was least-squares-fit to a theoretical expression for a nickel(II) dimer. Ginsberg, *et al.*,[3a] derived the magnetic susceptibility expression for a Ni(II) dimer assuming $g_x = g_y = g_z \equiv g$ and considering single-ion zero-field splitting as well as interdimer interactions. They found that the molar paramagnetic susceptibility for a nickel(II) dimer is

$$\chi_M = \frac{2Ng^2\beta^2}{3k}\left[\frac{F_1}{T - 4Z'J'F_1} + \frac{2F'}{1 - 4Z'J'F'}\right] + N\alpha$$

Here N, β, and k have the normal meaning, $N\alpha$ is TIP (-200×10^{-6} cgs/mol of dimer), and F_1 and F' are complicated functions of temperature, zero-field splitting D, and the *intradimer* exchange integral J. The effective *interdimer* exchange is $Z'J'$. The complete expressions are given in either ref 3a or 5. It is sufficient to note here that it has been shown[3a,5] that fitting nickel(II) dimer data to the above equation gives accurate values of the exchange integral J as well as g. The parameters D and $Z'J'$ are not well determined from magnetic susceptibility data[5] because the effects of these parameters are most important in the low-temperature region where experimental uncertainties (temperature determination) and impurity effects are greatest.

Fitting all of the χ data (4.2–283°K) for the second preparation of $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ to the above theoretical expression gives $J = -35.1$ cm^{-1}, $g = 2.325$, $D = 6.9$ cm^{-1}, and $Z'J' = 0.35$ cm^{-1}. [A referee has pointed out that this g value is somewhat larger than what one would expect. With $Dq = 1135$ cm^{-1} and $\lambda = -300$ cm^{-1}, calculation gives $g = 2 - 8\lambda/10Dq = 2.21$. A least-squares fit to the data has been found with $g = 2.20$; in this case $Z'J'$ is unchanged, D is very slightly reduced, and J is changed to -33 cm^{-1}.] If the five points in the low-temperature tail are removed, least-squares fitting gives essentially the same parameters. Least-squares fitting to the complete data set was also carried out where the susceptibility was taken as a mole fraction weighted

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Table II. Experimental and Calculated Magnetic Susceptibility Data for Preparation 2 of $[Ni_2tren(N_3)_2](BPh_4)_2$ [a]

	$10^3\chi_M$, cgsu		μ_{eff}/Ni, BM	
T, °K	Obsd	Calcd	Obsd	Calcd
283.0	7.39	7.41	2.892	2.896
247.7	8.07	8.06	2.827	2.825
218.3	8.71	8.66	2.758	2.750
188.4	9.30	9.33	2.647	2.651
173.5	9.66	9.66	2.589	2.589
156.7	10.00	10.04	2.503	2.508
138.3	10.39	10.40	2.397	2.399
117.2	10.73	10.71	2.242	2.240
103.4	10.83	10.78	2.116	2.111
85.7	10.57	10.62	1.903	1.907
73.6	10.21	10.26	1.733	1.738
66.0	9.81	9.89	1.609	1.616
59.5	9.40	9.46	1.496	1.500
53.8	8.95	8.95	1.387	1.388
47.8	8.35	8.25	1.263	1.255
41.0	7.19	7.15	1.086	1.083
31.5	5.68	4.90	0.846	0.786
18.7	4.46	0.98	0.562	0.263
9.3	5.71	0.23	0.461	0.093
7.3	6.74	0.22	0.443	0.081
5.6	8.10	0.22	0.426	0.071
4.2	9.94	0.22	0.409	0.061

[a] Diamagnetic correction used: -680.7×10^{-6} cgs/mol. Parameters: $J = -35.1$ cm^{-1}, $g = 2.325$, $D = 6.85$ cm^{-1}, $Z'J' = 0.50°$. Standard error: based on all 22 points, 0.184; ignoring lowest 5 points, 0.0168. Standard error given by the following equation: $SE = \Sigma_{i=1}{}^{n}[\mu_{eff}(obsd)_i - \mu_{eff}(calcd)_i]^2/(n-K)^{1/2}$, where n is the number of observables and K is the number of parameters.

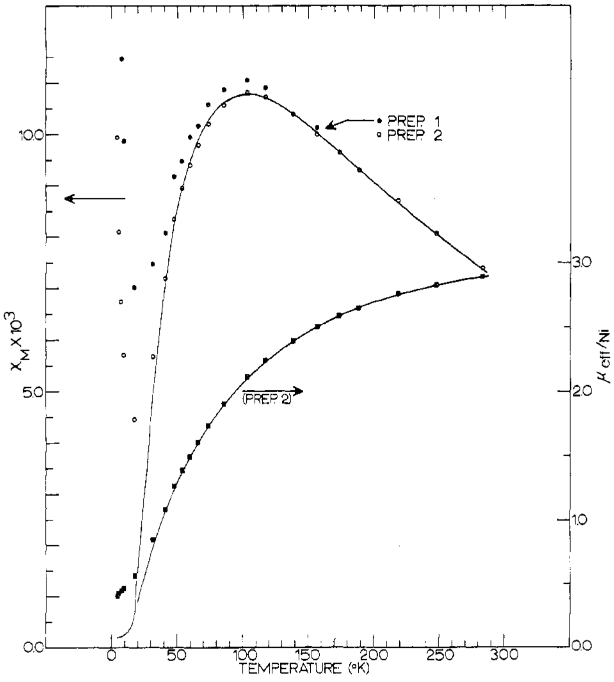
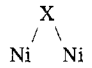


Figure 1. Molar susceptibility (cgs/mol) and effective moment (BM/nickel) curves for $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ in a magnetic field of 14.8 kG. Filled circles are χ_M experimental data for preparation 1. Open circles and filled squares are χ_M and μ_{eff} data for preparation 2. The lines are least-squares fit using a theoretical expression (see text).

average of the susceptibility of the dimer (using the above expression) and a monomer impurity (assumed Curie law behavior with $\mu_{eff} = 2.9$ BM). The fit is considerably improved, especially in the "tail" region; the value of D is somewhat decreased; however the calculated J and g values are essentially the same as above and thus appear to be accurately determined in spite of the presence of impurities.

Intradimer exchange integrals (J) have been determined for several nickel(II) dimers.[3a] When the Ni(II) centers are bridged as μ-oxo, di-μ-chloro, di-μ-bromo, or di-μ-thiocyanato systems, the exchange coupling is ferromagnetic ($J < +15$ cm^{-1}). In these cases the superexchange interaction is propagated through a ~90° pathway in the



bridge (crystal structure determinations have been carried out for these systems). Bridging two Ni(II) centers by an oxalate dianion leads to $J = -17$ cm^{-1}. In this case the superexchange does not go through an orthogonal bridge "junction" and the net interaction is antiferromagnetic.

As mentioned in the Introduction, there are two di-μ-azido bridging modes possible for $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$, the single-atom mode A and the end-to-end mode B. If we assume that in mode A the primary metal bridge bonding is σ overlap of the appropriate metal orbital with a nitrogen sp^2 hybrid orbital and that there is no direct metal-metal interaction, then exchange coupling *via* this mode of bridging would be ferromagnetic in nature due to the orthogonality of the sp^2 orbitals on the nitrogen. If the bridging is end-to-end (mode B), then the exchange coupling would be expected to be antiferromagnetic and analogous to what is observed for the μ-oxalato-nickel(II) dimer. Comparison of the exchange intergals [μ-oxalato ($J = -17$ cm^{-1}) and di-μ-azido ($J = -35$ cm^{-1})] leads one to believe that since both dimer systems couple antiferromagnetically and since the interaction is even stronger in the case of the di-μ-azido dimer, the two dimer systems are similar in symmetry and thus the azide dimer is bridged end to end. Other facts point to the same conclusion as the complex is further characterized below.

The ir spectrum of $[Ni_2(tren)_2(N_3)_2](BPh)_2$ pelleted in KBr is shown in Figure 2 and band positions are listed in Table II. The major feature of this spectrum is, of course, the $\nu_a(N_3)$ observed at 2075 cm^{-1}. This is the usual position for this type of band;[8,9] unfortunately, the position of this band cannot be used to infer the mode of azide bridging. The other vibrational modes of the azide group are expected at ~1300-1400 cm^{-1} (ν_s) and ~600-700 cm^{-1} (δ). The bending vibration (δ) is always found to be of low intensity and as such we cannot expect to locate it in a region where there are several strong counterion bands. The symmetric stretch, however, can be of varying intensity, depending upon the symmetry of the bound azide. If it is singly bound (either single nitrogen bridging or terminal), the charge distribution would be such as to produce a large oscillating dipole upon "symmetric" vibration. On the other hand if the azide is symmetrically bound (*i.e.*, end to end), there would be no effective dipole change in a symmetric vibration, and no ir band would be observed. Terminally[9] bound and single-nitrogen-bridged[20] azides commonly exhibit medium to strong $\nu_s(N_3)$ bands.

In the ir spectrum of $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ the region from 1300 to 1400 cm^{-1} contains several weak to medium bands due mainly to the tren ligand. In order to tell if one of these bands can be assigned to the $\nu_s(N_3^-)$ band it was necessary to find an analogous nickel dimer that would not have this band. It is known[3,4] that $[Ni_2(en)_4(NCS)_2]I_2$ has end-to-end di-μ-thiocyanato bridging. We prepared $[Ni_2(tren)_2(NCS)_2](BPh_4)_2$ and because it was found to have the same ferromagnetic interaction as reported for the iodide salt, it was concluded that the same di-μ-thiocyanato-bridged

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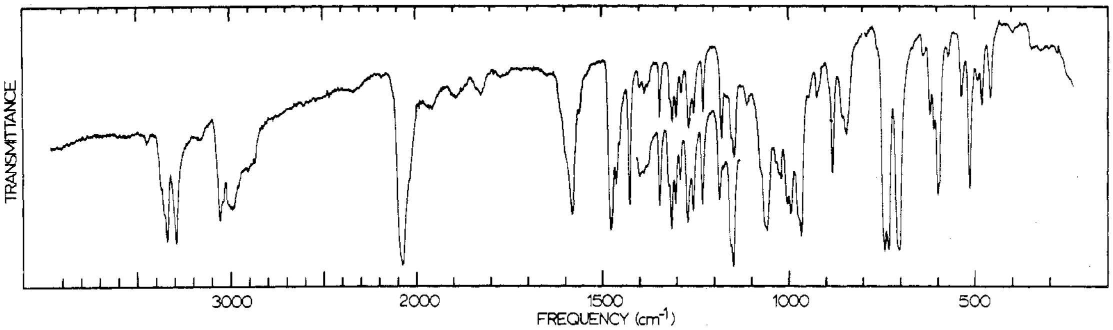

Figure 2. Infrared spectrum (4000–250 cm^{-1}) of $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ pelleted in KBr. Inset shows ~1100–1400-cm^{-1} region of $[Ni_2(tren)_2(NCs)_2](BPh_4)_2$ spectrum.

Table III. Infrared Data for Principal Azide, Oxalate, and Amine Bands

			ν(NH)		ν_{as}(OCO)	ν_s(OCO) or $\nu_a(N_3)$	δ(OCO)
$[Ni_2(tren)_2(C_2O_4)_2](BPh_4)_2$		3340 s 3370 w, sh	3290 s 3315 w, sh	3165 w, br	1642 vs	1308 m	781 m
$[Cu_2(tren)_2(C_2O_4)_2](BPh_4)_2$		3326 s 3354 m, sh	3278 s 3310 w, sh	3160 w, br	1630 vs	1290 m	781 mw
$[Ni_2(tren)_2(N_3)_2](BPh_4)_2$	3439 w[a]	3334 ms 3353 mw, sh 3367 w 3381 vw, sh	3285 ms 3309 w, sh 3297 w, sh	3153 w, br		2075 vs (2035 sh)	
$[Cu_2(tren)_2(N_3)_2](BPh_4)_2$		3368 ms 3340 ms 3308 ms 3289 w, sh	3275 ms 3250 mw, sh	31442 w, br		2038 vs	

[a] Possibly $\nu_a(N_3) + \nu_s(N_3)$.

dimer was present. This dimer cation does *not* have an NCS$^-$ band in the 1300–1400-cm^{-1} region and comparison of the ir spectrum of $[Ni_2(tren)_2(NCS)_2](BPh_4)_2$ in this region (see inset in Figure 2) with that for the azide compound shows that the 1300–1400-cm^{-1} regions are virtually identical. This rules against the presence in the azide spectrum of any appreciable intensity in the $\nu_s(N_3^-)$ band and indicates that the azide groups are probably end-to-end bridged. With respect to the above observations it is interesting to consider the assignment of the weak band at 3439 cm^{-1}. For $[(C_2H_5)_2InN_3]_2$ and related azide-bridged complexes[21] ($\nu_a + \nu_s$) bands are often observed at ~3400 cm^{-1}. If this is indeed the origin of the 3439-cm^{-1} band, then the lowest energy position for ν_s can be calculated to be ⩾1364 cm^{-1}. This high frequency may be taken[22] as indicating a highly symmetric N_3^- group.

The ir bands in the NH region of $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ have the appearance of an octahedrally coordinated tren complex with distortion leading to multiple shoulders on the major 3334-cm^{-1} $\nu_a(NH_2)$ and 3285-cm^{-1} $\nu_s(NH_2)$ bands.[23] The two highest energy shoulders are in a region often associated with vibrations of noncoordinated ("dangling") primary amine groups; however it is clear that this is not the case for this complex. Other complexes have had bands in this region even though their ligands were considered to be fully coordinated.[12] Finally, ir data for μ-oxalato $[Ni_2(tren)_2(C_2O_4)](BPh_4)_2$ are included in Table III for comparison. Except for small differences in the NH region and differences assignable to bridge vibrations, the ir spectra of $[Ni_2(tren)_2(C_2O_4)](BPh_4)_2$ and $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ are identical. The relevance of this comparison will become more apparent when the X-ray powder pattern data are discussed below.

Electronic spectral data for solid samples of the nickel azide- and oxalate-bridged systems are given in Table IV. Fitting the ν_1, ν_{E_g}, and ν_2 peaks $[^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^1E_g(D)$, and ${}^3T_{1g}(F)]$ to an energy level diagram for octahedral d^8 systems[24] leads to $Dq \cong 1170$ cm^{-1} and $B \cong 700$ cm^{-1} for the azide complex, while the oxalate numbers are similar. Both of these values are in the range typical of nickel(II) amine complexes. The electronic absorption spectra of these complexes are very similar, both in solution and as solids with the exception of the extinction coefficients for the ν_1 transition. The electronic bands of these two nickel(II) dimers are also more intense than bands associated with monomeric octahedral nickel(II) species.[25] Intensification of bands in dimeric complexes has been noted and it is thought that it arises from exchange effects.[26]

Figure 3 illustrates the X-ray powder diffraction data for $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ and $[Ni_2(tren)_2(C_2O_4)](BPh_4)_2$. The crystal structure of the oxalate dimer has not been reported, but based on ir data and the known structures[27] of $[Ni_2(en)_4(C_2O_4)](NO_3)_2$ and $[Cu_2(dien)_2(C_2O_4)](ClO_4)_2$ it is safe to presume that it is bis-bidentate. The geometry of the $Ni_2(C_2O_4)$ moiety can thus be inferred from other crystal structures. The powder patterns for the oxalate- and azide-bridged nickel dimers are quite similar. This *tends* to indicate that because the unit cell parameters are close to being the same and the distribution of electron density in the unit cell is similar, the dimer units should be of comparable size. If this is indeed true, then this would indicate that the azide

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Table IV. Electronic Spectral Data for Copper Oxalate and Azide Dimers

		Solid[a]		Solution[b,c]		
		Å	kK	Å	kK	ϵ/M
$[Ni_2(tren)_2(C_2O_4)_2](BPh_4)_2$	ν_3	3620	27.6	3540	28.2	
	ν_2	5520	18.1	5515	18.1	14.0
	νE_g	7860	12.7	7550	13.2	1.8
	ν_1	(9340)	(10.7)	9270	10.8	15.5
$[Ni_2(tren)_2(N_3)_2](BPh_4)_2$	ν_3	3572	28.0	3720	26.9	
	ν_2	5770	17.3	5790	17.3	13.2
	νE_g	8170	12.2	7920	12.6	1.8
	ν_1	9550	10.5	9560	10.5	28.6
$[Cu_2(tren)_2(C_2O_4)](BPh_4)_2$		6890	14.5	(6560 sh)	(15.2)	(15)
		(8270 sh)	(12.1 sh)	8190 br	12.2	150
$[Cu_2(tren)_2(N_3)_2](BPh_4)_2$		6700	14.9	6750	14.8	130
		8760	11.4[d]	8570	11.7	150
		9620 sh	10.4 sh			
$[Cu_2(dien)_2(N_3)_2](BPh_4)_2$		6430	15.5	6040	16.6	250
$[Cu_2(dien)_2(C_2O_4)_2](BPh_4)_2$		7000	14.3	6650	15.0	100

[a] KBr pellets with reference pellet of $NaBPh_4$ in KBr used. [b] DMF solutions of the nickel compounds and acetonitrile solutions of the copper compounds. [c] Molar extinction coefficients are given per metal atom unit. [d] The two lowest energy bands are in fact barely separable by eye, but since a splitting is indicated, two bands are reported. The 14.9-kK band is sharp and clearly separated from the lower two.

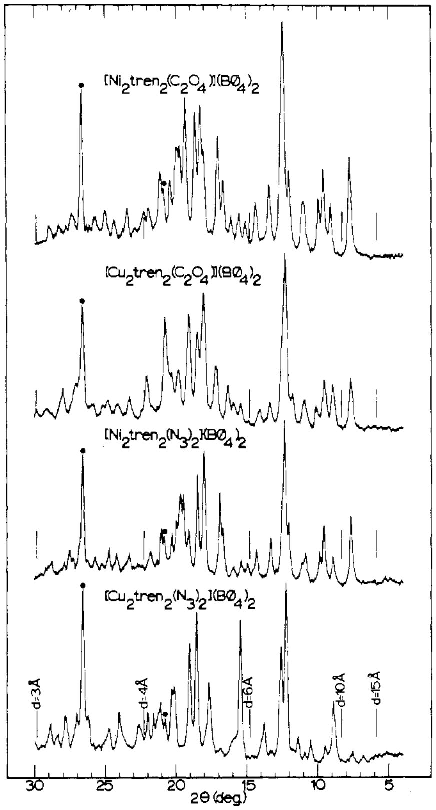

Figure 3. Comparison of X-ray powder diffraction patterns for $[M_2(tren)_2L_2](BPh_4)_2$, where M = Cu, Ni; L = N_3, $^1/_2C_2O_4$. The dots indicate lines due to the powdered quartz internal standard.

bridges in an end-to-end (mode B) fashion, for of the two modes it is clearly the only one yielding molecular dimensions close to those of an oxalate bridge. [Similar rationale has proven correctly to predict the end-to-end bridging character of the analogous nickel μ-cyanato complex.[6]] Molecular models also indicate that the single-nitrogen bridging is unlikely in $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$, without severe distortion of the octahedral geometry.

Summarizing the above material, it is our contention that the compound $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ is a di-μ-azido dimer with end-to-end bridging. Evidence for this is found mainly in the large antiferromagnetic interaction, the absence of intensity in a $\nu_s(N_3^-)$ ir band, and the similarity of powder patterns for the oxalate and azide nickel(II) dimers.

Copper(II) Azide and Oxalate Dimers. We have prepared several azide- and oxalate-bridged copper(II) dimers and have characterized them using ir, powder patterns, esr, electronic spectroscopy, and variable-temperature magnetic susceptibility data. It is out intention, as far as is possible, to interpret these data in terms of copper stereochemistry. This will set the stage for the next section in which magnetic exchange interactions in the azide and oxalate nickel(II) dimers will be compared with those for the analogous copper(II) systems. In this section it will be demonstrated that the copper and nickel oxalates seem to be fairly similar in their structures (X-ray structural information illustrating this fact for other μ-oxalato-copper and -nickel systems is available in ref 27), whereas the azide complexes are more varied, which is to be expected when one considers the flexibility of the di-μ-azido bridge plus the tendency of Cu(II) to form complexes distorted from regular symmetry.[28] The copper azide may, in fact, be bridged by a single nitrogen.

While the ir spectrum of $[Cu_2(tren)_2(C_2O_4)](BPh_4)_2$ is closely related to that of $[Ni_2(tren)_2(C_2O_4)](BPh_4)_2$ in the $\nu(NH_2)$ and ν(oxalate) bands (see Table III), it can be seen that the azide spectra differ in the number of $\nu(NH_2)$ bands. The CH and NH regions of $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ and $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ are reproduced in Figure 4. The nickel compound has shoulders on its two major $\nu(NH_2)$ peaks, while the copper azide exhibits a series of strong peaks spread over a wide range of frequency. The highest (3368 cm^{-1}) of these may be due to a dangling NH_2 group; however, this is not probable, for, as we will show, the symmetry about the copper is unusually low. A point of interest has arisen from a comparison of the ir spectra of the copper azide complex with that of $[Cu_2(tren)_2(NCS)_2](BPh_4)_2$, which we prepared. The ir spectra of these two compounds are nearly identical from 1600 to 500 cm^{-1}, the important exception being a medium to weak absorption in $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ at 1344 cm^{-1}. If this band corresponds to the $\nu_s(N_3)$ absorption, then this suggests that the copper azide complex is *not* end-to-end bridged, as was deduced for the nickel azide complex. The postulation of a single-nitrogen bridging in the copper azide would be commensurate with the apparent distortion from octahedral coordination in this system.

X-Ray powder patterns (see Figure 3) for $[Cu_2(tren)_2(C_2O_4)](BPh_4)_2$ and $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ again serve

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(28) B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 5, 143 (1970).

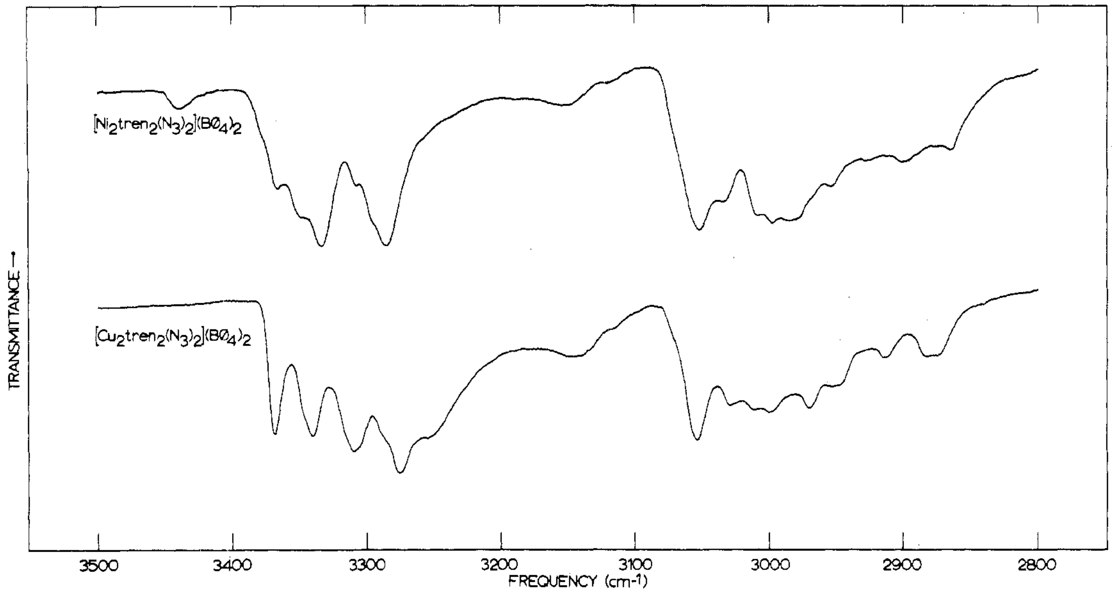

Figure 4. Infrared spectra of $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$ and $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ from 3500 to 2800 cm^{-1}.

to point out that whereas the copper and nickel oxalate systems are quite similar, the two tren azides differ. Although many low-angle (large *d* spacing) lines of the two azides coincide in location, the intensities are quite different. This indicates a somewhat different packing arrangement in the unit cell.

Electronic absorption spectra for Cu(II) complexes generally reflect the coordination geometry about the metal.[28,29] Usually small distortions, etc., lead to dramatic changes and quite often the broadness of the bands makes it difficult to identify individual transitions. Spectral data in the visible and near-ir region for solid samples and solutions of our Cu(II) systems are given in Table IV. There are two important features. The first is that there is evidence for more extensive distortion in $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ than in $[Cu_2(tren)_2(C_2O_4)](BPh_4)_2$; this is evidenced in the band splitting of the ~10.9-kK system in the spectrum of the former compound. Otherwise, the two spectra are similar. Second, if $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ is five-coordinate with a dangling amine group, one would expect its electronic spectrum to be more similar to that for $[Cu_2(dien)_2(N_3)_2](BPh_4)_2$ which consists of one single, fairly symmetrical peak.

The electronic absorption data of Ciampolini and coworkers[30,31] for five-coordinate dienMe-Cu complexes $[dienMe = CH_3N(CH_2CH_2N(CH_3)_2)_2]$ and five-coordinate trenMe-Cu systems $[trenMe = N(CH_2CH_2N(CH_3)_2)_3]$ also substantiate the stereochemistries that we have suggested. They found both $Cu(dienMe)Cl_2$ and $Cu(dienMe)Br_2$ (both halogens coordinated in each case) to exhibit single symmetrical electronic absorption bands at ~13.1 kK. This is similar to what we have observed (see Table IV) for $[Cu_2(dien)_2(N_3)_2](BPh_4)_2$ and $[Cu_2(dien)_2C_2O_4](BPh_4)_2$, which means that each of these copper atoms is five-coordinate and therefore each complex is dimeric. Furthermore, the spectra of Ciampolini and Nardi for [Cu(trenMe)X]X complexes[30] are different from ours for $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ in band positions and splitting, thus supporting the dimeric nature of this copper-tren-azide system and ruling against the possibility that it is really the five-coordinate complex $[Cu(tren)(N_3)](BPh_4)$.

Clear evidence for formulating the copper oxalate and azide systems as dimers is also found in the esr spectra for the complexes. Data were collected for polycrystalline solids, for solutions in some cases, and also for a single-crystal of $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$. Figure 5 depicts the full esr spectra of polycrystalline $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ and $[Cu_2(tren)_2(C_2O_4)](BPh_4)_2$ at ~110°K. Three features stand out. For each complex there is at ~1500 G a $\Delta m_s = \pm 2$ transition, which is about 3 orders of magnitude less intense than the full-field ($\Delta m_s = \pm 1$) transitions. These $\Delta m_s = \pm 2$ transitions have no possible assignment without the postulation of Cu-Cu pairs in the solid state. This indicates that indeed we are dealing with Cu(II) dimers. It is quite unlikely for a system with such large ligands and anions to have *intermolecular* exchange interactions of such a magnitude to give $\Delta m_s = \pm 2$ transitions. To check this full-field X-band esr spectra were recorded for [Cu(tren)(NCS)]SCN and $[Cu(bipy)_2I]ClO_4$, both known to be five-coordinate monomeric Cu(II) complexes, and it was not possible to detect a $\Delta m_s = \pm 2$ transition for these complexes.

The difference in line width in the full-field esr transitions in the above two Cu(II) complexes is notable. The azide-bridged dimer has a broader peak; a possible source of broadening could be unresolved zero-field splitting. The third feature which is of interest is that in the case of the azide dimer $g_{\parallel}$ is clearly *smaller* than $g_{\perp}$ ($g_{\parallel} = 2.02, g_{\perp} = 2.18$). Although this situation is most commonly found for trigonal-bipyramidal copper complexes, it has also been noted for tetragonally compressed octahedral species.[28] Again, precise structural conclusions cannot be drawn; however it is for the fourth time indicated that $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ has a symmetry very different from that of the other complexes. The μ-oxalato complex $[Cu_2(dien)_2(C_2O_4)](ClO_4)_2$ gives an axial esr spectrum with a $g_{\parallel}$ larger than $g_{\perp}$, whereas the interesting esr spectrum of $[Cu_2(dien)_2(N_3)_2](BPh_4)_2$ is shown in Figure 6. In this case the $\Delta m_s = \pm 2$ band is much stronger than in the tren complex and the full-field spectrum indicates distortion from axial symmetry. A distortion from axial symmetry might be expected to increase the $\Delta m_s = \pm 2$ transition moment integral, and this does serve to illustrate the fact that the origin of the 1500-G absorption *is intramolecular* in nature. Even further, if $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ were five-coordinate by virtue of a dangling amine,

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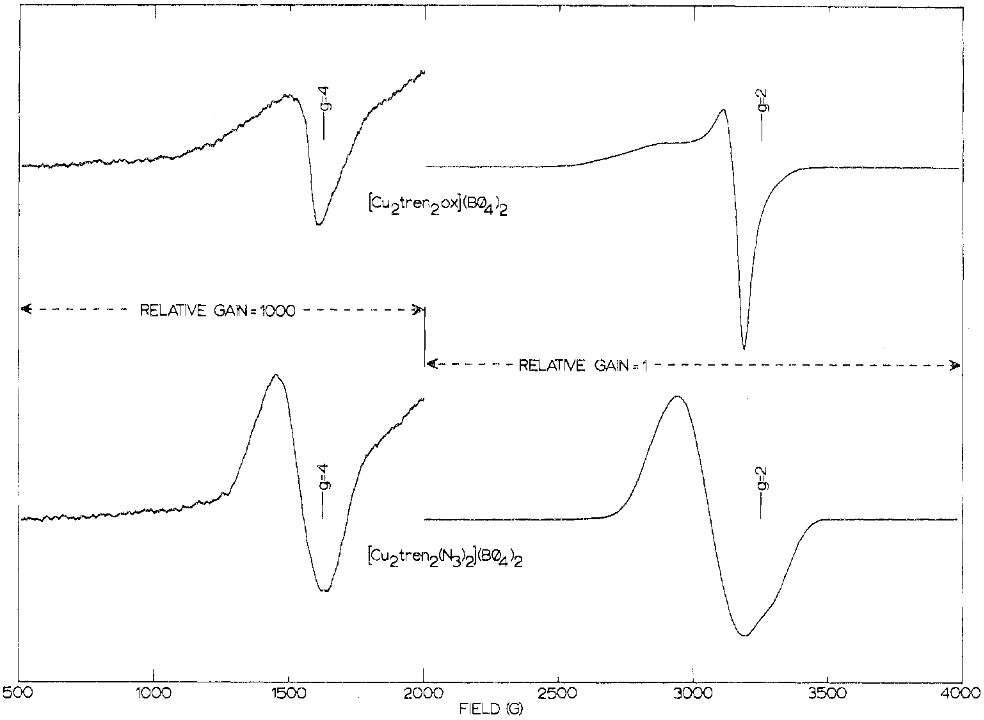

Figure 5. Esr spectra of $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ and $[Cu_2(tren)_2(C_2O_4)](BPh_4)$, showing both $\Delta m_S = \pm1$ and $\Delta m_S = \pm2$ transitions.

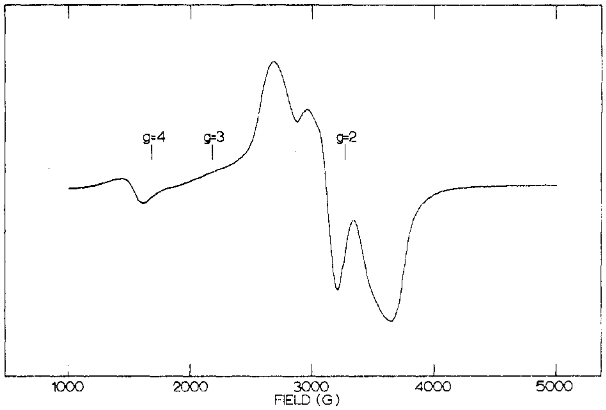

Figure 6. Esr spectrum of $[Cu_2(dien)_2(N_3)_2](BPh_4)_2$ in $\Delta m_S = \pm1$ and $\Delta m_S = \pm2$ regions.

then we would expect its esr to be more similar to that depicted in Figure 6.

In summary, it seems that the solid-state structures of the dimers $[Ni_2(tren)_2(C_2O_4)](BPh_4)_2$ and $[Cu_2(tren)_2(C_2O_4)](BPh_4)_2$ are similar, as would be expected from structurally characterized similar systems.[27] In the solid state the copper and nickel azide dimers show more of a variance in their structures. In particular, the copper-tren-azide dimer seems to be distorted. It is clear, however, that $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ is probably a dimer. In passing, we should mention that single crystals of $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ have been obtained suitable for preliminary X-ray photographs and single-crystal esr work. The space group has been determined to be either *Pca*2 or *Pbcm* with four dimer molecules per unit cell. Esr work has indicated that the molecules lie in two different orientations within the cell.

Molecular weight studies in acetonitrile and acetone demonstrate that the copper azide complexes are monomeric in solution. Dissociation upon dissolution of an end-to-end μ-azido dimer has been observed previously.[11] The effective molecular weight of a solution (over the concentration range of 7-3 mM) of $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ was determined by vapor pressure osmometry to be 313-290, which indicates dissociation into two copper monomers. At a concentration of 4 mg/ml the effective molecular weight (=329) of $[Cu_2(tren)_2(C_2O_4)](BPh_4)_2$ also indicates dissociation, while at 8 mg/ml this same copper oxalate has mol wt (eff) 441, which is larger than that expected for dissolution to give a dimer dication and two BPh_4^-. Unfortunately, the nickel complexes are not soluble enough for molecular weight determinations. Esr spectra of acetonitrile and acetone solutions of $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$ show four copper hyperfine lines, indicative of electron coupling to *one* copper as would be expected for a monomer $[Cu(tren)N_3]^+$. Upon freezing these solutions, axial spectra are observed where $g_\parallel$ is *greater* than $g_\perp$ (in contrast to what was seen for the solid) possibly indicating strong solvation of the copper in the sixth coordination site. Studies in frozen nitromethane glasses have indicated the presence of *two* copper species; further studies of these solution properties are being undertaken.

The magnetic susceptibilities of $[Cu(tren)_2(N_3)_2](BPh_4)_2$, $[Cu_2(tren)_2(C_2O_4)](BPh_4)_2$, $[Cu_2(dien)_2(N_3)_2](BPh_4)_2$, and $[Cu_2(dien)_2(C_2O_4)](ClO_4)_2$ have been measured in the range of 4.2-283.0°K and the data are presented in Table V. In each case the 283.0°K μ_{eff} value is in the range of 1.85-1.94 BM, as expected for a copper(II) complex, and there is relatively no temperature dependence in the μ_{eff} values. Contrary to the nickel(II) oxalate and azide dimers, these copper(II) dimers possess magnetic susceptibility curves with no indications of either antiferromagnetic or ferromagnetic interactions.

Exchange Mechanism. The apparent loss of an intradimer exchange interaction in replacing Ni(II) by Cu(II) in the above μ-oxalato and μ-azido dimers bears discussion. Naturally, in order most profitably to interpret the magnetic data, we should be cognizant of the structural characteristics of each system discussed. For this reason we will restrict our discussion of the exchange mechanism to the oxalate-bridged complexes, whose structures are better defined than those of the azide-bridged dimers.

As indicated above, both of the μ-oxalato systems $[Ni_2$-

Table V. Experimental Magnetic Susceptibility Data for Copper Oxalate and Azide Dimers[a]

	$[Cu_2(tren)_2ox](BPh_4)_2$		$[Cu_2(dien)_2ox](ClO_4)_2$		$[Cu_2(tren)_2(N_3)_2](BPh_4)_2$		$[Cu_2(dien)_2(N_3)_2[(BPh_4)_2$	
T, °K	$10^3\chi_M$	μ_{eff}/Cu	$10^3\chi_M$	μ_{eff}/Cu	$10^3\chi_M$	μ_{eff}/Cu	$10^3\chi_M$	μ_{eff}/Cu
283.0	3.04	1.871	3.07	1.864	3.32	1.939	3.02	1.850
247.7	3.40	1.836	3.55	1.876	3.71	1.916	3.45	1.848
218.3	3.84	1.832	4.08	1.888	4.28	1.934	3.96	1.859
188.4	4.52	1.844	4.67	1.875	4.87	1.916	4.55	1.852
156.7	5.49	1.854	5.56	1.866	5.81	1.908	5.39	1.838
117.2	7.26	1.844	7.36	1.857	7.84	1.916	7.19	1.836
94.5	9.06	1.850						
73.6	11.74	1.859	11.94	1.875	12.42	1.912	11.50	1.840
59.5	14.99	1.888	15.26	1.906	15.26	1.906	14.86	1.881
47.8	18.29	1.870	18.74	1.893	18.59	1.885	18.35	1.873
42.6	21.61	1.919						
35.8	25.83	1.923	26.18	1.936	27.04	1.967		
31.5	29.53	1.929						
26.0	34.67	1.899	35.37	1.918	35.90	1.932		
20.5	42.90	1.876	43.00	1.878	44.03	1.900	45.01	1.921
15.7	56.44	1.883	56.05	1.876	56.63	1.884	59.43	1.932
11.7	74.22	1.864	72.58	1.843	72.84	1.846	77.78	1.908
9.3	96.02	1.890	92.44	1.854	91.74	1.847	99.75	1.926
7.3	126.1	1.919	118.7	1.862	115.6	1.837	128.8	1.939
5.6	167.8	1.938	155.5	1.866	143.7	1.794	168.8	1.944
4.7	198.8	1.955	180.8	1.844	174.7	1.812	196.6	1.922
4.2	227.7	1.955	208.1	1.870	199.7	1.831	223.1	1.936

[a] Diamagnetic corrections used: -687.1×10^{-6} for tren oxalate; -265.0×10^{-6} for diene oxalate; -680.7×10^{-6} for tren azide; -625.8×10^{-6} for dien azide. χ in cgsu; μ_{eff} in BM.

$(tren)_2(C_2O_4)](BPh_4)_2$ and $[Cu_2(tren)_2(C_2O_4)](BPh_4)_2$ are octahedral with bis-bidentate bridging oxalates. These are, to our knowledge, the only isostructural *octahedral* copper and nickel dimers for each of which the magnetic data have been reported. This is a particularly salient point in view of the fact that whereas some planar or pseudotetragonal metal dimers show large exchange interactions despite the substitution of a different metal,[32] our octahedrally coordinated systems are unusual in that they show exchange only for the nickel dimers.

Before discussing the exchange mechanism in the oxalates, it is instructive to consider the interpretations given to the magnetic susceptibility data for the copper(II) formate systems.[33-36] The bridging geometry of the tetrahydrate[37] is quite similar to that of the oxalates (see Figure 7), although the formate is polymeric in nature, consisting of planes of single Cu-O-CH-O-Cu bridges. There is a royal blue anhydrous form of copper formate, which also possesses a three-atom formate-bridged structure; however, in this case (see Figure 7) the copper atoms are bonded in a syn,anti configuration such that there is no mirror plane across the bridge.[38] The symmetrical bridge of the tetrahydrate formate exhibits a net antiferromagnetic interaction, while the anhydrous formate has a net ferromagnetic interaction. Inoue and Kubo[35] have interpreted these observations, as well as their broad-line pmr data for the same systems, as indicating that in the tetrahydrate case the predominant exchange pathway is through the π system of the bridge, while for the anhydrous solid the most important exchange contribution results from the σ system.

There are two important points to be made about the formate analysis of Inoue and Kubo. First, the π mechanism they proposed involves "promotion" of an electron in a π-bonding d orbital (d_{xz}, say) to the in-plane $d_{x^2-y^2}$ orbital which contains the hole. This amounts to saying that there is some excited-state mixing such that the ground state contains an admixture of the "$d_{xz}{}^1$" excited state, the mixing coefficient being inversly proportional to the energy between the states (~20,000 cm^{-1}). Second, they assumed that any superexchange *via* a σ delocalization will result in a ferromagnetic coupling due to the orthogonality of the sp^2 hybrids used to form the σ-bond system. With respect to this second point we wish to raise the important question of whether or not a simple valence-bond description of bonding in a polyatomic bridge like formate or oxalate can be expected to give a realistic picture of a phenomenon as subtle as superexchange. In the formate bridge, the orthogonality between, for example, the oxygen sp^2 hybrid and the carbon sp^2 hybrid is just an artifact of the description. In reality there are molecular orbitals encompassing the whole molecule and the best description (*i.e.*, the coefficients on the various atomic orbitals) of the bridging system will undoubtedly *not* be such that you simply have sp^2 hybrids on the carbon and two oxygen centers.

In a previous paper[5] we qualitatively discussed exchange through a polyatomic bridging system in terms of the bridge molecular orbitals into which the metals atoms are bonded. It was concluded that, without consideration of excited-state mixing, there did not seem to be a ferromagnetic exchange pathway available for a polyatomic bridge that is sym-

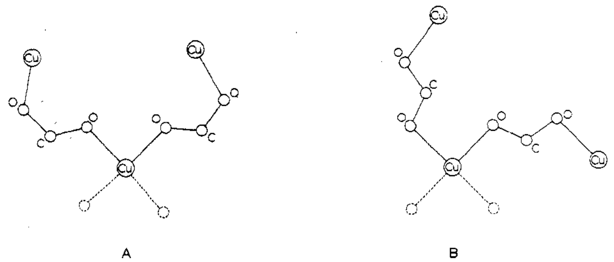

Figure 7. Crystalline structure of formate-bridging systems in "royal blue" anhydrous copper formate (A) and in copper formate tetrahydrate (B).

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metrically bridging two metals (*i.e.*, possessing a mirror plane perpendicular to the metal-metal vector as in copper formate tetrahydrate and $[Ni_2(tren)_2(C_2O_4)](BPh_4)_2$). In these cases, all first-order exchange pathways are seemingly antiferromagnetic because if one metal interacts with a given bridge orbital, the other metal will interact identically with the same bridge orbitals by virtue of the symmetry of the bridging. If, however, the bridging is geometrically asymmetric (no mirror plane), one metal might interact with a given bridge molecular orbital which is orthogonal to the appropriate metal orbitals on the second metal center. In this case ferromagnetic exchange pathways are available and a net ferromagnetic coupling might be observed for the dimer. Two cases of polyatomic geometrically asymmetric bridging have been reported: $[Ni_2(en)_4(NCS)_2]I_2$[3a] and the anhydrous copper formate;[35] both exhibit ferromagnetic coupling.

It is also relevant to note that Mays' single crystal ^{31}P and ^{7}Li nmr studies[39] point to antiferromagnetic coupling *via* a σ superexchange through Mn-O-P-O-Mn bridges in $LiMnPO_4$. This is another geometrically symmetric polyatomic bridge.

The interpretation of the difference in exchange effects for the nickel and copper oxalate systems can proceed in two ways. The first is qualitatively to discuss the d-orbital splitting on the metals, identify the d orbitals that contain the unpaired electrons, and then identify the possible exchange pathways through which the unpaired electrons interact. Consideration of the effects of excited-state mixing would also be desirable. The second approach is to do a molecular orbital calculation for the copper and nickel μ-oxalate dimers, or at least half of them, and to arrive at conclusions regarding the strength of the superexchange effect by "looking at " the overlap integrals and molecular orbital coefficients for those orbitals that contain the unpaired electrons.

If we define upon the molecular framework of $[Ni_2(tren)_2(C_2O_4)](BPh_4)_2$, at each metal center, a cartesian coordinate system analogous to that used for the formates, then the z axis will be perpendicular to the plane of the bridge and the x and y axes will each be directed at one oxygen and one nitrogen atom. Since we know that oxygen is a generally weaker field ligand than nitrogen, the octahedral e_g level will split into $d_{x^2-y^2}$ and d_{z^2} levels with the $d_{x^2-y^2}$ level lying lower in energy. In the copper complex the single unpaired electron on each metal center will be in the d_{z^2} level while the nickel complex will have one unpaired electron in each of the levels. The $d_{x^2-y^2}$ and d_{z^2} both participate only in σ interactions with the oxalate bridge and as such neither the copper nor nickel systems would have appreciable *first-order* exchange through the π system of the bridge. In this qualitative scheme the explanation of the loss in exchange interaction upon replacing nickel by copper in the μ-oxalato dimer would involve asserting that the $d_{x^2-y^2}$ orbital in the nickel system is more efficient than the d_{z^2} orbital (unpaired electrons in both copper and nickel cases) in transmitting an exchange interaction through the oxalate σ molecular orbitals. Alternatively, the explanation could be keyed on saying that first-order effects are not important and that configuration interaction in the nickel system provides a more viable exchange pathway (π pathway) than it does for the copper dimer.

Table VI. Normalized Molecular Coefficients for the Highest Two Occupied Orbitals of $Ni(NH_3)_4C_2O_4$ and $Cu(NH_3)_4C_2O_4$

	Coefficients			
	Nickel		Copper	
Atomic orbital	a_1 −9.32 eV	b_1 −9.84 eV	a_1 −8.89 eV	b_1 −9.81 eV
M 4s	0.012	. . .	−0.033	. . .
$3d_{z^2}$	0.217	0.001	−0.049	. . .
$d_{x^2-y^2}$	. . .	0.669	. . .	−0.175
d_{xz}	. . .	. . .	. . .	. . .
d_{yz}	. . .	. . .	. . .	. . .
d_{xy}	−0.070	. . .	0.030	. . .
$4p_x$	−0.011	0.005	−0.011	0.027
p_y	−0.011	−0.005	−0.011	−0.026
p_z	. . .	. . .	. . .	. . .
N(1) 2s	−0.025	. . .	0.011	. . .
$2p_x$	0.004	−0.001	0.003	−0.003
p_y	0.004	0.007	0.002	−0.002
p_z	0.106	. . .	0.053	. . .
N(3) 2s	0.012	−0.060	−0.005	0.028
$2p_x$	0.033	−0.227	−0.002	0.105
p_y	0.004	0.002	−0.004	0.002
p_z	. . .	0.002	−0.004	0.003
O(1) 2s	0.011	0.053	0.010	−0.005
$2p_x$	0.286	−0.055	−0.322	0.030
p_y	−0.321	−0.391	0.281	0.468
p_z	. . .	. . .	. . .	. . .
C(5) 2s	−0.069	0.001	0.068	0.003
$2p_x$	−0.189	0.029	0.199	−0.030
p_y	0.201	0.011	−0.208	−0.034
p_z	. . .	. . .	. . .	. . .
O(3) 2s	−0.009	0.034	0.016	0.004
$2p_x$	0.297	−0.242	−0.333	0.498
p_y	−0.326	−0.046	0.330	0.002
p_z	. . .	. . .	. . .	. . .

In an attempt to evaluate the differences in first-order σ superexchange between the nickel and copper oxalate dimers, extended-Huckel molecular orbital calculations (as per the Experimental Section) were performed on two model systems: $Ni(NH_3)_4C_2O_4$ and $Cu(NH_3)_4C_2O_4$. The expense of the calculations precluded considering the dimer complexes; however, orbital characteristics at the individual metal centers should be approximated, at least to the extent possible with the extended-Huckel technique. It must be remembered that we are doing very approximate calculations, in fact, calculations that do not take into account that we are dealing with open-shell systems. Some of the results of the calculations are given in Table VI. [Note that, in general, the molecular orbitals described by this table contain much less than the anticipated amount of metal character. While this seems to be an unfortunate artifact of the calculations, we will assume that the relative trends are reasonably well represented and will utilize the results on this more qualitative plane.] The axis system and details of structure used in these calculations are presented in Figure 8. In C_{2v} (local metal) symmetry the d_{z^2} orbital is of a_1 symmetry and the $d_{x^2-y^2}$ orbital is of b_1 symmetry. The molecular orbital coefficients are given in Table VI for the two highest energy filled levels for both the copper and nickel systems. In both cases the b_1 ($d_{x^2-y^2}$) is at lowest energy and thus for copper we have $(b_1)^2(a_1)^1$ and for nickel $(b_1)^1(a_1)^1$.

As has been frequently stated in the literature,[40-42] the magnitude of the exchange integral for a given metal-bridge-metal situation depends upon the overlap integrals involved in the metal-bridge bonding as well as on the intrabridge bonding and the relative energies of the metal and bridge orbitals. The copper system has one electron in the a_1 (d_{z^2}) level and in comparing this level with the a_1 level for the nickel system there does not seem to be nearly the difference requisite to explain the loss of exchange interaction in the

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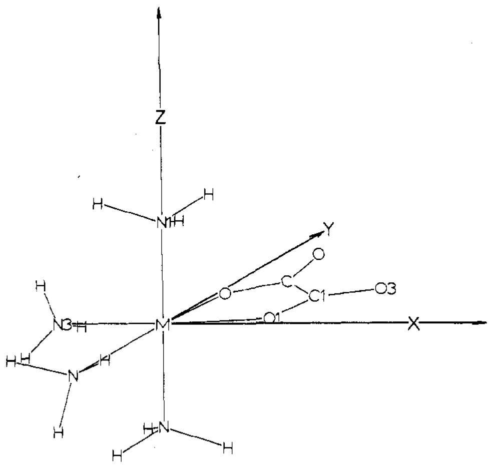

Figure 8. Details of assumed molecular structure of $M(NH_3)_4C_2O_4$ (M = Ni, Cu) used for molecular orbital calculations. Oxalate atoms and metal atom are coplanar. Metal–nitrogen and metal–oxygen distances are assumed to be 2.10 Å. Oxalate dimensions are MOC = 113°, OCO = 125°, C-C′ = 1.55 Å, and O-C = 1.25 Å.

copper case. In fact, the copper a_1 orbital places *more* of the unpaired electron density out onto the oxalate than does the nickel. If this were a dimer system, the *two* unpaired electrons in a copper dimer would seemingly be involved to a greater extent in spin polarization than the nickel electrons in the a_1 orbital; therefore this mechanism must be ruled out as the cause of the loss of interaction upon replacing nickel by copper. As advanced above, another qualitative explanation for the difference in interaction could lie in the character of the nickel b_1 ($d_{x^2-y^2}$) orbital. Our calculations have shown that of the orbitals wherein unpaired electrons reside, the nickel b_1 ($d_{x^2-y^2}$) orbital does bond *via* a $d_{x^2-y^2}$-bridge overlap which is significantly larger than is the d_{z^2}-bridge overlap. This would favor a larger exchange interaction. However, a relatively large $d_{x^2-y^2}$ coefficient in the b_1 nickel orbital, as well as small molecular orbital coefficients on the carbon for this case, seems to diminish the likelihood that the b_1 orbital is the predominant pathway of nickel exchange.

All in all, these molecular orbital calculations do not readily establish the mechanism of exchange leading to different magnetic effects for the copper and nickel systems. They do, however, seem to point out two things: (1) the character (population, energy, etc.) of the in-plane $d_{x^2-y^2}$ orbital could be of fundamental importance in determining the nature of the exchange and (2) a first-order σ-polarization mechanism is not indicated, and as such configuration interaction may be important in supporting a second-order π exchange.

We should note that as further experimental evidence of the importance of the in-plane $d_{x^2-y^2}$ orbital, a square-planar copper dimer with bis-bidentate 1,2,4,5-tetraaminobenzene bridging[43] possesses a distinct exchange interaction ($J = -12$ cm^{-1}).

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Registry No. $[Ni_2(tren)_2(N_3)_2](BPh_4)_2$, 40961-72-6; $[Ni_2(tren)_2(C_2O_4)](BPh_4)_2$, 40961-73-7; $[Cu_2(tren)_2(C_2O_4)](BPh_4)_2$, 41007-91-4; $[Cu_2(tren)_2(N_3)_2](BPh_4)_2$, 40961-74-8; $[Cu_2(dien)_2(N_3)_2](BPh_4)_2$, 40961-75-9; $[Cu_2(dien)_2(C_2O_4)](BPh_4)_2$, 40961-76-0; $[Cu_2(dien)_2(C_2O_4)](ClO_4)_2$, 21279-24-3; $Ni(NH_3)_4C_2O_4$, 15659-03-7; $Cu(NH_3)_4C_2O_4$, 40902-34-9.

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Stereoselectivity of *N*-(2-Pyridylmethyl)- and *N*-(6-Methyl-2-pyridylmethyl)-L-aspartic Acid Complexes of Copper(II) and Nickel(II) toward Optically Active Amino Acids

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Stability constants for a series of copper(II) and nickel(II) mixed-ligand complexes of amino acids and aspartic acid derivatives are reported. These constants indicate that the metal complexes of *N*-(2-pyridylmethyl)-L-aspartic acid and *N*-(6-methyl-2-pyridylmethyl)-L-aspartic acid coordinate the L enantiomers of alanine, phenylalanine, tryptophan, threonine, leucine, and valine in preference to their corresponding D isomers. These results are interpreted in terms of steric interactions of the α substituent of the amino acid and the pyridine residue of the aspartate derivative.

Introduction

There are few reports of stereoselectivity involving coordination of amino acidates (A^-) by complexes of labile metal ions, *i.e.*, examples in which equilibrium constants for the reactions

$$(\text{L-ligand})M^{n+} + \text{L-A}^- \rightleftharpoons (\text{L-ligand})M(\text{L-A})^{(n-1)+} \quad (1)$$

$$(\text{L-ligand})M^{n+} + \text{D-A}^- \rightleftharpoons (\text{L-ligand})M(\text{D-A})^{(n-1)+} \quad (2)$$

are different. Gillard, *et al.*,[2,3] found no stereoselective behavior for a series of bis(amino acidato)copper(II) complexes. ORD studies by Wellman, *et al.*,[4] supported this conclusion; they suggested there was little interaction between the two

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