III for the Mn compounds to be accurate to better than about ±40% due to the above assumptions and errors in $\langle r^{-3} \rangle$ and $Q$ values. Thus it is not at all surprising that the $(e^2qQ)_{calcd}$ values for $Mn(CO)_5X$ (X = Cl, Br, I) compounds do not give the same trend as $(e^2qQ)_{obsd}$ for these compounds. The signs of the $e^2qQ$ values should definitely be correct and $(e^2qQ)$ values should have semiquantitative significance.

Of particular interest are the positive signs of $e^2qQ$ (taking $Q$ positive) for $Mn(CO)_5X$ (X = Cl, Br, I, SnCl$_3$) and the negative sign for the hydride. The signs for the halides conflict with those calculated[5] using Fenske's orbital occupancy data.[6] This discrepancy in signs is almost certainly due to the overestimate of the $\sigma$-donor power of halides in the MO calculations, as noted by Spiess.[5] The field gradient $q$ can be expressed as

$$q = K[-N_{d_{z^2}} + N_{d_{x^2-y^2}} + {}^{1}\!/_2 N_{d_{xy}} - {}^{1}\!/_2(N_{d_{xz}} + N_{d_{yz}})] \tag{5}$$

and this can be rewritten for $Mn(CO)_5X$[7]

$$q \propto -\pi_{CO} + \pi_X + {}^{4}\!/_3\sigma_{CO} - {}^{4}\!/_3\sigma_X \tag{6a}$$

or

$$q \propto \Delta\sigma - \Delta\pi \tag{6b}$$

if we neglect crystal field contributions to the quadrupole splitting. The positive $e^2qQ$ value for $Mn(CO)_5X$ compounds indicates that CO is a better $\sigma$ donor and/or worse $\pi$ acceptor than Cl. Since CO is certainly a better $\pi$ acceptor than X from general chemistry and the photoelectron spectra of these compounds,[34] CO must be a much better $\sigma$ donor than Cl.

It is apparent then that as the $\sigma$-donor strength of L in $Mn(CO)_5L$ compounds increases, the $e^2qQ$ value becomes more negative; as the $\pi$ acceptor ability of L increases, the $e^2qQ$ value becomes more positive. Thus, we would expect compounds containing strong $\sigma$ donors such as L = H$^-$ to have relatively negative $e^2qQ$ values, while if L is a comparatively weak $\sigma$ donor (L = Cl, Br, I), the sign of $e^2qQ$ should be posi-

(34) S. Evans, J. C. Green, M. L. H. Green, A. F. Orchard, and D. W. Turner, *Discuss. Faraday Soc.*, 47, 112 (1969).

tive. The signs in Table III reflect the above ideas.

The correlation of $\sqrt{\Delta H}$ *vs.* chemical shift and the magnitude of the line widths strongly support the above treatment. The previous correlations of $\sqrt{\Delta H}$ *vs.* chemical shift by Onaka, *et al.*,[3] suggested that there should be a change in sign of $e^2qQ$ as predicted above and that the magnitude of $e^2qQ$ should follow the order $Mn(CO)_5H > Mn(CO)_5X > Mn(CO)_5$-SnCl$_3$ as predicted by the calculations in Table III. From the $\sqrt{\Delta H}$ *vs.* chemical shift correlation,[3] we suggest that all Mn-(CO)$_5$L compounds with chemical shifts below ~2150 ppm have positive $e^2qQ$ values, while those compounds having chemical shifts above this value have negative $e^2qQ$ values.

The positive correlations indicate strongly that both the chemical shift and $e^2qQ$ are mainly sensitive to $\sigma$ effects and it is interesting to note that the $\sqrt{\Delta H}$ ($\propto \sigma - \pi$) *vs.* chemical shift ($\propto \sigma + \pi$) plots are analogous to the quadrupole splitting ($\propto \sigma - \pi$)–center shift ($\propto \sigma + \pi$) plots noted earlier[26] for Fe$^{II}$ low-spin compounds. In both cases, if $\pi$ effects are dominant, a line of opposite slope to those observed should be obtained, while if $\pi$ effects are important, no correlations should be observed. Strong $\pi$ acceptors such as CO were found to lie off the line in the Fe$^{II}$ series,[26] as expected from the above ideas.

Finally, there is good qualitative agreement between observed relative $\Delta H$ values and those expected from the calculated $e^2qQ$ values in Table III. Thus the observed line widths for the $Mn(CO)_5X$ compounds are as follows (in gauss): Mn-(CO)$_5$SnCl$_3$, 0.18; Mn(CO)$_5$Cl, 0.18; Mn(CO)$_5$Br, 0.378; Mn-(CO)$_5$I, 0.557; HMn(CO)$_5$H, 2.39.[1,3] These values correlate reasonably well with $(e^2qQ)^2_{calcd}$, but more points are needed to establish a more quantitative correlation.

**Registry No.** Cl$_3$SiMn(CO)$_5$, 38194-30-8; Cl$_3$GeMn(CO)$_5$, 14768-39-9; Cl$_3$SnMn(CO)$_5$, 16165-09-6; (C$_6$F$_5$)$_3$SiMn(CO)$_5$, 25930-67-0; (C$_6$F$_5$)$_3$GeMn(CO)$_5$, 38135-65-8; (C$_6$F$_5$)$_3$SnMn-(CO)$_5$, 38135-66-9; Ph$_3$SiMn(CO)$_5$, 38194-32-0; Ph$_3$GeMn-(CO)$_5$, 38135-67-0; Ph$_3$SnMn(CO)$_5$, 34792-14-8; Ph$_3$PbMn-(CO)$_5$, 38135-69-2; Ph$_2$(C$_6$F$_5$)SnMn(CO)$_5$, 38135-70-5; Ph-(C$_6$F$_5$)$_2$SnMn(CO)$_5$, 37830-62-9; Ph$_2$ClSnMn(CO)$_5$, 38241-11-1; PhCl$_2$SnMn(CO)$_5$, 38135-72-7.

---

# Magnetization Studies of Bimetallic Copper(II) Complexes Which Have Triplet Ground States

KENNETH T. McGREGOR, DEREK J. HODGSON, and WILLIAM E. HATFIELD*

Magnetization studies have been carried out on the dimeric compounds [Cu(pyO)$_2$(NO$_3$)$_2$]$_2$, [Cu(2,2'-bipy)(OH)]$_2$SO$_4$·5H$_2$O, [Cu(2,2'-bipy)(OH)]$_2$(NO$_3$)$_2$, and [Cu(Et$_2$dtc)$_2$]$_2$ (pyO is pyridine N-oxide, 2,2'-bipy is 2,2'-bipyridyl, and Et$_2$dtc is N,N-diethyldithiocarbamate). The experimental data were compared with theoretical values calculated from the expression $\langle \mu \rangle = gS'B_{S'}(X)$, where $B_{S'}(X)$ is the Brillouin function and $S'$ is the effective spin. The data for each complex are consistent with a ferromagnetic intradimer interaction and an antiferromagnetic interdimer interaction and confirm the existence of a triplet ground state in each dimeric molecule.

## Introduction

Only recently have there been reports[1-4] of copper(II) dimers which exhibit spin–spin coupling resulting in triplet

(1) W. E. Hatfield, J. A. Barnes, D. Y. Jeter, R. Whyman, and E. R. Jones, *J. Amer. Chem. Soc.*, 92, 4982 (1970).

ground states. Although the theory of exchange interactions

(2) J. F. Villa and W. E. Hatfield, *Inorg. Chem.*, 10, 2038 (1971).
(3) J. A. Barnes, W. E. Hatfield and D. J. Hodgson, *Chem. Commun.*, 1593 (1970); J. A. Barnes, D. J. Hodgson, and W. E. Hatfield, *Inorg. Chem.*, 11, 144 (1972).
(4) K. T. McGregor, N. T. Watkins, D. L. Lewis, D. J. Hodgson, and W. E. Hatfield, submitted for publication.

has been developed[5] to a stage which includes ferromagnetic interactions, there are few examples of copper(II) dimers of this type. Some reasons for the absence of such examples have been discussed previously.[1] Here we wish to report the results of our magnetization studies on the bimetallic copper-(II) complexes, $[Cu(Et_2dtc)_2]_2$ ($Et_2dtc$ is $N,N$-diethyldithio-carbamate), $[Cu(pyO)_2(NO_3)_2]_2$ (pyO is pyridine $N$-oxide), $[Cu(bipy)OH]_2SO_4 \cdot 5H_2O$ (bipy is 2,2'-bipyridyl), and $[Cu(bipy)OH]_2(NO_3)_2$. Each of these complexes has a well-characterized structure and each has been reported to have a triplet ground state. The present studies more fully describe the magnetic properties of these complexes and contribute to our understanding of the nature of exchange interactions.

## Theory

The Hamiltonian for the spin-spin interaction of exchange coupled copper(II) ions may be written as

$$\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2 \qquad (1)$$

By consideration of the eigenvalues of (1) and the Boltzmann population distribution, the Van Vleck[6] equation for the magnetic susceptibility of such systems may be written. A modified version of the Van Vleck equation is

$$\chi_m = \frac{g^2 N\beta^2}{3k(T-\Theta)}[1 + (1/3)\exp(-2J/kT)]^{-1} + N\alpha \qquad (2)$$

Here $2J$ is the singlet-triplet energy level separation produced by the interaction of spins within the isolated dimers. The interaction among spins throughout the lattice is accounted for by the parameter $\Theta$.[7] It may be seen from (2) that a small $\Theta$ value is significant at low temperatures but is not significant at higher temperatures.

The Hamiltonian for the interacting dimers may be written as

$$\mathcal{H}_1 = -2J_1 \mathbf{S}'_i \overset{z}{\underset{j=1}{\Sigma}} \mathbf{S}'_j \qquad (3)$$

where $\mathbf{S}'$ is the effective dimer spin and the sum is taken over the $z$ nearest neighbors of the $i$th dimer. The classical molecular field treatment[8] of this interaction replaces the sum in (3) with an effective field $H_m$, which is assumed to be proportional to the magnetization $M$

$$H_m = N_w M = Ng\beta\langle\mathbf{S}'_j\rangle N_w \qquad (4)$$

where $\mathbf{S}'_j$ has been replaced with its average value. Using the expression

$$H_m = \frac{2zJ_1}{g\beta}\langle\mathbf{S}'_j\rangle$$

the molecular field coefficient $N_w$ can be written as

$$N_w = \frac{2zJ_1}{Ng^2\beta^2} \qquad (5)$$

By using the Curie-Weiss law for the magnetic susceptibility, $\chi = C/(T-\Theta)$, where the Weiss constant is given by

$$\Theta = \frac{2zJ_1S'(S'+1)}{3k}$$

the molecular field coefficient may be expressed in terms of $\Theta$ according to

$$N_w = \frac{3k\Theta}{Ng^2\beta^2S'(S'+1)} \qquad (6)$$

At low temperatures, where only the ground state is appreciably populated, eq 2 has the Curie-Weiss form, and the lattice interaction parameter may be used to estimate the molecular field coefficient.

These concepts have been used by Ginsberg and coworkers,[7] who have characterized some nickel(II) complexes in terms of both intra- and intermolecular interactions. The complex $Ni_4(OCH_3)_4(acac)_4(CH_3OH)_4$ is reported to exhibit ferromagnetic coupling for both types of interactions; the complex $[Ni(acac)_3]_3$, however, is reported to have a positive coupling constant within the trimer with an antiferromagnetic interaction between trimers.

## Experimental Section

**Preparation.** The preparations of $[Cu(Et_2dtc)_2]_2$ and $Cu[(bipy)-OH]_2SO_4 \cdot 5H_2O$ have been reported[2,3,9] previously. A sample of $[Cu(pyO)_2(NO_3)_2]_2$ was prepared by mixing solutions of copper(II) nitrate and pyridine $N$-oxide in 2,2-dimethoxypropane in the proper stoichiometric ratios. The pyridine $N$-oxide used was purified by vacuum distillation. The analytical data for these three complexes are shown in Table I. The sample of $[Cu(bipy)OH]_2(NO_3)_2$ was prepared by a metathetical reaction between the sulfate salt and $Ba(NO_3)_2$ in aqueous solution. The identity of the material was established by X-ray diffraction techniques. The unit cell and space group data were identical with those reported by Majeste and Meyers.[10]

**Magnetic Measurements.** The magnetic susceptibilities of a powdered sample of each complex were determined using a Foner-type vibrating-sample magnetometer.[11] Measurements were made at temperatures in the range of 1.5–10°K and at field strengths of 2.5, 5, 7.5, 10, 12.5, and 15 kG. The field strength was calibrated by nuclear (Li) resonance techniques. The temperatures were measured with a calibrated gallium arsenide diode and by a calibrated germanium-resistance thermometer. Mercury tetrathiocyanatocobaltate-(II) was used as a susceptibility standard.[12] All susceptibilities were corrected for the diamagnetism of the substituent atoms using Pascal's constants[13] and for the TIP of copper (estimated to be $60 \times 10^{-6}$ cgsu/Cu atom).

## Results and Discussion

**Tetrakis($N,N$-diethyldithiocarbamato)dicopper(II).** A plot of the experimental magnetization *vs.* $H/T$ for $[Cu(Et_2dtc)_2]_2$ is shown in Figure 1(a). The solid curves in Figure 1 are computer plots of the calculated magnetization

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

where $B_{S'}(X)$ is the Brillouin function[8]

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

Here $X = (H/T)(S'g\beta/k)$ where $S'$ is the effective spin and $H$ is the apparent field which is the sum of the external field and the molecular field, *i.e.*, $H = H_{ext} + H_m$. The molecular field was estimated by using eq 4 and 6. The experimental data are compared with calculated curves for the triplet state and for two doublet states. The data are consistent with a triplet ground state for the dimer with a small interdimeric antiferromagnetic interaction. The experimental data are fit by a $\Theta$ value of $-1.15°$ and a $g$ value of 2.05. This may be compared to the $\Theta$ value of $-1.37°$ and $\langle g \rangle$ of 2.05 which

(5) J. B. Goodenough, "Magnetism and the Chemical Bond," Interscience, New York, N. Y., 1963.

(6) J. H. Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, London, 1966, Chapters IX, XII.

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

(8) J. S. Smart, "Effective Field Theories of Magnetism," W. B. Saunders Co., Philadelphia, Pa., 1966, Chapter III.

(9) S. H. Laurie, *Aust. J. Chem.*, 20, 2609 (1967).

(10) R. J. Majeste and E. A. Meyers, *J. Phys. Chem.*, 74, 3497 (1970).

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

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

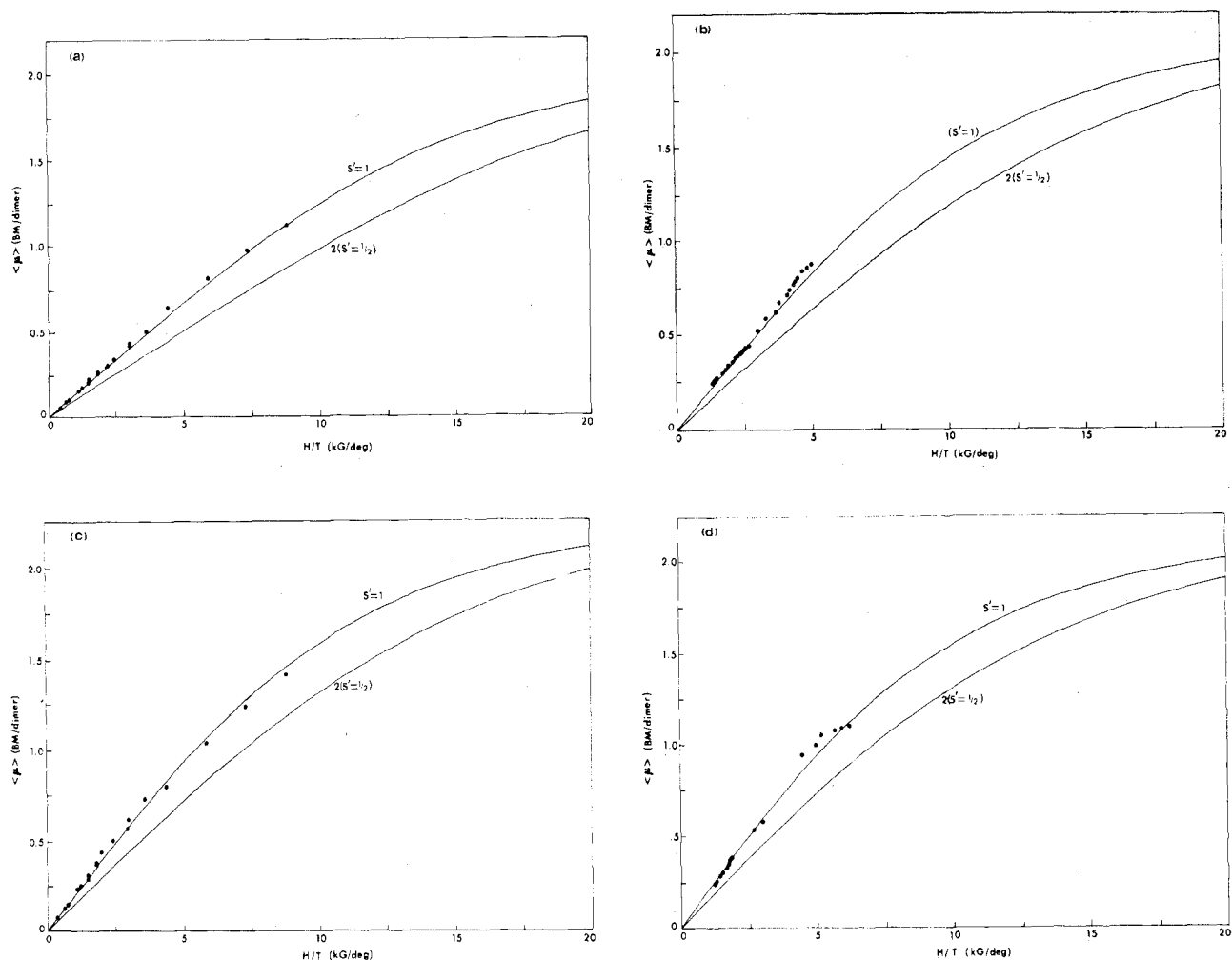(13) E. Konig, "Magnetic Properties of Transition Metal Compounds," Spinger-Velag, Berlin, 1966.

**Figure 1.** Magnetization data for the complexes: (a) $[Cu(Et_2dtc)_2]_2$, (b) $[Cu(pyO)_2(NO_3)_2]_2$, (c) $[Cu(bipy)OH]_2SO_4 \cdot 5H_2O$, and (d) $[Cu(bipy)OH]_2(NO_3)_2$. The solid curves are the calculated magnetizations for a triplet state and for two uncoupled doublet states. The experimental data are shown as dots.

**Table I.** Analytical Data

| | %C | | %H | | %N | |
|---|---|---|---|---|---|---|
| Complex | Found | Calcd | Found | Calcd | Found | Calcd |
| $[Cu(pyO)_2(NO_3)_2]_2$ | 32.09 | 31.80 | 2.55 | 2.67 | 14.72 | 14.83 |
| $[Cu(bipy)OH] SO_4 \cdot 5H_2O$ | 36.48 | 36.4 | 3.99 | 4.3 | 8.33 | 8.5 |
| $[Cu(Et_2dtc)_2]_2$ | 33.39 | 33.33 | 5.74 | 5.60 | 7.58 | 7.78 |

were determined from the magnetic susceptibility data reported[2] previously for this complex. The singlet-triplet separation, $2J$, was reported to be 24 cm$^{-1}$. Although the $\Theta$ values differ slightly, the results of both studies are suggestive of a small antiferromagnetic interaction between the triplet ground-state dimers. The estimated standard deviations of the values of the magnetic parameters are very large since, as has been discussed previously,[3] the Van Vleck equation is extremely insensitive to variations in large positive $J$ values.

The structure of $[Cu(Et_2dtc)_2]_2$, as determined by Bonamico, *et al.*,[14] is shown in Figure 2(a). The copper ions are in a distorted tetragonal-pyramidal environment with four sulfur atoms comprising the basal plane. The apical sulfur atom, at 2.85 Å, is part of the basal plane of an adjacent copper(II) ion. The copper-copper separation is 3.59 Å. Although the copper environment appears to be

pyramidal, a hydrogen atom of an ethyl group of an adjacent dimer is found in the sixth octahedral position 2.86 Å from the copper atom. This arrangement could serve as a pathway for the small lattice interaction which was observed.

**Di-$\mu$-(pyridine *N*-oxide)-bis[bis(nitrato)(pyridine *N*-oxide)-copper(II)].** The crystal structure of $[Cu(pyO)_2(NO_3)_2]_2$ has been determined by Scavnicar and Matkovic[15] and is shown schematically in Figure 2(b). Each copper ion of the dimeric unit is in a tetragonal-pyramidal environment with the basal plane composed of trans pyridine *N*-oxide and nitrate groups. The fifth position is occupied by an oxygen atom of a pyridine *N*-oxide group which is also in the basal plane of the other copper(II) ion; this axial Cu-O distance is 2.439 Å. The copper-copper separation is 3.458 Å and the Cu-O-Cu bond angle is 102.9°. Magnetic susceptibility data to 2.4°K and epr data for this complex have been reported.[1] A value for $2J$ of 15 cm$^{-1}$ with $\langle g \rangle = 2.11$ was determined from those studies. As seen in Figure 1(b), the magnetization data are consistent with a triplet ground state for the complex with $\langle g \rangle = 2.11$. The best fit $\Theta$ value of $-0.50°$ was used to account for a small antiferromagnetic lattice interaction. Such a lattice interaction was also suggested by the susceptibility data.

**Di-$\mu$-hydroxo-bis(2,2'-bipyridyl)dicopper(II) Sulfate Pentahydrate.** The structure of $[Cu(bipy)OH]_2SO_4 \cdot 5H_2O$,

(14) M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Crystallogr.*, 19, 886 (1965).

(15) S. Scavnicar and B. Matkovic, *Chem. Commun.*, 297 (1967); *Acta Crystallogr., Sect. B*, 25, 2046 (1969).
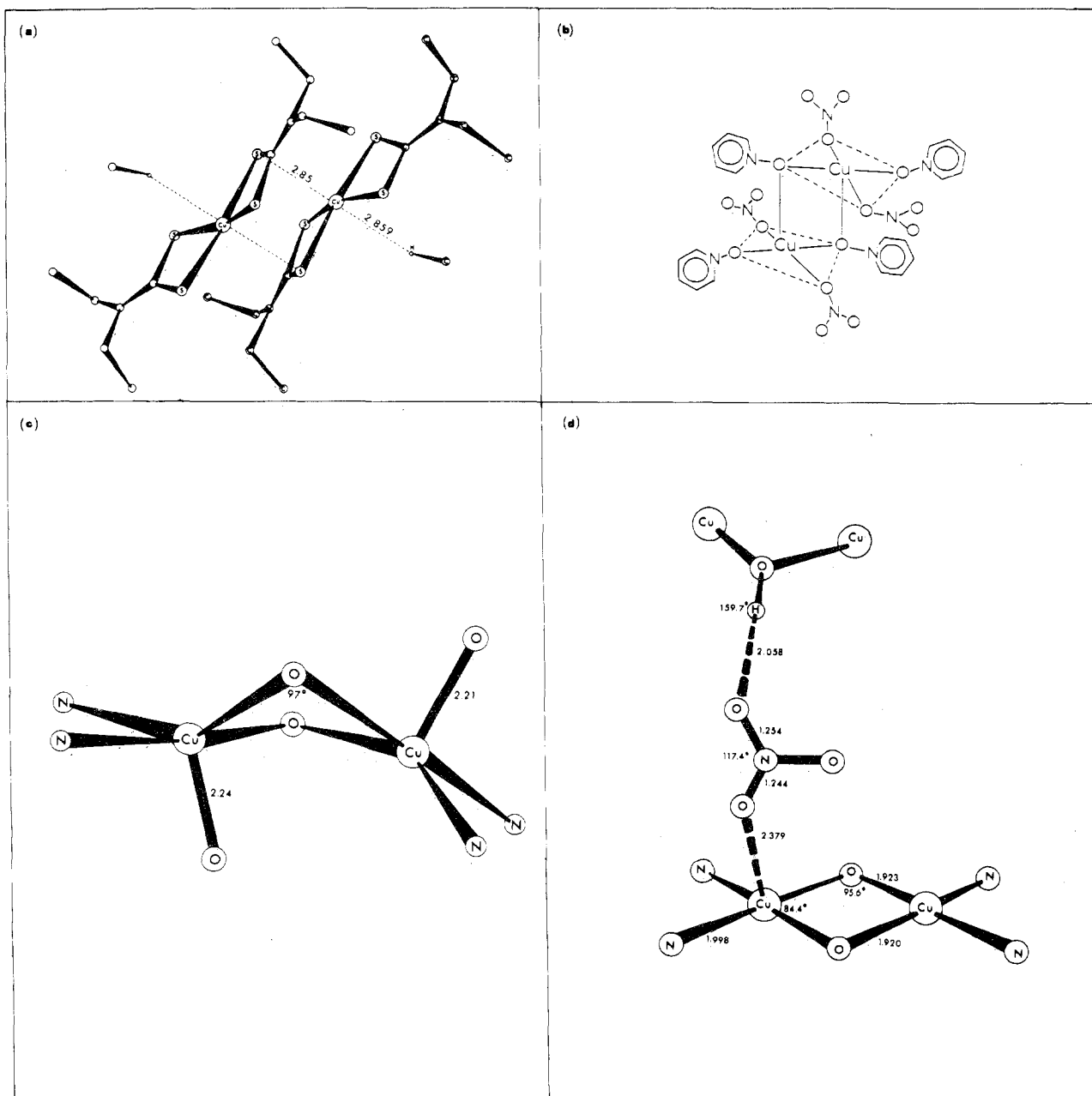
**Figure 2.** The structures of the complexes: (a) $[Cu(Et_2dtc)_2]_2$,[14] (b) $[Cu(pyO)_2(NO_3)_2]_2$,[15] (c) $[Cu(bipy)OH]_2SO_4 \cdot 5H_2O$,[16] and (d) $[Cu(bipy)OH](NO_3)_2$.[10]

as determined by Casey, *et al.*,[16] is shown in Figure 2(c). The basal plane of the distorted square-pyramidal environment of the copper(II) ions is composed of nitrogen atoms of a bipyridyl group and the oxygen atoms of the bridging hydroxy groups. The copper–copper separation is 2.893 Å and the Cu–O–Cu bridge angle is $97°$. The magnetic susceptibility and epr studies on this complex have been interpreted[3] in terms of a triplet ground state where $2J$ is 48 $cm^{-1}$ and $\langle g \rangle$ is 2.20. Figure 1(c) shows the magnetization data for the complex. The solid curves were calculated with the previously reported $g$ value and a $\Theta$ value of $-0.50°$. A best fit $\Theta$ value of $-1.00°$ was determined from the susceptibility study. The magnetization data suggest a somewhat smaller lattice interaction. Since the fifth coordination site of one of the copper(II) ions of each dimeric pair is occupied by a water molecule, it seems reasonable that hydrogen bond-

ing could provide a pathway for the lattice interaction. The absence of complete structural information does not permit a more detailed discussion of the interdimer interaction.

**Di-$\mu$-hydroxo-bis(2,2′-bipyridyl)dicopper(II) Nitrate.** The best least-squares fit of the magnetic susceptibility data of $[Cu(bipy)OH]_2(NO_3)_2$ yields a $2J$ value of 172 $cm^{-1}$ with a $g$ value of 2.10. A $\Theta$ value of $-0.45°$, which fits the experimental data, is suggestive of a small antiferromagnetic interaction between the triplet ground-state dimers. The magnetization data, shown in Figure 1(d), are consistent with these findings.

The structure of $[Cu(bipy)OH]_2(NO_3)_2$[10] is shown in Figure 2(d). The basal plane is composed of two cis hydroxo bridges and two nitrogen atoms of the bipyridyl group. The copper–copper separation is 2.847 Å and the Cu–O–Cu bridge angle is $95.6°$. The fifth coordination position is occupied by an oxygen atom of a nitrate group. Another oxygen atom of this nitrate group is hydrogen bonded to a hydroxo bridge of an adjacent dimer; this arrangement could

(16) A. T. Casey, B. F. Hoskins, and F. D. Whillans, *Chem. Commun.*, 904 (1970).

easily provide a pathway for the small lattice interaction.

## Conclusions

The magnetic and structural properties of these four complexes are summarized in Table II. The copper–copper separations of two of the complexes are greater than 3 Å, and this distance is considered to be too great to allow any significant orbital overlap between copper atoms; moreover, an interaction of this type must be antiferromagnetic in nature. The remaining two complexes, which are very similar in structure, show a negative correlation between the Cu–Cu separation and the value of $2J$. These facts indicate that the spin–spin interaction is of the type proposed by Goodenough,[5] in which the ligand atoms are instrumental in the exchange interaction. Further evidence for the superexchange mechanism is provided by the Cu–O–Cu bridge angles. The assumption that the s-orbital contribution increases as the bridge angle increases from 90° suggests that the value of $2J$ will decrease as the bridge angle increases; our experimental observations are consistent with this postulation.

The pathways available for the intradimer magnetic coupling have been discussed in some detail elsewhere.[2,3,5,17] All major pathways for the exchange interaction make positive contributions to $J$. Our magnetization studies, which are the first studies of this type of copper(II) compounds, provide strong evidence for the confirmation of the triplet ground state for these complexes.

The molecular field approximation used in the analysis of the data is basically that of Weiss. Although more sophisticated treatments could be used, the more simple method describes the experimental data reasonably well.

(17) R. L. Martin in "New Pathways in Inorganic Chemistry," E. A. V. Ebsworth, A. G. Maddock, and A. G. Sharpe, Ed., Cambridge University Press, London, 1968.

**Table II.** Structural and Magnetic Properties

| Complex | Bridge angle, deg | Cu–Cu, Å | $2J$, cm$^{-1}$ | $\Theta$, deg | Ref |
|---|---|---|---|---|---|
| [Cu(Et$_2$dtc)$_2$]$_2$ | | 3.59 | 24 | −1.15 | 2, 14 |
| [Cu(pyO)$_2$(NO$_3$)$_2$]$_2$ | 102.9 | 3.459 | 15 | −0.50 | 1, 15 |
| [Cu(bipy)OH]$_2$SO$_4$· 5H$_2$O | 97 | 2.893 | 48 | −0.50 | 3. 16 |
| [Cu(bipy)OH]$_2$(NO$_3$)$_2$ | 95.6 | 2.847 | 172 | −0.45 | 4, 10 |

Some comment should be made about the relation of the $\Theta$ value to the magnetic ordering temperature $T_i$ ($i$ = N or C, depending upon whether the ordering is antiferromagnetic or ferromagnetic, respectively). Although $\Theta$ may approximate $T_C$ for ferromagnetic ordering, this is not true for $\Theta$ and $T_N$ when antiferromagnetic ordering occurs.[8] Since the interdimer interactions of the systems studied here are antiferromagnetic, we are unable to predict the ordering temperature. It is noteworthy that all of the interdimer interactions that have been observed for copper(II) complexes have been antiferromagnetic in nature.

# Ligand-Bridged Five-Coordinate Nickel(II) Complexes

THOMAS D. DuBOIS* and FAITHEL T. SMITH

The tetradentate ligand 2,3-butanedione bis(2-diphenylarsinoethylimine), (C$_6$H$_5$)$_2$AsCH$_2$CH$_2$N=C(CH$_3$)C(CH$_3$)=NCH$_2$CH$_2$-As(C$_6$H$_5$)$_2$, forms the four-coordinate, square-planar [Ni(C$_{32}$H$_{34}$N$_2$As$_2$)](ClO$_4$)$_2$ complex and the five-coordinate, ligand-bridged [Ni(C$_{32}$H$_{34}$N$_2$As$_2$)X]$_n$(ClO$_4$)$_n$ (X = Cl, Br, I) complexes. The coordination compounds have been characterized by conductivity measurements, molecular weight measurements, proton magnetic resonance spectra, infrared spectra, electronic absorption spectra and elemental analyses. The electronic absorption spectra of the five-coordinate, ligand-bridged complexes of the type [Ni(C$_{32}$H$_{34}$N$_2$As$_2$)X]$_n$(ClO$_4$)$_n$ are consistent with a square-pyramidal arrangement of donor atoms about the nickel(II) ion.

## Introduction

In general it has been observed that five-coordinate, low-spin, trigonal-bipyramidal complexes of nickel(II) give electronic absorption spectra which are characterized by a rather intense symmetrical absorption band followed by a band of much lower intensity at higher energy. The positions of the absorption bands of the trigonal-bipyramidal complexes depend upon the relative crystal field strength of the donor atoms of the ligands.[1] In comparison the five-coordinate, low-spin, square-pyramidal complexes of nickel-

(II) give electronic absorption bands at relatively higher energies than the more intense band of the trigonal-bipyramidal complexes with the same or similar ligand donor atoms.[2-5]

The contour of the electronic absorption bands of the square-pyramidal complexes is quite sensitive to the arrangement of donor atoms in the base of the square pyramid. The

(1) G. Dyer and D. W. Meek, *Inorg. Chem.*, 6, 149 (1967), and references therein.

(2) G. A. Mair, H. M. Powell, and D. E. Henn, *Proc. Chem. Soc., London*, 415 (1961).

(3) G. A. Barclay, R. S. Nyholm, and R. V. Parish, *J. Chem. Soc.*, 4433 (1961).

(4) L. Sacconi and R. Morassi, *J. Chem. Soc. A*, 2997 (1968).

(5) P. L. Orioli and L. Sacconi, *Chem. Commun.*, 1310 (1968).