Inorg. Chem. **1982**, *21*, 68-72

Contribution No. 6347 from the Department of Chemistry, California Institute of Technology, Pasadena, California 91125,
and Contribution from the School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Binuclear Complexes of Macrocyclic Ligands. Variation of Magnetic Exchange Interaction in a Series of Heterobinuclear Cu^{II}-M^{II} Complexes

SUSAN L. LAMBERT,[1] CLIFFORD L. SPIRO,[2] ROBERT R. GAGNÉ,*[2] and DAVID N. HENDRICKSON*[1]

Received December 24, 1980

A series of heterobinuclear complexes of a ligand derived from the Schiff base condensation of 2 mol of 1,3-diaminopropane and 2 mol of 2,6-diformyl-4-methylphenol has been characterized with variable-temperature magnetic susceptibility (4.2-285 K). The complexes are of the composition $LCuMCl_2{\cdot}nH_2O$, where L is the rigid binucleating macrocyclic ligand. One metal ion, divalent copper ion, is held constant while M is varied across the series Mn(II), Fe(II), Co(II), and Ni(II). Both metal ions in a given binuclear unit have the same coordination geometry, square pyramidal with an N_2O_2 basal plane and an apically coordinated chloride anion. The susceptibility data for all the complexes were least-squares fit to susceptibility expressions derived from the isotropic spin Hamiltonian with the inclusion of a term to account for single-ion zero-field splitting for the metal M. A trend toward an increasingly antiferromagnetic exchange interaction is observed in the $LCuMCl_2$ series where the exchange parameter, J, was found to be -30, -71, and -103 cm^{-1} for the Mn(II), Fe(II), and Ni(II) complexes, respectively. The presence of spin-orbital coupling in $LCuCoCl_2$ makes a comparison with the other members of the series difficult. The data for $LCuCoCl_2$ were fit to an expression derived from a Hamiltonian which explicitly includes axial and rhombic single-ion zero-field effects, spin-orbit coupling for the cobalt ion, and an isotropic exchange interaction. The results for the $LCuMCl_2$ series are compared with the results for previously reported heterobinuclear series as well as with the results for the analogous LM_2Cl_2 series of homobinuclear compounds.

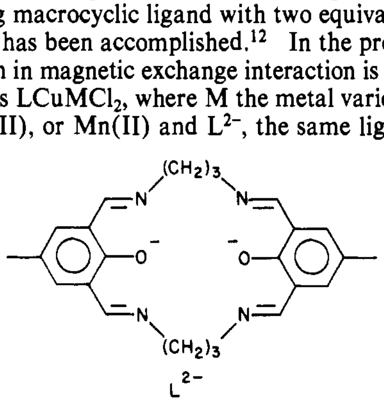
Introduction

There are basically two types of ligands that can simultaneously coordinate two metal ions. One type of binucleating ligand presents two equivalent coordination sites and the other has two inequivalent coordination sites. There are examples of either type which are macrocyclic.[3,4]

In recent papers we have used the Robson[5] macrocyclic binucleating ligand with equivalent N_2O_2 coordination sites to investigate the dependence of magnetic exchange interaction upon the metal ion in two different series of homobinuclear complexes. The first series[6] consisted of two identical ions each in square-pyramidal coordination sites. It was found that the net antiferromagnetic exchange interaction decreased monotonically in this series of homobinuclear complexes as the metal ion was changed in the order Cu(II), Ni(II), Co(II), Fe(II), and Mn(II). In the case of Mn(II), a cross-over to a feebly ferromagnetic ground state was observed. In the second series of homobinuclear complexes, each metal ion was constrained to lie within the plane of the macrocyclic ligand by virtue of two trans-axial ligands. The magnetic exchange interactions observed for these pseudooctahedrally coordinated metal ions were very similar to those observed for the five-coordinate complexes. This suggested that there is one major factor that determines the variation of magnetic exchange interaction in a series. The variation largely reflects the changing number of unpaired electrons and associated magnetic exchange pathways from one complex to another.

A number of mixed-metal complexes of binucleating ligands have been prepared and studied with the magnetic susceptibility technique.[8-10] Without exception, each of the binucleating ligands in these studies has two inequivalent coordination sites. Frequently, one metal ion is in a N_2O_2 coordination site and the other occupies an O_4 site. Such coordination site inequalities could dominate the overall exchange interaction. One notable result in this area is the synthesis of a Cu^{II}-V^{IV} complex in which there is an orthogonality of the magnetic orbitals centered on the two metal ions with a resulting net intramolecular ferromagnetic interaction.[11]

The formidable task of preparing and characterizing a series of mixed-metal complexes of a binucleating complexes of a binucleating macrocyclic ligand with two equivalent coordination sites has been accomplished.[12] In the present paper, the variation in magnetic exchange interaction is investigated for the series $LCuMCl_2$, where M the metal varied is Ni(II), Co(II), Fe(II), or Mn(II) and L^{2-}, the same ligand used in our previous studies,[6,7] results from the condensation of 2 mol of 2,6-diformyl-4-methylphenol with 2 mol of 1,3-diaminopropane.



L^{2-}

Experimental Section

Compound Preparation. All compounds in this study were prepared as reported.[12]

Physical Measurements. A PAR model 150A vibrating-sample magnetometer, operated at 13.5 kG, was used to collect the magnetic susceptibility data. Samples of $CuSO_4{\cdot}5H_2O$ were used as standards, and a calibrated GaAs diode was employed for sample-temperature determination. Corrections for the diamagnetism of the sample container and the background were made at all temperatures. A diamagnetic correction, estimated from Pascal's constants,[13] was used to calculate molar paramagnetic susceptibilities from the experimental susceptibilities. The molar paramagnetic susceptibilities were fit to

---

[1] University of Illinois.

[2] California Institute of Technology.

[3] Casellato, U.; Vigato, P. A.; Vidali, M. *Coord. Chem. Rev.* **1977**, *23*, 31.

[4] Groh, S. E. *Isr. J. Chem.* **1976/1977**, *15*, 277.

[5] Lambert, S. L.; Hendrickson, D. N. *Inorg. Chem.* **1979**, *18*, 2683.

[6] Sprio, C. L.; Lambert, S. L.; Smith, T. J.; Duesler, E. N.; Gagne, R. R.; Hendrickson, D. N. *Inorg. Chem.* **1981**, *20*, 1229.

[7] Pilkington, N. H.; Robson, R. *Aust. J. Chem.* **1970**, *23*, 2225.

[8] Kahn, O.; Tola, P.; Coudanne, H. *Chem. Phys.* **1979**, *42*, 355.

[9] O'Connor, C. J.; Freberg, D. P.; Sinn, E. *Inorg. Chem.* **1979**, *18*, 1077.

[10] Torihara, N.; Okawa, H.; Kida, S. *Chem. Lett.* **1978**, 185.

[11] Kahn, O.; Galy, J.; Tola, P.; Coudanne, H. *J. Am. Chem. Soc.* **1978**, *100*, 3931.

[12] Gagne, R. R.; Spiro, C. L.; Smith, T. J.; Hamann, C. A.; Thies, W. R.; Shiemke, A. D., submitted for publication in *Inorg. Chem.*

[13] Mulay, L. N.; Boudreaux, E. A. "Theory and Applications of Molecular Diamagnetism"; Wiley-Interscience: New York, 1976.

0020-1669/82/1321-0068$01.25/0

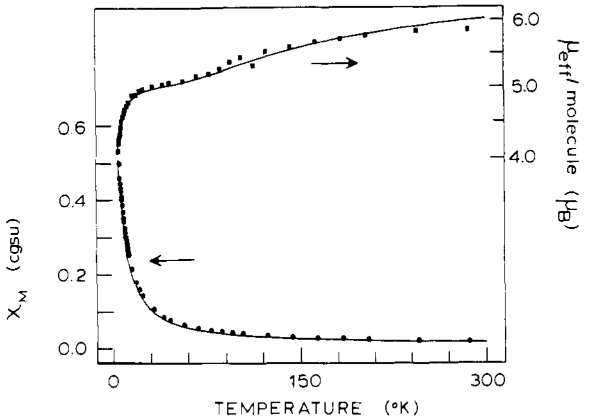


Figure 1. Molar paramagnetic susceptibility, χ_M, and effective magnetic moment per molecule, μ_{eff}, vs. temperature curves for $LCuMnCl_2$. The solid lines represent the least-squares fit of the data to the theoretical equation given in the text.

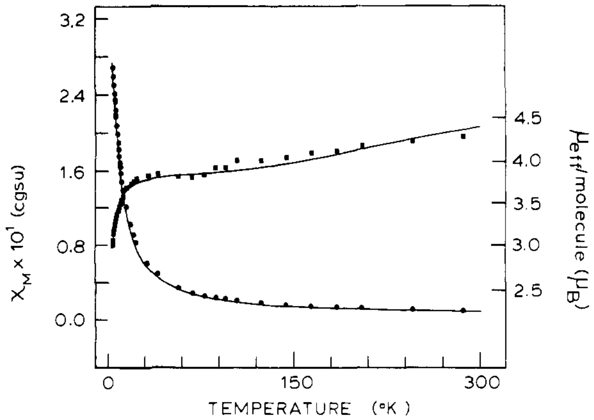


Figure 2. Molar paramagnetic susceptibility, χ_M, and effective magnetic moment per molecule, μ_{eff}, vs. temperature curves for $LCuFeCl_2{\cdot}2H_2O$. The solid lines represent the least-squares fit of the data to the theoretical equation given in the text.

the appropriate theoretical expressions by means of a least-squares fitting computer program.[14]

EPR spectra were recorded as described previously.[15]

Results

Variable-temperature (4.2–286 K) magnetic susceptibility data were collected for the compounds $LCuMnCl_2$, $LCuFeCl_2{\cdot}2H_2O$, $LCuCoCl_2{\cdot}H_2O$, and $LCuNiCl_2{\cdot}2H_2O$. These data are given in Tables I–IV.[16]

The data for $LCuMnCl_2$ are illustrated in Figure 1. An antiferromagnetic exchange interaction is present as indicated by the fact that the effective magnetic moment, μ_{eff}, decreases with decreasing sample temperature. When there is no magnetic exchange interaction present in such a Cu^{II}–Mn^{II} binuclear complex, the paramagnetic susceptibilities of the two different metal centers are added to give the paramagnetic susceptibility for the binuclear complex. Consequently, the spin-only value of μ_{eff} for the Cu^{II}–Mn^{II} binuclear complex would be expected to be 6.20 μ_B in the absence of an exchange interaction. An antiferromagnetic exchange interaction in a Cu^{II}–Mn^{II} binuclear complex leads to an $S = 2$ ground state with an $S = 3$ excited state. The observed value of μ_{eff} per binuclear complex is 5.83 μ_B at 285.5 K, which indicates that there is already some depopulation of the $S = 3$ excited state at this temperature. Furthermore, the observed temperature dependence of μ_{eff} can be understood qualitatively. In the region of ca. 286–70 K, μ_{eff} gradually decreases with decreasing sample temperature due to further depopulation of the $S = 3$ state. There is a plateau in the μ_{eff} vs. temperature curve (i.e., region of less change in μ_{eff}) from temperatures of ca. 60–15 K. In this region most of the molecules are in the $S = 2$ ground state where the spin-only value of μ_{eff} is 4.90 μ_B per binuclear complex. Below ca. 15 K there is a more pronounced decrease in μ_{eff} with decreasing temperature, and this most likely reflects zero-field interactions associated with the Mn(II) ion.

The data for $LCuMnCl_2$ were initially fit to the susceptibility expression (eq 1) derived from a spin Hamiltonian which

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left[\frac{10\exp(-6J/kT) + 28}{5\exp(-6J/kT) + 7}\right] \qquad (1)$$

included only an isotropic magnetic exchange interaction, $H = -2J\hat{S}_1{\cdot}\hat{S}_2$. A least-squares fitting of the data to eq 1 gave $J = -30\ cm^{-1}$ and $g = 2.03$; however, the data below ca. 30 K could not be satisfactorily fit by this equation. A term for the single-ion zero-field interaction of the Mn(II) ion was added to give the Hamiltonian $\hat{H} = 2J\hat{S}_1{\cdot}\hat{S}_2 - D\hat{S}_{z1}^2$, where D is the axial zero-field splitting parameter for the Mn(II) ion. The derivation of the resulting susceptibility eq 2 is shown in Appendix A.[16] The parameters obtained from a least-

$$\chi_M = (Ng^2\beta^2/kT)[8\exp(A) + 8\exp(B) + 2\exp(C) + 8\exp(E) + 2\exp(F)]/[2\exp(A) + 2\exp(B) + 2\exp(C) + \exp(D) + 2\exp(E) + 2\exp(F) + \exp(G)] \qquad (2)$$

$$\begin{aligned}
A &= (12J + 25D/4)kT \\
B &= [9J + 17D/4 + (9J^2 - 8DJ + 4D^2)^{1/2}]/kT \\
C &= [9J + 5D/4 + (9J^2 - 2DJ + D^2)^{1/2}]/kT \\
D &= (12J + D/4)/kT \\
E &= [9J + 17D/4 - (9J^2 - 8DJ + 4D^2)^{1/2}]/kT \\
F &= [9J + 5D/4 - (9J^2 - 2DJ + D^2)^{1/2}]/kT \\
G &= (6J + D/4)/kT
\end{aligned}$$

squares fit of the $LCuMnCl_2$ data to eq 2 are $J = -30\ cm^{-1}$, $g = 2.10$, and $D = -0.63\ cm^{-1}$. This fit is shown as the solid lines in Figure 1.

The magnetic susceptibility data for $LCuFeCl_2{\cdot}2H_2O$ are illustrated in Figure 2. Were no exchange interaction present in a Cu^{II}–Fe^{II} binuclear complex, the spin-only μ_{eff} per binuclear complex would be 5.21 μ_B. At 285.5 K the observed value of μ_{eff} per binuclear complex is 4.25 μ_B. Again there is a gradual decrease in μ_{eff} with decreasing sample temperature which indicates the presence of an antiferromagnetic exchange interaction. It is evident that the interaction in $LCuFeCl_2{\cdot}2H_2O$ is greater than it is in $LCuMnCl_2$ because the μ_{eff} value is depressed below the noninteracting spin-only μ_{eff} value to a greater degree for $LCuFeCl_2{\cdot}2H_2O$ at 285.5 K than for $LCuMnCl_2$. The data for $LCuFeCl_2{\cdot}2H_2O$ also show a low-temperature drop in μ_{eff} which is attributable to zero-field interactions at the Fe(II) center.

An expression was derived for the molar paramagnetic susceptibility, χ_M, of a Cu^{II}–Fe^{II} binulear complex including axial single-ion zero-field splitting for the $S_1 = 2$ Fe(II) ion and an isotropic magnetic exchange interaction as indicated in Appendix B.[16] The expression for χ_M is given in eq 3.

$$\chi_M = (Ng^2\beta^2/4kT) \times [25\exp(A) + 9\exp(B) + \exp(C) + 9\exp(D) + \exp(E)]/[\exp(A) + \exp(B) + \exp(C) + \exp(D) + \exp(E)] \qquad (3)$$

---

(14) Chandler, J. P. Program 66, Quantum Chemistry Program Exchange; Indiana University: Bloomington, IN.

(15) Felthouse, T. R.; Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 1077.

(16) Supplementary material.

$$A = (35J/4 + 4D)/kT$$

$$B = [25J/4 + 5D/2 + (25J^2/4 - 9DJ/2 + 9D^2/4)^{1/2}]/kT$$

$$C = [25J/4 + D/2 + (25J^2/4 - DJ/2 + D^2/4)^{1/2}]/kT$$

$$D = [25J/4 + 5D/2 - (25J^2/4 - 9DJ/2 + 9D^2/4)^{1/2}]kT$$

$$E = [25J/4 + D/2 - (25J^2/4 - DJ/2 + D^2/4)^{1/2}]/kT$$

A least-squares fit of the data for $LCuFeCl_2{\cdot}2H_2O$ to eq 2 is illustrated in Figure 2. The parameters obtained are $J = -71$ cm^{-1}, $g = 2.01$, and $D = -1.14$ cm^{-1}.

The magnetic susceptibility data for $LCuNiCl_2{\cdot}2H_2O$ are illustrated in Figure 3. The effective magnetic moment per binuclear complex at 285.5 K ($\mu_{eff} = 2.66\ \mu_B$) is considerably less than the 3.34 μ_B spin-only value expected for a Cu^{II}–Ni^{II} complex with no exchange interaction present. In contrast to $LCuMnCl_2$ and $LCuFeCl_2{\cdot}2H_2O$, the μ_{eff} vs. temperature curve for $LCuNiCl_2{\cdot}2H_2O$ does not show a decrease below ca. 30 K. The single-ion zero-field interaction for the Ni(II) ion apparently is weak. The value of μ_{eff} at 4.2 K is 1.86 μ_B, which reflects the fact that all of the binuclear complexes are in the $S = {}^1/_2$ ground state. As an aside it is clear that the sample of $LCuNiCl_2{\cdot}2H_2O$ examined is not simply a mixture of the two homobinuclear complexes because both of these are essentially diamagnetic at 4.2 K. The data for $LCuNiCl_2{\cdot}2H_2O$ were least-squares fit to eq 4 which was derived from the

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left[\frac{{}^1/_2 \exp(-3J/kT) + 5}{2\exp(-3J/kT) + 4}\right] \qquad (4)$$

simple spin Hamiltonian $\hat{H} = -2J\hat{S}_1{\cdot}\hat{S}_2$. The fit gives $J = -103$ cm^{-1} and $g = 2.17$ and is illustrated in Figure 3.

It was of interest to obtain the EPR spectrum for $LCuNi{\cdot}2H_2O$ because Gatteschi and co-workers[17] recently reported the 4.2 K EPR spectrum measured for a single crystal of LCu_2Cl_2 doped with 1% nickel. At 4.2 K the host is diamagnetic. In addition to a monomeric Cu(II) signal, a signal was identified that they attributed to the $LCuNiCl_2$ species with $g_1 = 2.09$ ($A_{Cu} = 49 \times 10^{-4}$ cm^{-1}), $g_2 = 2.41$, and $g_3 = 2.49$.

Figure 4 illustrates some of the EPR data that we obtained for $LCuNiCl_2{\cdot}2H_2O$. The upper tracing was obtained for a powdered sample of the compound at liquid-nitrogen temperatures and X-band frequencies. An asymmetric derivative is seen which can be simulated with $g_\perp = 2.28$ and $g_\parallel = 2.15$. An asymmetric derivative is also seen at Q-band frequencies for a sample at liquid-nitrogen temperature. In another experiment a sample of $LCuNiCl_2{\cdot}2H_2O$ was quickly dissolved in a 2:1 mixture of ethylene glycol and water and then immediately frozen to form a good glass at liquid-nitrogen temperature. The lower tracing in Figure 4 illustrates the X-band sspectrum obtained for this glass. A $g_\perp$ signal is seen at $g = 2.25$ together with a $g_\parallel = 2.11$ signal split by four copper hyperfine lines ($A_{Cu} = 52 \times 10^{-4}$ cm^{-1}). It is difficult at this time to explain the difference in value between the $g_2 = 2.41$ and $g_3 = 2.49$ signals reported by Gatteschi and our $g_\perp = 2.25$ signal.

The magnetic susceptibility data for $LCuCoCl_2{\cdot}H_2O$ are illustrated in Figure 5. At 285.5 K, μ_{eff} is 4.10 μ_B per binuclear complex. A spin-only value of 4.26 μ_B would be expected with $g = 2.0$ when $J = 0$ for a binuclear complex of Cu(II) and high-spin Co(II). It is clear that there is an antiferromagnetic interaction present. There is a maximum in the χ_M vs. T curve for $LCuCoCl_2{\cdot}H_2O$ at 9.3 K. The attenuation of μ_{eff} as the sample temperature approaches 4.2 K is most pronounced for $LCuCoCl_2{\cdot}H_2O$, in keeping with the expectation that the Co(II) ion would exhibit the greatest zero-field splitting. At 4.2 K the observed μ_{eff} is 1.13 μ_B compared to the value of 2.87 μ_B expected for all of the molecules in the $S = 1$ state.

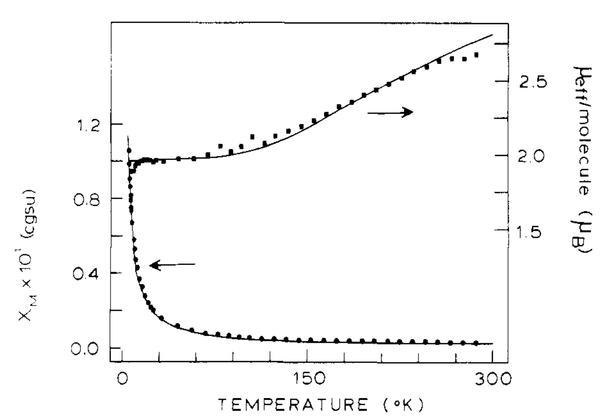


Figure 3. Molar paramagnetic susceptibility, χ_M, and effective magnetic moment per molecule, μ_{eff}, vs. temperature curves for $LCuNiCl_2{\cdot}2H_2O$. The solid lines represent the least-squares fit of the data to the theoretical equation given in the text.

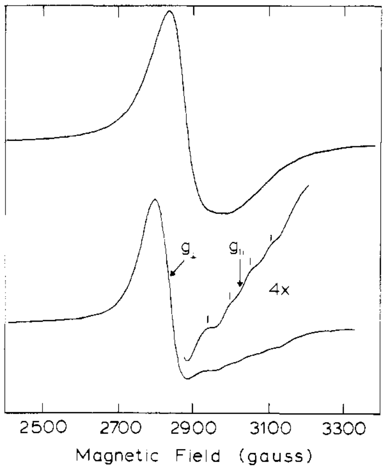


Figure 4. X-Band EPR data for $LCuNiCl_2{\cdot}2H_2O$. The upper tracing was obtained for a powdered sample of the compound at liquid-nitrogen temperature. The lower tracing was obtained from a 2:1 ethylene glycol and water glass at liquid-nitrogen temperature.

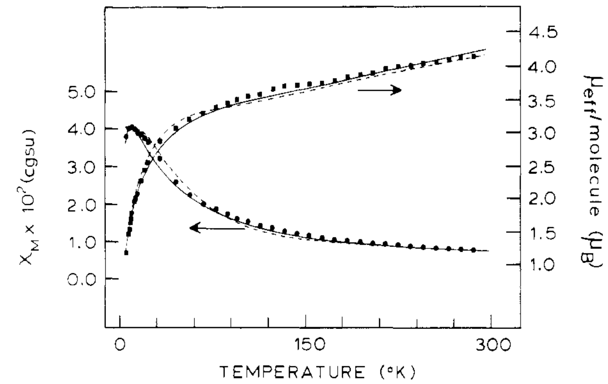


Figure 5. Molar paramagnetic susceptibility, χ_M, and effective magnetic moment per molecule, μ_{eff}, vs. temperature curves for $LCuCoCl_2{\cdot}H_2O$. The solid line represents the least-squares fit of the data to the equation derived from the spin Hamiltonian including zero-field effects. The dashed line represents the least-squares fit of the data to the equation derived from the real Hamiltonian including zero-field and spin–orbit effects.

---

[17] Banci, L.; Bencini, A.; Gatteschi, D.; Dei, A. *Inorg. Chim. Acta* **1979**, *36*, L419.

The data for $LCuCoCl_2{\cdot}H_2O$ were least-squares fit to eq 5 which can be derived (see Appendix C[16]) from the spin

$$\chi_M = (2Ng^2\beta^2/k(T-\Theta))[\exp(A) + 4\exp(C) + \exp(E)]/[2\exp(A) + \exp(B) + 2\exp(C) + \exp(D) + 2\exp(E)] \quad (5)$$

$$A = [4J + 5D/4 - (4J^2 - 2DJ + D^2)^{1/2}]/kT$$
$$B = (2J + D/4)/kT$$
$$C = (6J + 9D/4)/kT$$
$$D = (6J + D/4)/kT$$
$$E = 4J + 5D/4 + (4J^2 - 2DJ + D^2)^{1/2}]/kT$$

Hamiltonian $\hat{H} = -2J\hat{S}_1{\cdot}\hat{S}_2 - D\hat{S}_{z1}{}^2$. In contrast to the $LCuMnCl_2$ and $LCuFeCl_2{\cdot}2H_2O$ cases, it was necessary to include a Curie–Weiss parameter, Θ, in order to adequately fit the data for $LCuCoCl_2{\cdot}H_2O$. In fitting these data the parameters J and g were found to be highly correlated. With g values of 2.50, 2.60, 2.70, 2.80, and 2.90, J values of −63, −80, −100, −124, and −157 cm^{-1}, respectively, were obtained. The quality of the least-squares fit did not vary much in this range. The "best" fit in this range is found with $g = 2.80$ where $J = -124$ cm^{-1}, $D = -2.56$ cm^{-1}, and $\Theta = -27.8$ K. This fit is illustrated as the solid lines in Figure 5. The relatively large value of g for this Cu^{II}–Co^{II} complex is somewhat in keeping with average g values quoted for square-pyramidal Co(II) and Cu(II) complexes. In the case of Cu(II) complexes, $\bar{g}$ would be close to 2.1, whereas values of $\bar{g}$ for five-coordinate Co(II) complexes fall in the range of 3.6–3.8.[18-20]

The magnetic susceptibility data for $LCuCoCl_2{\cdot}H_2O$ were also least-squares fit to the Hamiltonian used by Kahn and co-workers[9] for the complex $CuCo(fsa)_2en{\cdot}3H_2O$, where $(fsa)_2en^{4-}$ is the bichelating ligand derived from the Schiff base *N*,*N'*-bis(2-hydroxy-3-carboxylbenzilidene)-1,2-diaminoethane. The form of this Hamiltonian is given in eq 6. As can be seen,

$$\hat{H} = D\hat{L}^2{}_{z(Co)} + {}^1\!/\!_2E[\hat{L}^2{}_{+(Co)} + \hat{L}^2{}_{-(Co)}] - {}^3\!/\!_2k\lambda\hat{L}_{Co}{\cdot}\hat{S}_{Co} - J\hat{S}_{Cu}{\cdot}S_{Co} + \beta[-{}^3\!/\!_2k\hat{L}_{\mu(Co)} + gS_\mu]H_\mu \qquad \mu = x, y, z \quad (6)$$

this Hamiltonian is not strictly a spin Hamiltonian for it explicitly takes into account the orbital angular momentum of the Co(II) ion. As detailed by Kahn et al., the above Hamiltonian matrix is numerically diagonalized with each setting of the parameters employing the $24|M_LSM_S\rangle$ functions as a basis set. We applied the same constraints that they used to avoid overparameterization. The rhombic zero-field splitting parameter E was assumed to be 0. The spin–orbit coupling constant, λ, was held constant at −160 cm^{-1}, which is somewhat less than the free-ion value of −170 cm^{-1}. The g value was held constant at 2.05 for reasons explained in ref 9. Least-squares fitting the data for $LCuCoCl_2{\cdot}H_2O$ with these constraints gave $J = -81$ cm^{-1}, $D = 1289$ cm^{-1}, and $k = -0.85$; this fitting is illustrated in Figure 5. It is not simply possible to compare the parameters obtained in this manner with those obtained above; however, it is interesting that the J values obtained in the two different approaches are of comparable magnitude.

Discussion

A major task in understanding magnetic exchange interactions is to sort out the various effects of molecular and electronic structure on coupling parameters. Our approach has been to control molecular structures to as great an extent as is possible and to vary simultaneously the electronic properties of the paramagnetic centers. We have accomplished this through the use of the symmetric binucleating ligand L^{2-}.

Table V. Exchange Parameters J (cm^{-1}) for Binuclear Complexes of $H_4(fsa)_2en$ and $H_4(fsa)_2pn$

	$H_4(fsa)_2en$[10]	$H_4(fsa)_2en$[8,21]	$H_4(fsa)_2pn$[10]
Cu^{II}–Cu^{II}	−330		−328
Cu^{II}–Ni^{II}	−75	−83.4	−34
Cu^{II}–Co^{II}	−35	−31	−36
Cu^{II}–Mn^{II}	−22	−32.5	−36

Initially we reported[5] the magnetic exchange parameters for the homobinuclear complexes LMn_2Cl_2, LFe_2Cl_2, LCo_2Cl_2, LNi_2Cl_2, and LCu_2Cl_2. A two-electron interval was accomplished while the square-pyramidal coordination geometries were held nearly constant in moving stepwise across this series. The trend observed is toward an increased net antiferromagnetic interaction across the transition series from manganese to copper.

We then reported[6] on the exchange interaction for a second series of homonuclear complexes of the same ligand, but where the metals were constrained to lie within the ligand plane, in contrast to the previous case where the metals were allowed to project from opposite sides of the ligand. In spite of the gross changes in molecular geometry, only small differences in coupling between the first homobinuclear series and the second homobinuclear series were observed. Our conclusion was that for these species molecular structure was less significant than electronic structure (i.e., number of unpaired electrons and the exchange pathways) in attenuating the exchange coupling parameter.

As a further check, the analogous heteronuclear series was explored; the data are reported herein. Again, large changes were observed in traversing this series, this time representing one-electron intervals. In addition, the monotonic trend toward increasing net antiferromagnetic interaction in moving from Mn to Cu was confirmed.

Other series of heterobinuclear complexes have been characterized by variable-temperature magnetic susceptibility. Though these systems lack the symmetry of that reported herein, they are useful for comparison to the symmetric systems studied in our laboratories. For example Okawa and co-workers[10] have prepared a large number of heterobinuclear complexes. Their binucleating ligands are generally prepared by condensing 2 mol of 3-formylsalicylic acid with 1 mol of a diamine. A square-planar N_2O_2 coordination site is provided for a Cu(II) ion while the second divalent metal ion interacts with four oxygen atoms of the binucleating ligand and two axially coordinated H_2O molecules. When the diamine used is ethylenediamine, the binucleating ligand is identified as $H_4(tsa)_2en$; with 1,3-propylenediamine it is called $H_4(tsa)_2pn$. Three heterobinuclear complexes [Cu^{II}–Ni^{II}, Cu^{II}–Co^{II}, and Cu^{II}–Mn^{II}] of both $H_4(fsa)_2en$ and $H_4(fsa)_2pn$ were studied with variable-temperature magnetic susceptibility. The J values that they obtained are listed in Table V. It can be seen that the same general trend that we observed is apparent in their data. The net antiferromagnetic interaction increases as the metal ion interacting with the N_2O_2/Cu^{II} ion varies in the order Mn(II), Co(II), Ni(II), and Cu(II). The one exception occurs in the case of CuCo(fsapn) where $J = -36$ cm^{-1}. However, it is important to note that Okawa and co-workers, unfortunately, only collected their susceptibility data down to 77 K. This leads to reduced accuracy in the determination of the smaller J values.

Kahn and co-workers[8,21] have singled out the $H_4(fsa)_2en$ series of heterobinuclear complexes for more detailed studies.

---

(18) Kennedy, F. S.; Hill, H. A. O.; Kaden, T. A.; Vallee, B. L. *Biochem. Biophys. Res. Commun.* **1972**, *48*, 1533.

(19) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1980**, *19*, 1301.

(20) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1979**, *18*, 2526.

(21) Tola, P.; Kahn, O.; Chauvel, C.; Coudanne, H. *Nouv. J. Chim.* **1979**, *1*, 467.

Variable-temperature magnetic susceptibility data for $CuNi(fsa)_2en$, $CuCo(fsa)_2en$, and $CuMn(fsa)_2en$ were collected from 300 to 5 K. The data for $CuNi(fsa)_2en{\cdot}3H_2O$ were fit to a susceptibility equation derived from a spin Hamiltonian which included only an isotropic magnetic exchange interaction. Least-squares fitting of the data yielded $J = -83.4$ cm^{-1} ($-2J\hat{S}_1{\cdot}\hat{S}_2$ form of Hamiltonian). The magnetic exchange interaction was determined in an analogous manner for $CuMn(fsa)_2en{\cdot}2H_2O$ yielding $J = -32.5$ cm^{-1}. Examination of Table V shows that the J values obtained by Kahn et al. for the Cu–Ni and Cu–Mn complexes of $H_4(fsa)_2en$ are appreciably different than those obtained by Okawa et al. The variable-temperature magnetic susceptibility data obtained by Kahn for $CuCo(fsa)_2en{\cdot}2H_2O$ were fit to eq 6 to give an exchange parameter of $J = -31$ cm^{-1}.

Kahn and co-workers[8,21] have also investigated a molecular orbital model to rationalize the exchange parameters observed for their heterobinuclear complexes. In their model the experimentally observed exchange parameter J is taken as the sum of a negative contribution, J_1, and a positive contribution, J_2, which arise from the one-electron and two-electron parts of the Hamiltonian operator, respectively. They found that the antiferromagnetic contribution J_1 is given by eq 7 where

$$J_1 = -(2/n_A n_B) \sum_{i=1}^{n_A(<n_B)} S_i(\Delta_i^2 - \delta_i^2)^{1/2} \qquad (7)$$

n_A and n_B are the number of unpaired electrons associated with the transition metal ions A and B, respectively. The parameter S_i is the overlap integral, $\langle \phi_{A_i} | \phi_{B_i} \rangle$, between the two unpaired-electron atomic orbitals, one on each of the two metal centers. The energy difference between the two basis atomic orbitals ϕ_{A_i} and ϕ_{B_i} is gauged by δ_i, whereas Δ_i is the energy difference between the resulting two molecular orbitals ϕ_{A_i} and ϕ_{B_i}. The ferromagnetic contribution (J_2) to the exchange parameter is determined by C_{ij} which is the two-electron exchange integral as given in eq 8 and 9.

$$J_2 = (2/n_A n_B) \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} C_{ij} \qquad (8)$$

$$C_{ij} = \langle \phi_{A_i}(1)\phi_{B_j}(2) | r_{12}^{-1} | \phi_{A_i}(2)\phi_{B_j}(1) \rangle \qquad (9)$$

In order to apply the above equations to explain the observed J values for the heterobinuclear complexes, Kahn and co-workers made three simplifying assumptions. First, the contribution from J_2 was assumed to be constant across the series and small compared to J_1. Second, it was assumed that the overlap and energy-difference parameters, S_{ij}, δ_{ij}, and Δ_{ij}, are constant across a series. Third, only the $\phi_A = \phi_B = d_{x^2-y^2}$ term was considered in the eq 7 for J_1. In this third case, thus, the one unpaired copper electron is located in a $d_{x^2-y^2}$ orbital and only the interactions with the unpaired electron located in a $d_{x^2-y^2}$ orbital on the second metal would be considered. Within the limits set by these assumptions the value of $-J$ varies as 5:2.5:1 in the series [Cu, Cu], [Cu, Ni], and [Cu, Mn], respectively. Experimentally, they found that $-J$ varies as 10.6:2.6:1 as the second copper ion is replaced by nickel and manganese, respectively. They concluded that in the absence of structural data it was not possible to explain quantitatively the deviations from the theoretical expectations. The bridgehead angle at the phenoxide oxygen, ∠Cu–O–M, could be changing as M is changed, for example.

The value of $-J$ varies as 9.8:3.4:1 in the $LCuMCl_2$ series studied in this work as M is varied in the series Cu(II), Ni(II), and Mn(II), respectively. The trends are similar to those found by Kahn and co-workers. It is our opinion that several factors contribute to make $-J$ vary across the series differently than is predicted by the simple theory. For example, the [Cu, Cu] complex probably exhibits a greater overlap (S_{ij}) of $d_{x^2-y^2}$ orbitals than is present in the [Cu, Ni] complex. It is likely that the Cu(II) ion is closer to being in the plane of the binucleating ligand. As pointed out by Kahn, it is also likely that δ_{ij} is smaller for the [Cu, Cu] complex than it is for the [Cu, Ni] complex. In comparing the J values for the [Cu, Cu] and [Cu, Ni] complexes, it would also be interesting to know what the contribution of the added unpaired d_{xy} nickel electron is to be the observed net interaction for the [Cu, Ni] complex.

Sinn and co-workers[9] recently reported X-ray structural and magnetic susceptibility data for a series of heterobinuclear complexes with the composition $Cu((prp)_2en)M(hfa)_2$, where M is Cu(II), Ni(II), Co(II), or Mn(II), $(prp)_2en$ is 2-hydroxypropiophenone imine and hfa is hexafluoroacetylacetonate. The $Cu((prp)_2en)$ units are square planar, and the two oxygen atoms of the N_2O_2 ligand coordination sphere also chelate the metal ion of the $M(hfa)_2$ unit. Thus the Cu(II) ion has a square-planar N_2O_2 coordination geometry, whereas the M metal ion coordination geometry is a distorted O_6 octahedron. Fitting the susceptibility vs. temperature data for these complexes gave J values of −13.2 (Mn), −16.3 (Co), −48.0 (Ni) and −44.8 cm^{-1} (M = Cu). Sinn and co-workers examined the structural features of this series of heterobinuclear complexes and concluded that the magnitude of the J value reflects the Cu–O–M angle. Furthermore, they concluded that since the difference in J values between various $Cu((prp)_2en)M(hfa)_2$ complexes could be entirely accounted for by changes in structural features, other factors such as the number of unpaired d electrons are unimportant or at least less important than structural factors.

In light of the extensive experimental data reported here and elsewhere[5,6,9,11,12,21] as well as theoretical calculations,[9,12,21] we feel that Sinn's conclusions should be reexamined.

Acknowledgment. We are grateful for support from NIH Grant No. HL13652 (to D.N.H.) and NSF Grant No. CHE79-27141 (to R.R.G.).

Registry No. $LCuMnCl_2$, 79329-66-1; $LCuFeCl_2$, 79329-67-2; $LCuCoCl_2$, 79329-68-3; $LCuNiCl_2$, 71722-81-1.

Supplementary Material Available: Tables I–IV (calculated and observed magnetic susceptibility data) and Appendixes A–C (derivations of susceptibility expressions) (17 pages). Ordering information is given on any current masthead page.