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Magnetic Exchange Interactions in Binuclear Transition-Metal Complexes. 20.[1] Variation in Magnetic Exchange Interaction for a Series of Metal(II) Complexes of a Binucleating Ligand

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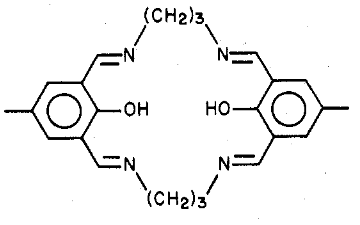
Received March 29, 1979

Variable-temperature magnetic susceptibility data, measured down to 4.2 K, are reported for Cu(II), Ni(II), Co(II), Fe(II), and Mn(II) complexes of the binucleating ligand formed from the condensation of 2 mol of 2,6-diformyl-4-methylphenol with 2 mol of 1,3-diaminopropane. A strong antiferromagnetic exchange is present in the binuclear Cu(II) complex and is characterized by $J = -294$ cm^{-1}, where the spin Hamiltonian is taken as $\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2$ for all the complexes. The net antiferromagnetic interaction decreases monotonically in the series Cu(II), Ni(II) ($J = -27$ cm^{-1}), Co(II) ($J = -9.3$ cm^{-1}), and Fe(II) ($J = -4.2$ cm^{-1}) and finally becomes a net ferromagnetic exchange interaction with the Mn(II) complex where $J = +0.2$ cm^{-1}. The variation in J value across the series is attributed to (1) the changing number of unpaired electrons and associated exchange pathways and (2) the increasing metal–ligand plane distance in going from Cu(II) to Mn(II).

Introduction

There is a growing interest in binuclear transition-metal complexes derived from binucleating ligands.[3,4] The impetus for the study of these complexes derives from three areas of interest. First, it is of interest to see whether the coupled (i.e., interacting) metal ions in such complexes exhibit chemical reactivities that are different from mononuclear complexes. Several metalloenzymes, such as cytochrome oxidase and nitrogenase, have coupled metal centers and catalyze important reactions under mild conditions. Second, it is important to ascertain whether complexes of binucleating ligands have electronic structural features that reflect the interaction between the metal ions. For example, the separation between successive one-electron redox waves in these complexes could be dependent on the interaction.[5] Third, metal complexes of binucleating ligands can provide interesting cases for the study of magnetic exchange interactions.

Pilkington and Robson[6] in 1970 reported the preparation and characterization of a series of transition-metal complexes with the binucleating ligand L. Divalent manganese, iron, cobalt, nickel, copper, and zinc have been complexed with this ligand to give complexes with the general composition of LM_2X_2, where M is the metal and X^- is a coordinated anion. Crystal structures have been reported for $LCo_2Br_2\cdot CH_3OH$[7] and $LCu_2Cl_2\cdot 6H_2O$.[8] In each case it was found that the metal ion coordination geometry is essentially[9] square pyramidal. The molecular structures of the two binuclear complexes can be schematically represented as follows:



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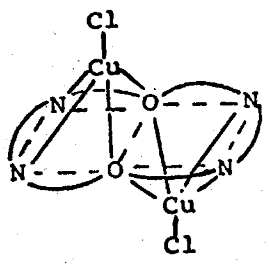

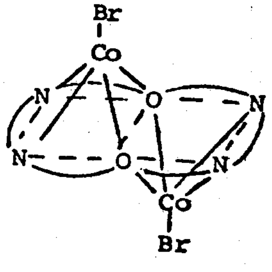

Variable-temperature magnetic susceptibility data were reported[6] in the temperature range of 100–300 K for the series of binuclear complexes. A strong antiferromagnetic exchange interaction was found for $LCu_2Cl_2\cdot 6H_2O$, whereas, in the range of 100–300 K only weak interactions were suggested for $LNi_2Cl_2\cdot 2H_2O$, $LCo_2Cl_2\cdot 2CH_3OH$, $LFe_2Cl_2\cdot 2CH_3OH$, and $LMn_2Cl_2\cdot 2H_2O$.

In this paper, we report the magnetic susceptibilities of the series of LM_2X_2 complexes measured from 285 to 4.2 K. A marked dependence of the nature of the magnetic exchange interaction upon the divalent metal ion is demonstrated.

Table I. Analytical Data

compd		% C	% H	% N	% metal
LMn_2Cl_2	obsd	49.30	4.61	9.59	18.95
	calcd	49.40	4.49	9.64	18.83
LFe_2Cl_2	obsd	49.08	4.35	9.84	18.85
	calcd	49.27	4.48	9.58	19.09
$LCo_2Br_2\cdot CH_3OH$	obsd	42.24	4.25	8.16	16.67
	calcd	42.14	4.24	7.90	16.54
$LNi_2Cl_2\cdot 2H_2O$	obsd	45.72	4.80	8.69	18.76
	calcd	45.97	4.82	8.97	18.72
$LCu_2Cl_2\cdot 6H_2O$	obsd	40.99	5.38	7.90	17.99
	calcd	40.67	5.40	7.94	17.93

Experimental Section

Compound Preparation. Samples of $LCu_2Cl_2\cdot 6H_2O$, $LNi_2Cl_2\cdot 2H_2O$, $LCo_2Br_2\cdot CH_3OH$, and LMn_2Cl_2 were prepared as reported previously.[6,10] As an added precaution, a second sample of LMn_2Cl_2 was prepared in Schlenk glassware with use of an argon atmosphere. Both of the manganese samples were found to give good analyses for the nonsolvated compound. Contrary to a suggestion in a previous paper,[6] we find that the iron compound LFe_2Cl_2 is oxygen sensitive in solution. Samples prepared without the careful exclusion of oxygen exhibited ^{57}Fe Mössbauer spectra with both Fe(II) and Fe(III) signals. The sample of LFe_2Cl_2 studied in this work was prepared with the rigorous exclusion of oxygen. A freshly prepared[11] sample of $FeCl_2\cdot 2H_2O$ was used as starting material. 1,3-Diaminopropane and 2,6-diformyl-4-methylphenol were distilled to remove any impurities. The reaction was carried out in a Schlenkware apparatus under purified argon gas. The product was removed from the apparatus in a Vacuum Atmospheres, Inc., inert-atmosphere glovebox and stored under argon. The solid did appear to be fairly air stable. Analytical data for all of the compounds were secured in the microanalytical laboratory at the University of Illinois and are collected together in Table I.

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. A correction for the diamagnetism of the sample container and the background was made at all temperatures. A diamagnetic correction, estimated from Pascal's constants, was used to calculate molar paramagnetic susceptibilities from the experimental susceptibilities. The resulting molar paramagnetic susceptibilities were

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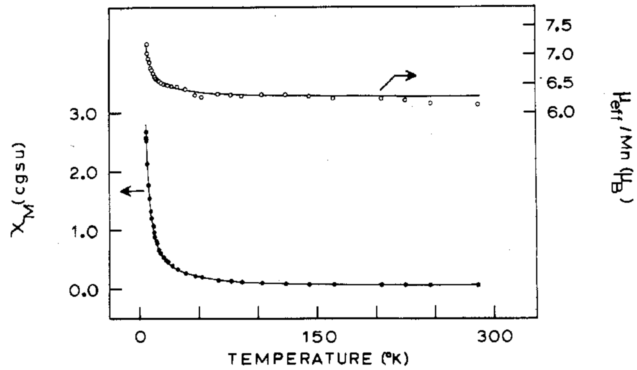

Figure 1. Molar paramagnetic susceptibility per binuclear complex and effective magnetic moment per Mn(II) ion vs. temperature for LMn_2Cl_2. The solid lines result from a least-squares fit to the theoretical equation for an isotropic exchange interaction.

fit to the appropriate theoretical expressions by means of a computer least-squares-fitting program.[12] ^{57}Mössbauer data were collected on a previously described spectrometer.[13]

Results and Discussion

Variable-temperature (4.2–285 K) magnetic susceptibility data were collected for the compounds LMn_2Cl_2, LFe_2Cl_2, $LCo_2Br_2{\cdot}CH_3OH$, $LNi_2Cl_2{\cdot}2H_2O$, and $LCu_2Cl_2{\cdot}6H_2O$. The data are given in Tables II–VI.[14]

The data for LMn_2Cl_2 are illustrated in Figure 1. A weak ferromagnetic exchange interaction is present in this binuclear manganese(II) complex. The effective magnetic moment per manganese(II) ion, μ_{eff}/Mn, increases appreciably as the temperature is decreased below ca. 50 K until a value of μ_{eff}/Mn = 7.07 μ_B is reached at 4.6 K.

For comparison purposes, we decided to fit the magnetic susceptibility data for this manganese(II) complex as well as the data for the other four binuclear complexes to the theoretical susceptibility equation that results from a consideration of only an isotropic exchange interaction with $\hat{H} = -2J\hat{S}_1{\cdot}\hat{S}_2$. The molar paramagnetic susceptibility for a binuclear complex with $S_1 = S_2 = S$ was given by Earnshaw et al.[15] as

$$\chi_M = (Ng^2\beta^2/3kT)\{\sum_{S'} S'(S'+1)(2S'+1)\Omega(S')\exp(-E_{S'}/kT)\}/\{\sum_{S'}(2S'+1)\Omega(S')\exp(-E_{S'}/kT)\}$$

In this expression, S' is the quantum number for a given coupled energy level of the binuclear complex and can take values of $2S$, $2S - 1$, $2S - 2$, ..., 0. The energy of the S' level is given as

$$E_{S'} = -J[S'(S'+1) - 2S(S+1)]$$

The quantity $\Omega(S')$ is the degeneracy of the given S' energy level.

The susceptibility data for LMn_2Cl_2 were least-squares fit to the appropriate form of the above χ_M expression to give the parameters $J = +0.2$ cm^{-1} and $g = 2.11$. The fit is reasonable in spite of the fact that no account was taken of possible single-ion zero-field interactions for an $S = {}^5/_2$ manganese ion. For the purposes of this paper it is totally adequate to use the above simple χ_M expression to calculate J values that can be compared in the series of binuclear complexes.

The χ_M and μ_{eff}/Fe data in Figure 2 are from a sample of LFe_2Cl_2 which was prepared under conditions where O_2 was meticulously excluded. An antiferromagnetic exchange interaction is present. Magnetic susceptibility vs. temperature data obtained for two other preparations of LFe_2Cl_2 which were not prepared under such careful conditions were quite similar with the exception that in the low-temperature region the susceptibility exhibited an increase after the maximum. Iron-57 Mössbauer spectra indicated the presence of high-spin ferric ions in these samples. As can be seen in Figure 2 for the case of the purest sample of LFe_2Cl_2, χ_M vs. temperature peaked at ca. 33 K with the μ_{eff}/Fe varying from 5.17 μ_B at 245 K to 1.01 μ_B at 4.2 K. These data were least-squares fit to the form of the above χ_M expression where $S_1 = S_2 = 2$ to give the parameters $J = -4.2$ cm^{-1} and $g = 2.27$. The fit is reasonable; the deviation in χ_M at low temperatures is most likely due to a small amount (less than ca. 1%) of ferric impurity. The ^{57}Fe Mössbauer spectrum of this sample at room temperature showed only an Fe(II) quadrupole-split doublet with $\Delta E_Q = 3.601$ mm/s and $\delta = 0.9408$ mm/s vs. iron metal.

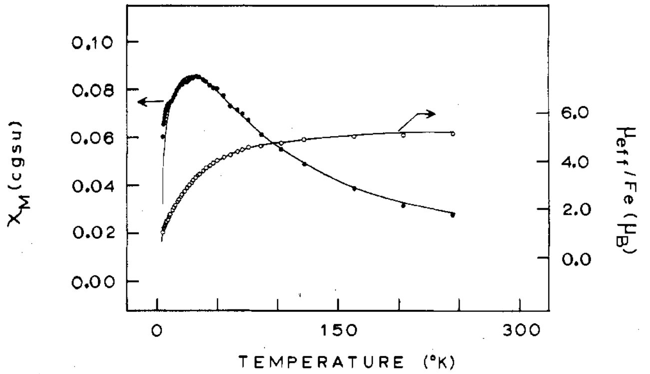

Figure 2. Molar paramagnetic susceptibility per binuclear complex and effective magnetic moment per Fe(II) ion vs. temperature for LFe_2Cl_2. The solid lines result from a least-squares fit to the theoretical equation for an isotropic exchange interaction.

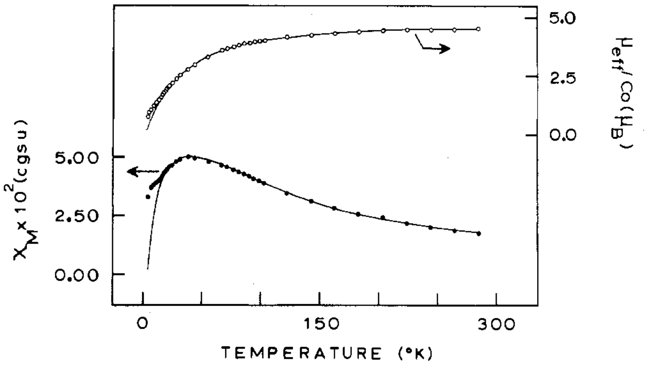

Figure 3. Molar paramagnetic susceptibility per binuclear complex and effective magnetic moment per Co(II) ion vs. temperature for $LCo_2Br_2{\cdot}CH_3OH$. The solid lines result from a least-squares fit to the theoretical equation for an isotropic exchange interaction.

The magnetic susceptibility vs. temperature data of $LCo_2Br_2{\cdot}CH_3OH$ are shown in Figure 3. These data fit to $J = -9.3$ cm^{-1} and $g = 2.49$, indicating an increased antiferromagnetic interaction in the $S_1 = S_2 = {}^3/_2$ binuclear cobalt(II) complex beyond that seen for the iron(II) complex. The slight increase in χ_M observed at low temperature relative to the theoretical fit in Figure 3 is most likely due to a small amount of a paramagnetic impurity.

The magnetic susceptibility data for $LNi_2Cl_2{\cdot}2H_2O$ are illustrated in Figure 4, where it is seen that there is a broad peak in the susceptibility vs. temperature curve in the range of 80–100 K. A second sample of $LNi_2Cl_2{\cdot}2H_2O$ was prepared to confirm the appearance of the susceptibility curve. This second sample was highly crystalline and gave susceptibility vs. temperature data that were essentially superimposable with the data given in Figure 4. Fitting of the data to the appropriate form of the above χ_M expression gave the parameters $J = -27$ cm^{-1} and $g = 2.19$. Ginsberg et al.[16] derived the equations for the susceptibility of a binuclear nickel(II) complex treating an isotropic magnetic exchange interaction as well as single-ion zero-field interactions $D\hat{S}_z^2$ and *inter*dimer

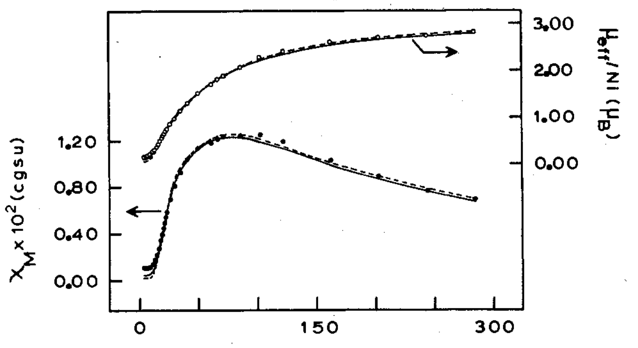

Figure 4. Molar paramagnetic susceptibility per binuclear complex and effective magnetic moment per Ni(II) ion vs. temperature for $LNi_2Cl_2 \cdot 2H_2O$. The solid and dashed lines result from least-squares fits to two different theoretical χ_M equations; see text.

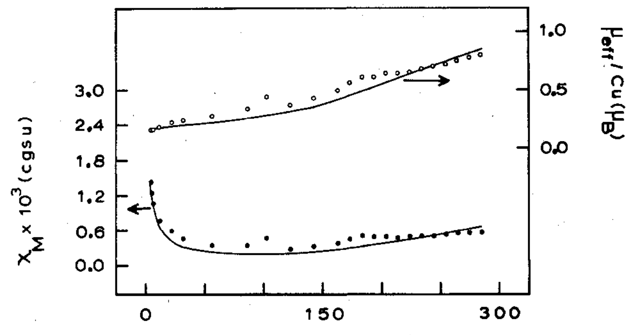

Figure 5. Molar paramagnetic susceptibility per binuclear complex and effective magnetic moment per Cu(II) ion vs. temperature for $LCu_2Cl_2 \cdot 4H_2O$. The solid lines result from a least-squares fit to the Bleaney–Bowers χ_M equation for a copper(II) dimer.

Table VII. Magnetic Susceptibility Parameters

	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
S	5/2	2	3/2	1	1/2
J, cm^{-1}	+0.20	−4.15	−9.33	−36.0	−294
$4JS^2$, cm^{-1}	+5.0	−66.4	−84.0	−144	−294
g (calcd)	2.11	2.27	2.49	2.15	2.06
ionic radius, Å	0.82	0.78	0.74	0.70	0.65

interactions with a parameter $Z'J'$. The data for $LNi_2Cl_2 \cdot 2H_2O$ were also least-squares fit to these equations to give $J = -36$ cm^{-1}, $g = 2.15$, $D = 23.6$ cm^{-1}, and $Z'J' = -0.54$ K. Both of the theoretical fits are illustrated in Figure 4 where it can be seen that the two theoretical fits are very similar.

Figure 5 shows the susceptibility and μ_{eff}/Cu vs. temperature data obtained for $LCu_2Cl_2 \cdot 4H_2O$. It is clear that there is a relatively strong antiferromagnetic exchange interaction present in this complex. This is what was found by Pilkington and Robson.[6] The susceptiblity data were least-squares fit to the appropriate form of the above χ_M expression (equivalent to the Bleaney–Bowers equation[17]) to give $J = -294$ cm^{-1} and $g = 2.057$.

Table VII summarizes the exchange parameters for the five binuclear complexes studied in this work. There is a trend toward decreasing antiferromagnetic exchange interaction on moving across the series from $LCu_2Cl_2 \cdot 4H_2O$ to LFe_2Cl_2 until with LMn_2Cl_2 there is a net ferromagnetic interaction. Glick and Lintvedt[18] have reported that for binuclear β-polyketonate complexes, the antiferromagnetic interaction observed for copper(II) complexes ($-J$ = 400–700 cm^{-1}) is considerably greater than that observed for a nickel(II) complex ($J = -25$ cm^{-1}). This is in keeping with the magnitude of change that is observed in going from $LCu_2Cl_2 \cdot 4H_2O$ to $Ni_2Cl_2 \cdot 2H_2O$. Very recently, Blake and Hatfield[19] reported the preparation of three linear-chain (assumed structures) compounds where the divalent metal ions in the chain are bridged by dimethylpyrazine ligands. They found that the exchange parameters did not vary much: $J = -0.2$ cm^{-1} for cobalt(II), $J = -0.4$ cm^{-1} for nickel(II), and $|J| < 0.1$ cm^{-1} for copper(II).

To compare the exchange interaction across the LM_2X_2 series one must account for the presence of different numbers of low-lying energy levels from one complex to another. Nesbet has shown[20] that $4JS^2$ is the quantity that should be compared from one metal to another. Values of $4JS^2$ are given in Table VII for the LM_2X_2 series, and it can be seen that there still is a monotonic change from Cu(II) to Mn(II). The low symmetry (C_s point group) about the metal ions leads to a situation where there is no degeneracy in the five d orbitals. All five binuclear complexes have high-spin divalent metal ions. Thus, starting with the Cu(II) complex with one unpaired electron per metal, the number of unpaired electrons per metal increases by one for each member in the series Cu(II), Ni(II), Co(II), Fe(II), and Mn(II). Because of the low symmetry of the ligand field, the electronic ground states of each of these metal ions would be orbitally nondegenerate. The question is, then: Why does the magnitude of antiferromagnetic exchange interaction decrease in going through the series from the Cu(II) complex to the Mn(II) complex?

The results of two previous studies can provide a guide for understanding the change in magnetic exchange interaction in the series LM_2X_2. An antiferromagnetic exchange interaction has been noted[21] for the series MnO, FeO, CoO, and NiO. The Nêel temperatures increase regularly from 116 to 523 K in going from MnO to NiO. Each of these compounds has a rock salt structure and the exchange interaction occurs through linear M–O–M units. According to Anderson's theory,[22] superexchange occurs because the metal d orbitals in which the unpaired spins reside overlap with filled s and p orbitals of the bridging diamagnetic ion. If the unpaired electron orbitals on the two metals interact via an overlap with orbitals of the bridge, then an antiferromagnetic interaction develops. If there is an orthogonality of two orbitals in a given selection of unpaired-electron metal orbitals and bridge orbitals, then a ferromagnteic interaction develops. Nesbet[23] has shown that the decreasing antiferromagnetic exchange interaction in the series NiO to MnO is interpretable in terms of a few simple ideas. The strongest antiferromagnetic interaction is due to a σ type of interaction between the metal e_g orbitals and σ orbitals of the oxide ion. This σ interaction should decrease from NiO to MnO because the M–O bond becomes less covalent on going from NiO to MnO. In addition, ferromagnetic interaction pathways are being introduced progressively from NiO to MnO and this would also lead to a reduced *net* antiferromagnetic interaction. There are two unpaired e_g electrons in NiO. Across the series, there is an addition of one more unpaired d-orbital electron per change in metal, until MnO is reached where there are two e_g and three t_{2g} electrons. Unpaired electrons in t_{2g} orbitals introduce ferromagnetic exchange pathways.

In more recent work, Hatfield and Hodgson[24] have studied the magnetic exchange interaction in a series of eight di-μ-hydroxo-bridged copper(II) complexes of the form $Cu_2B_2(OH)_2$, where B is a bidentate nitrogen ligand. Each copper(II) ion has a square-pyramidal coordination geometry, and in a given $Cu_2B_2(OH)_2$ complex the two coordination planes are coplanar. The results show that there is a linear relationship between the exchange parameter J and the Cu–O–Cu bridging angle. The bridging angles range from 95.6 to 104.1° and J varies between +86 to −254 cm^{-1}. For an angle greater than ca. 97.6° the interaction is antiferromagnetic, while angles less than 97.6° lead to a ferromagnetic interaction.

The marked decrease in antiferromagnetic exchange interaction across the LM_2X_2 series from $LCu_2Cl_2 \cdot 4H_2O$ to LMn_2Cl_2 is due then to several factors. For $LCu_2Cl_2 \cdot 4H_2O$, the X-ray structure[8] shows that the two Cu–O–Cu bridging angles are 104.5°. The two copper(II) ions are located 0.21 Å on opposite sides of the L ligand plane. The intramolecular Cu···Cu distance is 3.133 (1) Å and, therefore, any direct magnetic exchange interaction is negligible. Although the J vs. Cu–O–Cu angle correlation of Hatfield and Hodgson[24] is not strictly applicable, the 104.5° Cu–O–Cu angle in $LCu_2Cl_2 \cdot 4H_2O$ would be expected to lead to an antiferromagnetic interaction as observed. The fact that the Cu(II) ions in $LCu_2Cl_2 \cdot 4H_2O$ are somewhat displaced from the L ligand plane leads to some reduction in the effectiveness of this interaction, because the dominant exchange pathway consists of two $d_{x^2-y^2}$ orbitals, one on each copper(II) ion, interacting via the s and p orbitals of the oxide ion. The σ overlap will be reduced by moving the Cu(II) ion out of the plane.

In going from $LCu_2Cl_2 \cdot 4H_2O$ to $LNi_2Cl_2 \cdot 2H_2O$, the reduction in *net* antiferromagnetic exchange interaction results partially from the fact that the Ni(II) ion is displaced further from the L ligand plane than the Cu(II) ion. The $d_{x^2-y^2}$–(s,p)–$d_{x^2-y^2}$ overlap is reduced. The Ni–O interaction is also probably less covalent. In addition, for $LNi_2Cl_2 \cdot 2H_2O$, there are now two unpaired electrons per metal ion and the introduction of an unpaired electron in a d_{z^2} orbital would bring about ferromagnetic exchange pathways and reduce the *net* antiferromagnetic exchange interaction.

The X-ray structure[7] of $LCo_2Br_2 \cdot CH_3OH$ shows that the cobalt(II) ions are displaced 0.2985 (11) Å from the L ligand plane. This further displacement of the metal ion, together with the addition of more ferromagnetic exchange pathways due to additional unpaired electrons, leads to a further reduction in the *net* antiferromagnetic interaction. The process probably continues with LFe_2Cl_2, where the weakest antiferromagnetic interaction is found. And finally, an appreciable metal ion displacement coupled with a large number of ferromagnetic exchange pathways leads to a *net* ferromagnetic interaction for LMn_2Cl_2. A crystal structure is needed, of course, to ascertain the exact displacement of the manganese(II) ions in this complex; however, it is clear the relatively large ionic radius of the Mn^{2+} ion would necessitate its placement at the greatest distance from the L ligand plane in the series.

Acknowledgment. We are very grateful for support from National Institutes of Health Grant HL 13652 and for experimental assistance from Mr. Stephen L. Kessel.

Registry No. LMn_2Cl_2, 71184-06-0; LFe_2Cl_2, 47737-31-5; $LCo_2Br_2 \cdot CH_3OH$, 57913-33-4; $LNi_2Cl_2 \cdot 2H_2O$, 30893-96-0; $LCu_2Cl_2 \cdot 6H_2O$, 30893-92-6.

Supplementary Material Available: Tables II–VI giving observed and theoretically calculated magnetic susceptibility data (7 pages). Ordering information is given on any current masthead page.

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