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Magnetic Exchange Interactions in Binuclear Transition-Metal Complexes. 15. Copper(II) and Nickel(II) Complexes Bridged by Imidazolate, Benzimidazolate, Biimidazolate, and Bibenzimidazolate Ions[1]

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The preparation and characterization of 13 binuclear copper(II) complexes bridged by imidazolate (Im⁻), 2-methylimidazolate (2-MeIm⁻), benzimidazolate (BzIm⁻), biimidazolate (BiIm²⁻), and bibenzimidazolate (BiBzIm²⁻) are reported together with one binuclear nickel(II) complex bridged by BiIm²⁻. Antiferromagnetic exchange interactions are present in many of the copper compounds where the exchange parameter, J, varies from −49 cm⁻¹ to a value in the range ca. $0.02 < |J| <$ ca. 0.5 cm⁻¹. In the series $[Cu_2(tren)_2(bridge)]X_3$, where tren is 2,2′,2″-triaminotriethylamine, the strongest interaction is found when the bridge is 2-MeIm⁻ ($J = −49$ cm⁻¹, X = ClO₄⁻), followed by the Im⁻ complex ($J = $ ca. −38 cm⁻¹), then the BzIm⁻ complex ($J = −24$ cm⁻¹), with the weakest interaction seen for the BiIm²⁻-bridged compound ($|J| < $ ca. 0.5 cm⁻¹). Copper hyperfine structure in the EPR spectra of the last compound indicates that there is a magnetic exchange interaction present. The variation in magnitude of exchange parameters in the above series is explained in terms of differences in molecular orbitals of the bridge, angle of bonding of the bridge to the copper(II) ion, and in the case of the BiIm²⁻ complex a change in ground state. As expected, the compound $[Cu_2(phen)_4(Im)](ClO_4)_3 \cdot 3H_2O$ shows a weaker interaction ($J = −24$ cm⁻¹) compared to the analogous tren compound. The intermediate level of interaction ($J = −35$ cm⁻¹) in $[Cu_2(bpy)_4(Im)](PF_6)_3 \cdot H_2O$ was unexpected on the basis of previous work. Except for $[Cu_2(dpt)_2(BiIm)](BPh_4)_2 \cdot 2CH_3CN$ ($J = −1.9$ cm⁻¹), several complexes of the composition $[Cu_2(triamine)_2(L)](BPh_4)_2$, where L is either BiIm²⁻ or BiBzIm²⁻, did not exhibit any signs of an interaction in susceptibility data recorded to 4.2 K. The antiferromagnetic interaction in $[Ni_2(tren)_2(BiIm)](BPh_4)_2$ ($J = −2.9$ cm⁻¹) is weaker than that previously seen for the analogous oxalate compound.

Introduction

The interaction of imidazole and benzimidazole or their derivatives with transition-metal ions is believed to be important in determining the activity of many biologically important molecules and metalloproteins.[4] Very recently, interest in imidazolate (Im)-bridged transition-metal ions has increased due to the involvement of imidazolate ion as a bridging ligand between Cu(II) and Zn(II) ions in the enzyme superoxide dismutase (SOD).[5-8] X-ray crystallographic studies[5] have indicated that the Cu²⁺ and Zn²⁺ ions exist in distorted square-planar and tetrahedral coordination environments, respectively. In the case of the 4-Cu²⁺ SOD protein, it was also found that the two Cu²⁺ ions in each subunit are antiferromagnetically coupled with a singlet–triplet separation (2J) of approximately −52 cm⁻¹.[6]

Imidazolate ions are known to bridge metal ions in polymeric materials with the composition M(Im)₂.[4] Imidazolate bridges between Cu(II) ions are present in polymeric Cu(ImH)₂(Im)Cl[9] and in the semipolymeric material Cu₃(ImH)₈-(Im)₂(ClO₄)₄.[10] The first reported *nonpolymeric* complex with imidazolate bridging between Cu(II) ions is the tetramer [Cu₂(bpim)(Im)]₂(NO₃)₄·4H₂O[7] where bpim is 4,5-bis[2-(2-pyridyl)ethyliminomethyl]imidazolate. Very recently two imidazolate-bridged binuclear Cu(II) complexes have been characterized.[8] Magnetic susceptibility measurements for all three of these nonpolymeric Cu(II) complexes revealed that the Cu(II) ions are involved in antiferromagnetic exchange interactions propagated by the Im⁻ bridge.

Not only are there few complexes with benzimidazolate ion (BzIm⁻) as a bridging ligand but there are only a limited number of transition-metal complexes containing BzIm⁻ as a ligand.[4] No discrete dimers are known; however, the capability of BzIm⁻ to bridge two metal ions is indicated by the isolation of M(BzIm)₂ complexes where M = Co(II),[11] Pd(II),[12] and Cu(II).[4] The dianions of 2,2′-biimidazole (BiImH₂) and 2,2′-bibenzimidazole (BiBzImH₂) can function as bis-bidentate ligands, bridging between two transition-metal ions. Two papers have appeared recently that describe the preparation and X-ray crystallographic characterization of the first complexes incorporating BiIm²⁻ as a bridging ligand between

metal ions. The complexes are M₂(COD)₂(BiIm)[13] and M₄(CO)₈(BiIm)₂,[14] where M = Rh(I) and Ir(I) and COD is 1,5-cyclooctadiene. Even more recently, the compounds [(η⁵-C₅H₅)₂Ti]₂(BiIm) and [(η⁵-C₅H₅)₂Ti]₂(BiBzIm) have been reported.[15] The BiIm²⁻ and BiBzIm²⁻ ions bridge between two (cp)₂Ti^{III} (cp = η⁵-C₅H₅) moieties in these complexes; an antiferromagnetic exchange interaction between two d¹ ions is present in each molecule. The reaction of CuCl₂ with BiBzImH₂ in acetone has been reported to be complex, yielding a series of products that are thought to be polymeric.[16]

In this paper, we report the preparation and characterization with EPR and magnetic susceptibility of several binuclear Cu(II) complexes and one binuclear Ni(II) complex bridged by imidazolate and benzimidazolate and by the dianions biimidazolate and bibenzimidazolate.
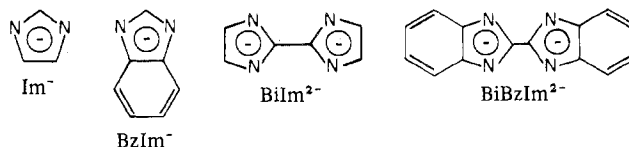
The complexes prepared are [Cu₂(tren)₂(L)]X₃, where tren is 2,2′,2″-triaminotriethylamine, L = Im⁻ or 2-MeIm⁻, and X = ClO₄⁻ or PF₆⁻; [Cu₂(tren)₂(BzIm)](ClO₄)₃; [Cu₂(phen)₄(Im)](ClO₄)₃·3H₂O, where phen is 1,10-phenanthroline; [Cu₂(bpy)₄(Im)](PF₆)₃·H₂O, where bpy is 2,2′-bipyridine; [M₂(tren)₂L](BPh₄)₂, where M = Cu(II) or Ni(II) and L = BiIm²⁻; [Cu₂("dien")₂L](BPh₄)₂ where "dien" is variously dien (diethylenetriamine), dpt (dipropylenetriamine), or Me₅dien (1,1,4,7,7-pentamethyldiethylenetriamine) and L is BiIm²⁻ or BiBzIm²⁻. The complexes provide several new simple binuclear Cu(II) complexes with imidazolate-like bridging units. It is of interest to see how dependent on the Cu(II) ion coordination geometry the exchange interaction between two imidazolate-bridged Cu(II) ions is. In previous work from these laboratories the magnitude of a magnetic exchange interaction between two Cu(II) ions was found to depend on the orbital ground state of the Cu(II) ions.[17] For example, complexes of the type [Cu₂("dien")₂(C₂O₄)]X₂[18] and [Cu₂("dien")₂(N₃)₂]X₂,[19] where the oxalate dianion or two

azide anions bridge between two Cu(II) ions, did show such a dependence.

Experimental Section

Compound Preparation. Diethylenetriamine (Union Carbide), dipropylenetriamine (Aldrich), 2,2',2''-triaminotriethylamine (Aldrich), 1,1,4,7,7-pentamethyldiethylenetriamine (Ames Laboratories), 1,10-phenanthroline (J. T. Baker), and 2,2'-bipyridine (Aldrich) were used as received. Biimidazole was prepared according to a literature procedure[20] and bibenzimidazole was prepared according to a modified literature procedure.[15] Imidazole (Aldrich), 2-methylimidazole (Aldrich), and benzimidazole (Aldrich) were used as purchased. Benzimidazole was recrystallized from hot water. Elemental analyses were performed by the microanalytical laboratory of the School of Chemical Sciences, University of Illinois. The analytical data are compiled in Table I.[21]

Samples of [Cu$_2$(tren)$_2$(Im)](X)$_3$, where X = ClO$_4^-$ and PF$_6^-$, were prepared by the following procedure. To an aqueous solution (20 mL) of ca. 1.0 g (4 mmol) of CuSO$_4$·5H$_2$O was added ca. 0.6 mL of tren followed by ca. 0.14 g (2 mmol) of imidazole and NaOH in slight excess. The mixture was filtered and an aqueous solution (8 mL) of NaClO$_4$ or [Et$_4$N]PF$_6$ was added yielding blue solids. Stoichiometric amounts or excess (up to eightfold) of the counterion salt led to precipitation. Preparation 1 of [Cu$_2$(tren)$_2$(Im)](PF$_6$)$_3$ is a sample obtained by precipitation with [Et$_4$N]PF$_6$. However, two observations have to be noted. First, if NH$_4$PF$_6$ is used instead of [Et$_4$N]PF$_6$, formation of the monomeric copper compound results if a stoichiometric amount of NaOH is used, whereas the dimer forms if excess NaOH (twofold) is used. In the latter case, the material has to be recrystallized from water. Preparation 2 of [Cu$_2$(tren)$_2$-(Im)](PF$_6$) is such a recrystallized sample. Second, in the precipitation with NaClO$_4$, excess NaClO$_4$ results in the formation of crystalline [Cu$_2$(tren)$_2$(Im)](ClO$_4$)$_3$·xNaClO$_4$ where the value of x depends upon the amount of NaClO$_4$ used. In this case, recrystallization from water yields the desired product. Hydroxide-bridged species are not formed (vide infra).

[Cu$_2$(tren)$_2$(BzIm)](ClO$_4$)$_3$. Preparation 1 of this compound was obtained as in the case of [Cu$_2$(tren)$_2$(Im)](ClO$_4$)$_3$, except that triethylamine (2 mL) was used as the base. Addition of an aqueous solution of NaClO$_4$ gave a blue powder. Unrecrystallized benzimidazole reagent was used in this preparation. Preparation 2 of this compound was obtained by taking some of the above blue powder and dissolving it in 75 mL of H$_2$O which was warmed. Filtration of the resulting solution and rapid evaporation of the filtrate in a hood gave a dark blue crystalline sample of [Cu$_2$(tren)$_2$(BzIm)](ClO$_4$)$_3$. In attempting to prepare another sample of this dark blue crystalline material, a turquoise crystalline sample was obtained, and this is identified as preparation 3 of this same compound. Most likely, the three preparations only differ in the relative amounts of a small percentage of a monomeric impurity (vide infra).

The crystalline complex **[Cu$_2$(tren)$_2$(Im)](BPh$_4$)$_2$(ClO$_4$)** was made by metathesis of [Cu$_2$(tren)$_2$(Im)](ClO$_4$)$_3$·1.5NaClO$_4$ in water with NaBPh$_4$. Alternatively, metathesis of [Cu$_2$(tren)$_2$(Im)](ClO$_4$)$_3$ in MeOH–H$_2$O (4:1) yields the same light blue product.

The preparation of **[Cu$_2$(tren)$_2$(2-MeIm)](ClO$_4$)$_3$·H$_2$O**, where 2-MeIm is the monoanion of 2-methylimidazole, was accomplished in a similar fashion to [Cu$_2$(tren)$_2$(Im)](ClO$_4$)$_3$ except that the reaction was run in a MeOH–H$_2$O (1:1) solution. The mixture was refluxed for 1 h followed by filtration and then addition of an aqueous solution of NaClO$_4$. The blue solid that precipitated was recrystallized from water.

Preparation 1 of **[Cu$_2$(tren)$_2$(2-MeIm)](PF$_6$)$_3$** was obtained by dissolving 2.0 g (8 mmol) of CuSO$_4$·5H$_2$O in a 1:2 MeOH–H$_2$O solution (75 mL) to which was added 1.2 mL of tren. The solution was heated to boiling and then filtered. A solution of ca. 0.2 g (4 mmol) of 2-methylimidazole in 20 mL of MeOH and 2 mL of Et$_3$N was added. The resulting solution was filtered twice and continually heated. A hot solution of 3.0 g of KPF$_6$ in 20 mL of H$_2$O was added and, as the solution was stirred while still hot, a very fine precipitate of [Cu$_2$(tren)$_2$(2-MeIm)](PF$_6$)$_3$ separated. The filtrate also gave more product as it was cooled in the refrigerator. Preparation 2 of this compound was obtained from two recrystallizations of a sample prepared as above. The recrystallizations were carried out from a hot solution of 1:1 CH$_3$OH–H$_2$O (40 mL) with ca. 2 mL of Et$_3$N added.

The compound **[Cu$_2$(phen)$_4$(Im)](ClO$_4$)$_3$·3H$_2$O** was prepared by the following procedure. To an aqueous solution (60 mL) of ca. 0.50 g (2 mmol) of CuSO$_4$·5H$_2$O was added ca. 4 mmol of phen·H$_2$O. Stirring the mixture results in the formation of a precipitate that disappears upon adding a small volume of an aqueous solution of stoichiometric amounts of imidazole and NaOH. The solution is then filtered followed by addition of an aqueous solution of NaClO$_4$. Rapid addition of the NaClO$_4$ solution gave a light blue powder (preparation 1), while dropwise slow addition of the NaClO$_4$ solution gave a dark blue-green material (preparation 2). Both samples analyzed as [Cu$_2$(phen)$_4$(Im)](ClO$_4$)$_3$·3H$_2$O.

The compound **[Cu$_2$(bpy)$_4$(Im)](PF$_6$)$_3$·H$_2$O** was prepared by adding 0.09 g (1.3 mmol) of imidazole and 0.16 g (2.9 mmol) of KOH to a light blue aqueous solution (150 mL) of 0.50 g (2.0 mmol) of CuSO$_4$·5H$_2$O and 0.64 g (4.0 mmol) of 2,2'-bipyridine. The deep blue solution that results is filtered and an aqueous solution (10 mL) of 0.38 g (2.3 mmol) of NH$_4$PF$_6$ is added to precipitate the compound as a dark blue-green powder. Reproducibility of the compound preparation is a sensitive function of the amount of KOH used. The above quantities of reactants were selected to effect reproducibility. In some instances, the compound precipitates as a dihydrate.

Preparation of the **[Cu$_2$("dien")$_2$(L)](BPh$_4$)$_2$** complexes, where "dien" = dien, Me$_5$dien, and dpt and L = BiIm^{2-} and BiBzIm^{2-}, was accomplished by the following general procedure. To an anhydrous methanol solution (300 mL) of ca. 0.50 g (2 mmol) of CuSO$_4$·5H$_2$O was added ca. 2 mmol of "dien" followed by ca. 1 mmol of L and NaOCH$_3$ (fourfold excess). Both L and NaOCH$_3$ were added as solids. The mixture was then stirred and boiled until most of L disappeared. Prolonged boiling could result in the formation of polymers. The solution was then filtered and a methanol solution of ca. 0.5 g of NaBPh$_4$ was added. Precipitation of [Cu$_2$(dien)$_2$-(BiIm)](BPh$_4$)$_2$ as a light lavender microcrystalline solid occurred only when the methanol solution was added to an equal volume of water. The complex [Cu$_2$(dien)$_2$(BiBzIm)](BPh$_4$)$_2$ precipitated in methanol as a lead gray microcrystalline solid. Stirring the solid in ethyl alcohol removes a yellow impurity which is probably unreacted bibenzimidazole. To get pure and microcrystalline solids of [Cu$_2$-(Me$_5$dien)$_2$(BiIm)](BPh$_4$)$_2$ and [Cu$_2$(Me$_5$dien)$_2$(BiBzIm)](BPh$_4$)$_2$ addition of 40 mL of acetonitrile to the methanol solution just before adding the methanol solution of NaBPh$_4$ proved very important; otherwise the product would form as a light lavender powder that is contaminated with polymers. Recrystallization of the powders from CH$_3$CN yields good quality crystals of [Cu$_2$(Me$_5$dien)$_2$(BiIm)](BPh$_4$)$_2$ and [Cu$_2$(Me$_5$dien)$_2$(BiBzIm)](BPh$_4$)$_2$·CH$_3$CN. In the case of [Cu$_2$(dpt)$_2$(BiIm)](BPh$_4$)$_2$ it was not possible to obtain pure material even with the use of CH$_3$CN as described previously. Slow evaporation of an acetonitrile solution of the crude product results in the formation of [Cu$_2$(dpt)$_2$(BiIm)](BPh$_4$)$_2$·2CH$_3$CN. Two samples (preparations 1 and 2) were prepared in the same manner.

Samples of **[M$_2$(tren)$_2$(BiIm)](BPh$_4$)$_2$**, where M = Cu(II) and Ni(II), were prepared in a method analogous to that used for the [Cu$_2$("dien")$_2$(L)](BPh$_4$)$_2$ compounds described above. CuSO$_4$·5H$_2$O and NiSO$_4$·6H$_2$O were used as starting materials. The [Ni$_2$-(tren)$_2$(BiIm)](BPh$_4$)$_2$ precipitated in methanol as light purple microcrystals. On the other hand, [Cu$_2$(tren)$_2$(BiIm)](BPh$_4$)$_2$ was obtained as blue-lavender microcrystalline material only when the 350-mL methanol solution containing NaBPh$_4$ was added to 1 L of water. With time, the color changed to blue-green due to the incorporation of 1 mol of water/mol of dimer. In all cases the solid product was collected, washed with ether, and dried in a vacuum desiccator over P$_4$O$_{10}$.

Physical Measurements. Variable-temperature (4.2–286 K) magnetic susceptibilities were measured with a Princeton Applied Research Model 150A vibrating-sample magnetometer operating at 12.7 G and calibrated as described in a previous paper.[1] All data were corrected for diamagnetism[22,23] and TIP (taken as 120 × 10^{-6} cgsu per Cu(II) dimer and 200 × 10^{-6} cgsu per Ni(II) dimer). Least-squares fitting of the magnetic susceptibilities to the Bleaney–Bowers equation[24] ($\hat{H} = 2J\vec{S}_1\cdot\vec{S}_2$) for Cu(II) dimers and to the equations given by Ginsberg[25] for Ni(II) dimers was performed with a new version of the minimization computer program STEPT.[26]

EPR spectra of powder samples were recorded with a Varian E-9 X-band spectrometer and a Varian E-15 Q-band spectrometer operating at 9.1–9.5 and 35 GHz, respectively. The X-band frequency was determined using a Hewlett-Packard Model 5240A 12.4-GHz digital frequency meter while the Q-band frequency was calibrated

with DPPH ($g = 2.0036$). X-band spectra were recorded at ~300 and ~80 K. Q-band spectra were taken at ~300 and ~110 K.

The MO calculations were performed using the CNDO/2 method.[27] The sources of the molecular dimensions used in the Im⁻ and BzIm⁻ calculations are mentioned in the Exchange Mechanism section of the Results and Discussion.

Results and Discussion

Compound Preparation and Formulation. In this work it was found to be relatively easy to prepare binuclear copper(II) complexes bridged by the monoanion of imidazole as well as binuclear copper(II) and nickel(II) complexes bridged by the dianion of biimidazole. The imidazolate-bridged compounds can be precipitated with various counterions from aqueous solutions of copper(II) complexes and imidazole if the appropriate amount of base is added. Many of the compounds could be recrystallized from water; hydroxide was added to keep the imidazole in the deprotonated form in solution. Several of the compounds prepared in this study were reproducibly obtained in a crystalline form, e.g., $[Cu_2(tren)_2(Im)](PF_6)_3$, $[Cu_2(tren)_2(Im)](BPh_4)_2ClO_4$, $[Cu_2(bpy)_4(Im)](PF_6)_3 \cdot 2H_2O$, $[Cu_2(Me_5dien)_2(BiIm)](BPh_4)_2$, $[Cu_2(dien)_2(BiIm)](BPh_4)_2$, $[Cu_2(dien)_2(BiBzIm)](BPh_4)_2$, and $[M_2(tren)_2(BiIm)](BPh_4)_2$ where M = Cu(II) or Ni(II). The crystallinity of these compounds provides the best assurance of their purity.

Before the physical data are presented for the compounds in this study, there are two questions that should be addressed. Since several of the compounds were prepared from a basic aqueous media, it is possible that the compounds contain hydroxide ions, perhaps even functioning as bridging anions. The second question relates to whether the compounds contain binuclear complexes or are polymeric in structure.

Evidence indicating that there are *not* hydroxide ion bridges present in these compounds has been obtained for some of the compounds. It is possible that the compound we formulate as $[Cu_2(tren)_2(Im)](PF_6)_3$ is, in fact, $[Cu_2(tren)_2(OH)]$-$(PF_6)_3(ImH)$. As will be shown, the compound does exhibit susceptibility data characteristic of the presence of an antiferromagnetic exchange interaction (μ_{eff}/Cu = 1.66 μ_B at 244.6 K and T_N =71.5 K) and, as such, there is some bridging species between the copper(II) ions. In the second formulation, this bridging function is filled by a single hydroxide ion and the imidazole is not deprotonated. Analytical data would not easily differentiate between the two formulations. In separate experiments,[28] we have prepared authentic samples of $[Cu_2(tren)_2(OH)]X_3$, where X is either PF_6^- or ClO_4^-. Both of these compounds exhibit quite strong antiferromagnetic interactions, where, for example, the μ-hydroxo-bridged PF_6^- compound has μ_{eff}/Cu = 0.77 μ_B at 270 K. It is clear, then, that such a hydroxide-bridged copper(II) species is not present in the present Cu–tren compounds.

A strong case can also be made for the fact that, in many of the compounds in this study, the cations are binuclear and there is not some type of polymeric structure present. It is highly probable that the bis-bidentate BiIm²⁻ and BiBzIm²⁻ bridges would afford binuclear complexes based on our previous work.[15,29] Several of these complexes, notably $[Cu_2(tren)_2(BiIm)](BPh_4)_2$ and $[Cu_2(dien)_2(BiIm)](BPh_4)_2$, show copper hyperfine structure (vide infra) that is *only* explicable in terms of the presence of a binuclear cation.

The presence of a binuclear cation in the $[Cu_2(tren)_2Y]X_3$ compounds, where Y is Im⁻, 2-MeIm⁻, or BzIm⁻ and X is a counterion such as ClO_4^-, PF_6^-, or a combination of ClO_4^- and BPh_4^-, can also be argued. The tren ligand enforces a trigonal-bipyramidal geometry on the copper(II) ion as has been found in all previous structures involving the Cu(tren)²⁺ unit.[30-33] The EPR spectra (vide infra) of these compounds do, in fact, establish that (distorted) trigonal-bipyramidal

copper(II) coordination geometries are found in the $[Cu_2$-$(tren)_2Y]X_3$ compounds. With such a coordination geometry only one axial coordination site is available for the bridging species. Under these circumstances it is hard to imagine how a polymeric association would result with an Im⁻ bridge. In other words, the tripodal nature of the tren ligand prevents the formation of a polymeric association.

Only two compounds in this paper, $[Cu_2(bpy)_4(Im)]$-$(PF_6)_3 \cdot 2H_2O$ and $[Cu_2(phen)_4(Im)](ClO_4)_3 \cdot 3H_2O$, present very much problem in terms of their molecular structure in the solid state. The appearance of the maxima in susceptibility vs. temperature curves (vide infra) for these two compounds suggest that the cations are binuclear; i.e., the maxima are relatively sharp compared with the broader maxima seen for polymeric compounds. Well-formed crystals of the bpy compound have been obtained and a single-crystal X-ray diffraction study is in progress.[34]

X-ray diffraction data have also been collected for $[Cu_2$-$(tren)_2(Im)](PF_6)_3$. At first, the precession photography for this compound was analyzed to indicate the tetragonal space group of $P4_22_12$, and reflection data were collected. No solution could be found with this data set using either heavy-atom or direct methods. The precession photographs were reanalyzed and it was decided that the system was orthorhombic with a space group of $C222$.[35] Apparently, there is a pseudotetragonal symmetry present in the system. Work continues on the solution to the structure of this compound, but it does appear that there is a possibility of disorder in the system.

Magnetic Susceptibility. Variable-temperature magnetic susceptibility data were collected for 12 of the 13 copper(II) complexes prepared in this study and also for $[Ni_2(tren)_2$-$(BiIm)](BPh_4)_2$. In many cases, data were collected for several preparations of the same compound. The data are given in Tables II–XVI.[21] Four of the copper(II) compounds did not show any signs of a magnetic exchange in the susceptibility data taken down to ca. 4.2 K and these four compounds are $[Cu_2(tren)_2(BiIm)](BPh_4)_2$, $[Cu_2(Me_5dien)_2(BiIm)](BPh_4)_2$, $[Cu_2(dien)_2(BiIm)](BPh_4)_2$, and $[Cu_2(dien)_2(BiBzIm)]$-$(BPh_4)_2$. Data were not collected for $[Cu_2(Me_5dien)_2$-$(BiBzIm)](BPh_4)_2$.

The susceptibility data for the eight copper(II) compounds that did show antiferromagnetic interactions were least-squares fit to the Bleaney–Bowers equation[24] for isotropic exchange in a copper(II) dimer (eq 1). In this equation for the corrected

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left\{\frac{2}{3 + \exp(-2J/kT)}\right\} + N\alpha + PAR\left(\frac{4.2}{T}\right)$$

(1)

molar paramagnetism (χ_M) of an exchange interacting dimer, the symbols have their usual meaning. The temperature-independent paramagnetism, $N\alpha$, for a copper(II) dimer was taken as 120×10^{-6} cgsu/mol of dimer. The third term (PAR) in eq 1 was added to account for the presence of the small amount (~1-3%) of a paramagnetic (monomeric) impurity which is found in some samples of binuclear copper(II) complexes. There are potentially, then, three parameters in eq 1, the exchange parameter J, the g factor, and PAR, the paramagnetism of the impurity at 42 K. For each interacting copper(II) dimer, two different approaches were tried in fitting the data. In both approaches, the value of PAR was held fixed at the susceptibility value found at 4.2 K. On the one hand, g was held fixed at a value appropriate for the high-temperature data and J was varied as the only parameter. On the other hand, both g and J were varied to get the best least-squares fit of the data. In the case of $[Cu_2(dpt)_2$-$(BiIm)](BPh_4)_2 \cdot 2CH_3CN$ PAR was fixed at zero while all other parameters were varied.
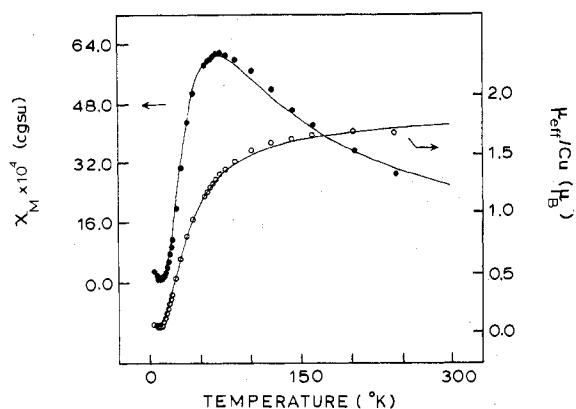
Figure 1. Molar paramagnetic susceptibility (χ_M in cgsu per dimer) and effective magnetic moment per copper ion (μ_{eff}/Cu(II) in μ_B) of [Cu$_2$(tren)$_2$(Im)](PF$_6$)$_3$ plotted as a function of temperature. The experimental data are represented as circles and the lines result from a least-squares fit to eq 1.
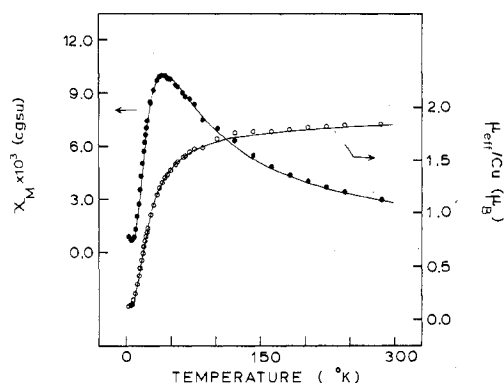

Figure 2. Molar paramagnetic susceptibility (χ_M in cgsu per dimer) and effective magnetic moment per copper ion (μ_{eff}/Cu(II) in μ_B) of [Cu$_2$(tren)$_2$(BzIm)](ClO$_4$)$_3$ plotted as a function of temperature. The experimental data are represented as circles and the lines result from a least-squares fit to eq 1.

The corrected molar magnetic susceptibility vs. temperature curves for [Cu$_2$(tren)$_2$(Im)](PF$_6$)$_3$, [Cu$_2$(tren)$_2$(Im)]-(BPh$_4$)$_2$(ClO$_4$), and [Cu$_2$(tren)$_2$(Im)](ClO$_4$)$_3$ are indicative of antiferromagnetic exchange interactions with susceptibility maxima at 71.5 K. Figure 1 illustrates the data obtained for preparation **2** of the PF$_6^-$ compound. The second approach for fitting the data gave an excellent fit. The solid lines in Figure 1 result from a fit where both g and J are varied to the final values of J = −38 cm^{-1} and g = 2.072. PAR was fixed at 0.00015 cgsu. Preparation **1** of this PF$_6^-$ compound gave similar data, only the susceptibility did not drop to as low a value at 4.2 K, a fact that is characteristic of the presence of a greater amount of monomeric impurities. Interestingly, the least-squares fitting of the data for preparation **1** gave an identical J = −38 cm^{-1}, but a slightly different g value of 2.119. Table XVII gives the least-squares fitting parameters for the two other [Cu$_2$(tren)$_2$(Im)]$^{3+}$ compounds, and it can be seen that the J values for these three compounds are quite close. This is clear evidence for the fact that the counterions are not part of the exchange pathway.

The susceptibility data for preparation **3** of the compound [Cu$_2$(tren)$_2$(BzIm)](ClO$_4$)$_3$, as illustrated in Figure 2, were least-squares fit by varying g and J to give the final values of J = −24 cm^{-1} and g = 2.134. PAR was fixed at 0.0008 cgsu. This fit is represented by the solid lines in Figure 2. The g value obtained in the fitting is in excellent agreement with the g value of 2.127 obtained from the EPR spectrum (vide infra) for [Cu$_2$(tren)$_2$(BzIm)](ClO$_4$)$_3$. Table XVII gives the

Table XVII. Magnetic Exchange Least-Squares Fitting Parameters

compd	J, cm^{-1}	g
[Cu$_2$(tren)$_2$(Im)](PF$_6$)$_3$		
prepn 1	−38	2.119
prepn 2^f	−38	2.072
[Cu$_2$(tren)$_2$(Im)](ClO$_4$)$_3$	−38	2.107
[Cu$_2$(tren)$_2$(Im)](BPh$_4$)$_2$(ClO$_4$)	−40	2.050^a
[Cu$_2$(tren)$_2$(BzIm)](ClO$_4$)$_3$		
prepn 1	−21	2.091
prepn 2	−22	2.134
prepn 3^g	−24	2.134
[Cu$_2$(tren)$_2$(2-MeIm)](PF$_6$)$_3$		
prepn 1^h	−42	2.160^a
prepn 2	−40	2.053
[Cu$_2$(tren)$_2$(2-MeIm)](ClO$_4$)$_3$·H$_2$O	−49	2.082
[Cu$_2$(bpy)$_4$(Im)](PF$_6$)$_2$·H$_2$O	−35	2.083
[Cu$_2$(phen)$_4$(Im)](ClO$_4$)$_3$·3H$_2$O		
prepn 1^i	−24	2.190^a
prepn 2	−26	2.043
[Cu$_2$(tren)$_2$(BiIm)](BPh$_4$)$_2$	< ca. 0.5^b	
[Ni$_2$(tren)$_2$(BiIm)](BPh$_4$)$_2$	−2.9	2.082
[Ni$_2$(tren)$_2$(Ox)](BPh$_4$)$_2$^{c}	−15.6	
[Cu$_2$(dpt)$_2$(BiIm)](BPh$_4$)$_2$·2CH$_3$CN		
prepn 1	−2.1	2.007
prepn 2	−1.9	2.094
[Cu$_2$(dpt)$_2$(Ox)](BPh$_4$)$_2$	−5.7^d	
[Cu$_2$(Me$_5$dien)$_2$(BiIm)](BPh$_4$)$_2$	< ca. 0.5^b	
[Cu$_2$(Me$_5$dien)$_2$(Ox)](BPh$_4$)$_2$	−3.4^d	
[Cu$_2$(dien)$_2$(BiIm)](BPh$_4$)$_2$	< ca. 0.5^b	
[Cu$_2$(dien)$_2$(Ox)](BPh$_4$)$_2$	−7.3^e	
[Cu$_2$(Me$_5$dien)$_2$(BiBzIm)](BPh$_4$)$_2$	< ca. 0.5^b	
[Cu$_2$(dien)$_2$(BiBzIm)](BPh$_4$)$_2$	< ca. 0.5^b	

^{a} In the least-squares fitting procedure, this g value was held fixed. ^{b} In these cases there are no signs of an exchange interaction in the susceptibility data taken down to 4.2 K and, as such, $J < 0.5$ cm^{-1}. ^{c} See the Ph.D. thesis of D. M. Duggan, University of Illinois. The abbreviation Ox stands for the oxalate ion, C$_2$O$_4^{2-}$. ^{d} See ref 18. ^{e} G. R. Hall, D. M. Duggan, and D. N. Hendrickson, *Inorg. Chem.*, 14, 1956 (1975). $^{f-i}$ Susceptibility data are represented in Figures 1, 2, 3, and 5.
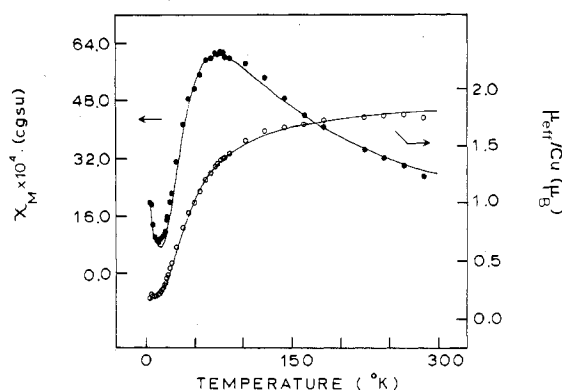

Figure 3. Molar paramagnetic susceptibility (χ_M in cgsu per dimer) and effective magnetic moment per copper ion (μ_{eff}/Cu(II) in μ_B) of [Cu$_2$(tren)$_2$(2-MeIm)](PF$_6$)$_3$ plotted as a function of temperature. The experimental data are represented as circles and the lines result from a least-squares fit to eq 1.

least-squares fitting parameters for preparations **1** and **2**. It is apparent that the parameters of the three preparations are quite close which indicates that the data are reproducible and, as in the case of [Cu$_2$(tren)$_2$(Im)](PF$_6$)$_3$, the J value can be determined independent of a small and variable amount of monomeric impurities.

It was of interest to see what effect substituting the Im$^-$ bridge would have on the level of antiferromagnetic interaction. The compounds [Cu$_2$(tren)$_2$(2-MeIm)](PF$_6$)$_3$, [Cu$_2$(tren)$_2$-(2-MeIm)](ClO$_4$)$_3$·H$_2$O, and [Cu$_2$(tren)$_2$(BzIm)](ClO$_4$)$_3$ were prepared. The susceptibility data for preparation **1** of the first compound are given in Table VII^{21} and are illustrated in Figure
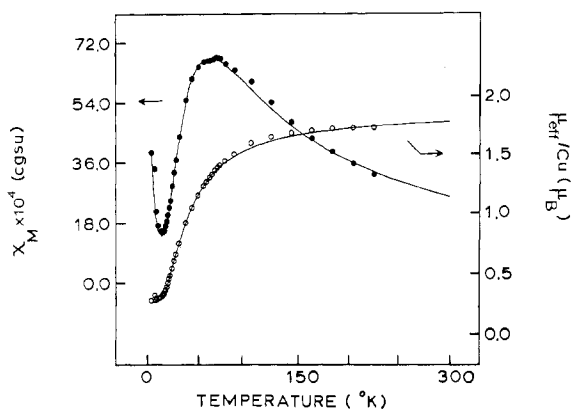
Figure 4. Molar paramagnetic susceptibility (χ_M in cgsu per dimer) and effective magnetic moment per copper ion (μ_{eff}/Cu in μ_B) of [Cu$_2$(bpy)$_4$(Im)](PF$_6$)$_3$·H$_2$O plotted as a function of temperature. The experimental data are represented as circles and the solid lines result from a least-squares fit to eq 1.

Figure 5. Molar paramagnetic susceptibility (χ_M in cgsu per dimer) and effective magnetic moment per copper ion (μ_{eff}/Cu in μ_B) of [Cu$_2$(phen)$_4$(Im)](ClO$_4$)$_3$·3H$_2$O plotted as a function of temperature. The experimental data are represented as circles and the solid lines result from a least-squares fit to eq 1.

3. The increase in χ_M at the lowest temperatures is due again to a monomeric impurity. A very good fit is obtained by fixing the g value at 2.160, fixing PAR at 0.00195 cgsu, and varying J. A value of -42 cm^{-1} is obtained for the J value. The susceptibility data for preparation **2** of the same compound exhibited a greater increase in χ_M at the lowest temperatures; this is due, of course, to a greater amount of a monomeric impurity. However, as can be seen in Table XVII, the least-squares fitting J value obtained is not much different. The susceptibility data for the compound [Cu$_2$(tren)$_2$(2-MeIm)](ClO$_4$)$_3$·H$_2$O are given in Table VIII.[21] An excellent least-squares fit is obtained by varying J and g and fixing PAR as 0.0127 cgsu. The values of the final fitting parameters are $J = -49$ cm^{-1} and $g = 2.082$. The more negative value of J for the ClO$_4^-$ salt compared to the PF$_6^-$ salt could be due to enhanced intermolecular interactions propagated by the good hydrogen-bonding ClO$_4^-$ ion. However, due to the anion independence of J in the [Cu$_2$(tren)$_2$Im]$^{3+}$ case, another explanation will be presented in the Exchange Mechanism section.

Our previous work[17-19] has shown that changing the non-bridging ligand can lead to an appreciable change in the magnitude of the magnetic exchange interaction in a copper(II) binuclear complex. Consequently, the compounds [Cu$_2$(bpy)$_4$(Im)](PF$_6$)$_3$·H$_2$O and [Cu$_2$(phen)$_4$(Im)]-(ClO$_4$)$_3$·3H$_2$O were prepared. Figure 4 shows the data for the former. The solid lines in this figure result from fitting the data to two parameters, J and g, and fixing the value of PAR. The least-squares fitting parameters are $J = -35$ cm^{-1} and $g = 2.083$. PAR was fixed at 0.0039 cgsu. Two preparations, **1** and **2**, of the phen compound were studied. Figure 5 shows the data for preparation **1**. Least-squares fitting of these data with g fixed at 2.190, PAR fixed at 0.0036 cgsu, and J as a parameter yields the solid lines presented in Figure 5. The value of J obtained is -24 cm^{-1}. Preparation **2** exhibited more monomeric impurity (Table X).[21] Least-squares fitting of the data for preparation **2** gave a J value of -26 cm^{-1} (Table XVII) which is quite close to that obtained for preparation **1**.

Only one copper(II) complex bridged by either BiIm^{2-} or BiBzIm^{2-} exhibited an antiferromagnetic interaction in the susceptibility data taken to 4.2 K. As indicated in Table XI,[21] μ_{eff}/Cu for both preparations **1** and **2** of [Cu$_2$(tren)$_2$-(BiIm)](BPh$_4$)$_2$·2CH$_3$CN is essentially constant down to ca. 11.1 K, whereupon there is a drop to 1.16 μ_B and 1.21 μ_B, respectively, at 4.2 K. Both data sets were least-squares fit by varying J and g while fixing PAR at 0.0 cgsu. For preparation **2** the least-squares-fit parameters are $J = -1.9$ cm^{-1} and $g = 2.094$. Table XII[21] and Figure 6 show that
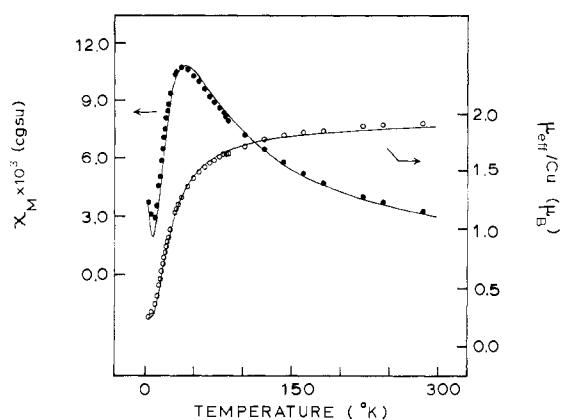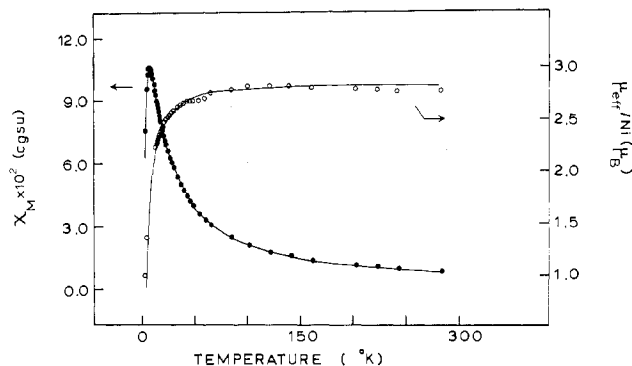

Figure 6. Molar paramagnetic susceptibility (χ_M in cgsu per dimer) and effective magnetic moment per nickel ion (μ_{eff}/Ni(II) in μ_B) of [Ni$_2$(tren)$_2$(BiIm)](BPh$_4$)$_2$ plotted as a function of temperature. The experimental data are represented as circles and the lines result from least-squares fits to theoretical equations presented in ref 25.

[Ni$_2$(tren)$_2$(BiIm)](BPh$_4$)$_2$ does exhibit a maximum at ca. 9.1 K in the χ_M vs. temperature curve. Ginsberg et al.[25] derived the susceptibility expression for a dimeric Ni(II) complex involved in an isotropic magnetic exchange interaction. Least-squares fitting of the experimental data to the theoretical expression was carried out varying the exchange parameter J, g, the single-ion zero-field splitting parameter D, and the intercluster interaction $Z'J'$. The fitting gave $J = -2.9$ cm^{-1}, $D = 53$ cm^{-1}, $g = 2.082$, and $Z'J' = 1.80$ K. The fitting is shown in Figure 6 as solid lines, which can be seen to fit the data reasonably well, particularly the peak in χ_M curve.

Electron Paramagnetic Resonance. Several of the Cu(II) dimers in this work were prepared as BPh$_4^-$ salts in an attempt to provide a magnetically dilute environment for the dimers. Eliminating or reducing the *inter*dimer dipolar and exchange interactions with a large counterion can lead to the resolution of Cu(II) hyperfine structure and other features in the EPR spectra of these compounds. In previous papers[18,19] we have discussed the various EPR observables for a Cu(II) dimer.

The compounds with the composition [Cu$_2$("dien")$_2$(L)]-(BPh$_4$)$_2$, where "dien" is variously dien, Me$_5$dien, or dpt and L is BiIm^{2-} or BiBzIm^{2-}, give very similar EPR spectra. The general features of a typical spectrum are a weak and broad resonance around g_1 ($g_{||}$) = 2.2 and two other signals around $g_2 = 2.1$ and $g_3 = 2.04$. The g_3 signal is the most intense, while the g_2 signal is of intermediate intensity. In addition, samples of [Cu$_2$(Me$_5$dien)$_2$(BiIm)](BPh$_4$)$_2$ and [Cu$_2$(dpt)$_2$(BiIm)]-(BPh$_4$)$_2$·2CH$_3$CN show an additional weak feature between the g_1 and g_2 signals.

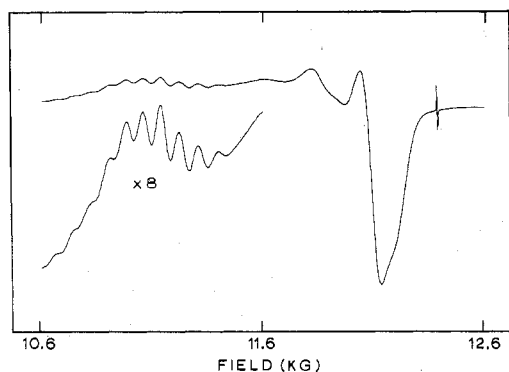**Figure 7.** Q-Band ($\sim$35 GHz) EPR spectrum of a powdered sample of $[Cu_2(tren)_2(BiIm)](BPh_4)_2$ at ca. 110 K with DPPH as a frequency calibrant.

Figure 8. High-field portion of the X-band (9.090 GHz) EPR spectrum of a powdered sample of $[Cu_2(tren)_2(BiIm)](BPh_4)_2$ showing the $\Delta M_s = 1$ region recorded at ca. 80 K.

The Q-band as well as the X-band spectra of $[Cu_2(tren)_2(BiIm)](BPh_4)_2$ proved to be the most interesting of all because of the appearance of a rich pattern of copper hyperfine structure. The Q-band EPR spectrum of a powdered sample of $[Cu_2(tren)_2(BiIm)](BPh_4)_2$ at ca. 110 K is shown in Figure 7. The g value pattern is the same as those observed for $[Cu_2("dien")_2(L)](BPh_4)_2$ above. The spectrum in Figure 6 is similar to the previously reported[18] spectra of oxalate-bridged $[Cu_2(Me_5dien)_2(C_2O_4)](BPh_4)_2$ and cyanate-bridged $[Cu_2(Me_5dien)_2(NCO)_2](BPh_4)_2$. The cyanate ions are probably bridged in an end-to-end fashion in the latter compound (cf. the analogous N_3^- compound[19]), and it has been pointed out that the two cyanate ions can be considered as a pseudooxalate bridge with a missing C–C bond. Similarly, the $BiIm^{2-}$ bridge can be considered as an analogue of the oxalate ($C_2O_4^{2-}$) bridge. The inset in Figure 7 shows that there are 10 copper hyperfine lines on the parallel signal of $[Cu_2(tren)_2(BiIm)](BPh_4)_2$ with interline spacings ranging from 68 to 83 G and an average spacing of 76 G. The 10 lines result from the overlapping of two seven-line copper hyperfine patterns where the positioning of the two seven-line patterns depends on zero-field splitting. The observation of such a hyperfine structure means that electrons are exchanging between the two Cu(II) ions via the $BiIm^{2-}$ bridge at a rate that is faster than the EPR time scale. The hyperfine pattern also indicates that there is a magnetic exchange interaction where $|J| >$ ca. 0.02 cm^{-1}. This limiting value is determined by the magnitude of the Cu(II) hyperfine interactions. Because the spectrum does not show second-order effects and it does show an interaction with both Cu(II) ions, the exchange interaction exceeds the copper hyperfine interaction. On the other hand, the magnetic susceptibility data to 5.1 K for this same compound did *not* show any signs of an exchange interaction. This means that $|J| <$ ca. 0.05 cm^{-1}, thus bracketing the exchange parameter to $0.02 < |J| < 0.5\ cm^{-1}$.

The X-band spectrum of $[Cu_2(tren)_2(BiIm)](BPh_4)_2$ provides additional convincing support for the presence of a weak exchange interaction. The $\Delta M_s = 1$ region is illustrated in Figure 8. At least seven copper hyperfine lines are seen on the $g_{\parallel}$ signal with spacings ranging from 60 to 77 G and an average spacing of 73 G. The $\Delta M_s = 2$ region of the X-band spectrum, as illustrated in Figure 9 for a sample at ca. 80 K, offers the most definitive proof of the presence of an *intra*dimer magnetic exchange interaction. A derivative pattern showing seven hyperfine lines is seen, where the spacings range from 72 to 90 G with an average of 80 G. There is only one seven-line pattern expected, because there is no zero-field splitting expected for the $\Delta M_s = 2$ transition.

The compound $[Cu_2(dien)_2(BiIm)](BPh_4)_2$ also shows a pattern of 10 copper hyperfine lines on the $g_{\parallel}$ signal in the Q-band spectrum, as illustrated for the analogous tren
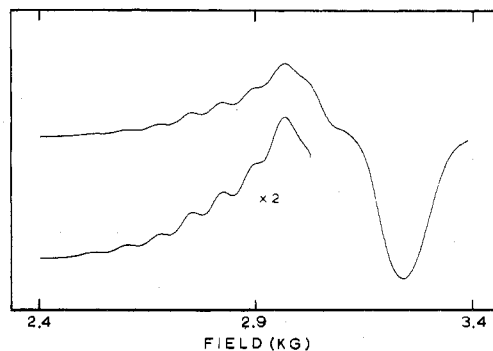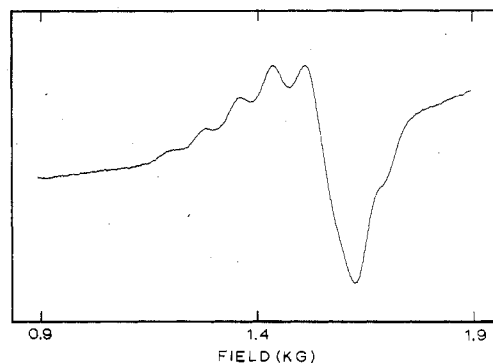

Figure 9. Low-field portion of the X-band (9.090 GHz) EPR spectrum of a powdered sample of $[Cu_2(tren)_2(BiIm)](BPh_4)_2$ showing the $\Delta M_s = 2$ region recorded at ca. 80 K.

compound in Figure 7. The compounds $[Cu_2(Me_5dien)_2(L)](BPh_4)_2$, where L is $BiIm^{-2}$ or $BiBzIm^{2-}$, show some features (i.e., bumps) on their Q-band, $g_{\parallel}$ signals which are part of a hyperfine pattern that could not be further resolved even at low temperatures. The most featureless Q-band $g_{\parallel}$ signal was found for $[Cu_2(dpt)_2(BiIm)](BPh_4)_2 \cdot 2CH_3CN$. The similarity of the EPR spectra of the $BiIm^{2-}$ and the $BIBzIm^{2-}$ "dien" complexes, particularly in the $g_{\parallel}$ region, with the spectra of $[Cu_2(tren)_2(BiIm)](BPh_4)_2$ indicates that there is probably also a weak magnetic exchange interaction present in these complexes. Again, the exchange parameter for each complex would be in the range $0.02\ cm^{-1} < |J| < 0.5\ cm^{-1}$.

The Q-band and X-band EPR spectra of $[Cu_2(tren)_2(Im)](X)_3$, where X is either ClO_4^- or PF_6^-, and $[Cu_2(tren)_2(Im)](BPh_4)_2(ClO_4)$ are characteristic of variable amounts of zero-field splitting. On the one hand, the Q-band spectrum of the ClO_4^- salt is a typical trigonal-bipyramidal spectrum with $g_{\perp} = 2.140$ and $g_{\parallel} = 2.045$. The $g_{\parallel}$ and $g_{\perp}$ signals are broader than those of the monomer, $[Cu(tren)(ImH)](ClO_4)_2$. The X-band spectrum of the ClO_4^- dimer shows a single symmetrical derivative at $g = 2.131$. No $\Delta M_s = 2$ transition was observed at "half-field". The Q-band spectrum of the PF_6^- dimer shows three g values: $g_1 = 2.120$, $g_2 = 2.117$, and $g_3 = 2.056$. The g_1 and g_2 signals are much broader than those observed in the ClO_4^- dimer spectrum. It is suggested that there is a very weak *inter*molecular magnetic exchange interaction present in the ClO_4^- dimer salt and this eliminates the *intra*dimer zero-field splitting in the spectrum. In the PF_6^- dimer salt, the *inter*molecular exchange interaction is reduced in magnitude and the spectral features are broadened. Finally, in the case of the mixed-anion salt $[Cu_2(tren)_2(Im)](BPh_4)_2(ClO_4)$, both the Q-band and the X-band spectra show zero-field splitting features. In the Q-band spectrum there is a signal at $g = 2.265$ with its zero-field-split partner occurring at a magnetic field position

above DPPH and with a g of 1.970. In addition, there is a strong signal at $g = 2.071$ and a weak one at $g = 2.180$. A low-intensity $\Delta M_s = 2$ transition is observed at 5650 G. The X-band spectrum of this mixed-anion salt shows a relatively intense $\Delta M_s = 2$ transition at ca. 1500 G. It is stronger than that of the PF_6^- dimer salt and it is also only ca. 20 times weaker than the signals in the $\Delta M_s = 1$ region. In the $\Delta M_s = 1$ region, two features of a zero-field split transition with g values of 2.597 and 1.887 are observed; the latter signal is of greater intensity. Another signal is observed at $g = 2.275$. Thus, the zero-field splitting effects are most evident in the mixed-anion salt. It is to be remembered that the intensity of the $\Delta M_s = 2$ transition depends, to second order, on the magnitude of zero-field splitting.

The X-band spectrum of $[Cu_2(tren)_2(2\text{-MeIm})](ClO_4)_4 \cdot H_2O$ is a typical trigonal-bipyramidal Cu(II) spectrum with $g_\perp = 2.146$ and $g_\parallel = 2.057$. A $\Delta M_s = 2$ transition is seen at ca. 1500 G. Two broad bumps at high and low field, which are reminiscent of zero-field splitting, are observed. Since this compound shows a $\Delta M_s = 2$ signal while the imidazolate analogue does not, it is possible that the effective zero-field splitting is of greater magnitude for the 2-methylimidazolate dimer. This is reflected in the Q-band spectrum of the compound, where two zero-field split signals occurred at g values of 2.306 and 1.964 with a strong signal at a g value of 2.119 together with a "bump" at $g = 2.177$. The X-band spectrum of the PF_6^- salt is similar to that of the ClO_4^- salt, except that the g signal is not as well resolved.

Interestingly, in the $\Delta M_s = 1$ region of both the Q-band and X-band spectra of $[Cu_2(tren)_2(BzIm)](ClO_4)_3$, a single symmetrical line is seen with g values of 2.115 (Q-band) and 2.127 (X-band). The appearance of a single line in an exchanging Cu(II) dimer can be the result of an exchange averaging.

The X-band spectrum of $[Cu_2(phen)_4Im](ClO_4)_3 \cdot 3H_2O$ consists of a single asymmetrical derivative with a g value of 2.112; a $\Delta M_s = 2$ transition is observed. On the other hand, the Q-band spectrum is more complex in that it shows two broad bumps at low and high field with g values of 2.297 and 1.989, respectively. These are again probably zero-field split features of the $g_\parallel$ signal. At intermediate fields, a strong signal at $g = 2.076$ and a weak signal at $g = 2.187$ are seen. These represent the $g_\perp$ region of the $\Delta M_s = 1$ transition.

The Q-band spectrum of the compound $[Cu_2(bpy)_4(Im)](PF_6)_4 \cdot H_2O$ shows a strong symmetrical line at $g = 2.108$ and two other weak "bumps" symmetrically situated around the $g = 2.108$ signal. The g values of these latter two features are 2.172 and 1.967. Because the smaller g value is less than 2.00, it again seems that these two weak absorptions are the zero-field-split $g_\parallel$ signal. The X-band spectrum of $[Cu_2(bpy)_4(Im)](PF_6)_3 \cdot H_2O$ is similar to the Q-band spectrum in that it shows a strong line at $g_1 = 2.163$ and two other weak features at $g_2 = 2.596$ and $g_3 = 1.844$. The g_1 signal is broader and more asymmetric than the Q-band signal.

Exchange Mechanism. Table XVII summarizes the exchange parameters for the 14 compounds from this study and for other related compounds. As can be seen, the exchange parameters for the 14 compounds vary from -49 cm^{-1} to a value that is not detectable in magnetic susceptibility data taken to 4.2 K; i.e., $|J| <$ ca. 0.5 cm^{-1}. This full range of exchange parameters is encountered in the series of six compounds with the formulation of $[Cu_2(tren)_2(L)](X)_n$, where the bridge L is variously Im$^-$, 2-MeIm$^-$, BzIm$^-$, or BiIm^{2-}. The 2-MeIm$^-$ complex has the strongest antiferromagnetic interaction, followed by the Im$^-$ complex and then the BzIm$^-$ complex; the weakest antiferromagnetic interaction is found for the BiIm^{2-} complex. It is important to understand this variation in exchange parameter. The superexchange in-

teraction between pairs of Cu(II) ions in the 4-Cu^{2+} SOD protein is characterized by $J = -26$ cm^{-1}, and it is interesting to know how important the Cu(II) coordination geometry and ground electronic state are in determining the magnitude of this antiferromagnetic interaction.

Various X-ray structures[30-33] have been reported for salts containing Cu(tren)X$^+$ ions. The tripodal ligand tren tends to enforce a trigonal-bipyramidal structure, which is what is found for these five-coordinate Cu(II) complexes. The fifth ligand X occupies an axial coordination site in the distorted trigonal-bipyramidal structure. It is safe to assume that the variation in exchange parameter for $[Cu_2(tren)_2(L)](X)_3$ when L is varied from 2-MeIm$^-$ to Im$^-$ to BzIm$^-$ is a reflection of the change in the bridge and not a change in Cu(II) coordination geometry. The magnitude of antiferromagnetic exchange is a reflection of the interaction of the orbitals of the bridging species with the Cu(II) orbitals in which the unpaired electrons reside. The orbital ground state of a Cu(II) ion in a trigonal-bipyramidal geometry is d_{z^2}. Interaction of the two d_{z^2} orbitals in a dimer occurs if there are bridge orbitals of the correct symmetry and energy. Consequently, two molecular orbitals form; one is the bonding combination and the other is the antibonding combination. If the two metal centers in a dimer are designated A and B, the two molecular orbitals are $\phi_1 \approx d_{z^2}{}^A + d_{z^2}{}^B$ and $\phi_2 \approx d_{z^2}{}^A - d_{z^2}{}^B$. The difference in energy between these two molecular orbitals determines the magnitude of antiferromagnetic interaction. The bonding combination is generally the most important.[36] The bridge in these tren complexes is expected to occupy an axial position with the metal d_{z^2} orbital pointing directly at the N atom lone pair of the bridge. As such, the d_{z^2} orbital exists in the plane of the bridge. Various X-ray crystal structures[4-6] of compounds containing the imidazolate anion show that it is planar but asymmetric. Therefore, the assumption of C_s symmetry of the bridge is a valid one. With this symmetry the d_{z^2} orbitals will interact with the σ framework of the bridge rather than the π system. The extent of overlap of d_{z^2} orbitals with the appropriate σ orbitals of the bridging species and the energy difference between the metal d_{z^2} orbital and the bridge molecular orbitals are two important factors that determine the energy separation (the J value) between the ϕ_1 and ϕ_2 molecular orbitals.

Taking the imidazolate dimer as a reference point, the angle (α) of attachment of each Cu(tren)$^{2+}$ unit to the bridge, $\angle$Cu–N–C(2), would be expected to change somewhat in the series Im$^-$, 2-MeIm$^-$, and BzIm$^-$. In the 2-methylimidazolate dimer, the C(2) atom is substituted with a methyl group, and this should cause the angle α to increase due to a tendency of the tren ligand to avoid steric interaction with the methyl group. On the other hand, the angle α would probably be decreased in the benzimidazolate as a result of the Cu(tren)$^{2+}$ moiety moving away from the added carbon skeleton on the C(4) and C(5) atoms of the imidazole. CNDO/2 molecular orbital calculations on the imidazolate anion suggest that the highest occupied σ molecular orbital of Im$^-$ which could provide a bonding interaction pathway for the d_{z^2} orbitals of the two Cu(II) ions has major contributions from two nitrogen orbitals and these are oriented as indicated:
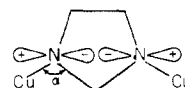
If the above Im$^-$ orbital is a major antiferromagnetic exchange pathway, then increasing α in going from Im$^-$ to 2-MeIm$^-$ could lead to a more favorable situation for overlap, and this would explain the somewhat greater interaction in the 2-MeIm$^-$ dimer relative to the Im$^-$ dimer. The decreased $\angle$Cu–N–C(2) expected in the BzIm$^-$ dimer could lead to a
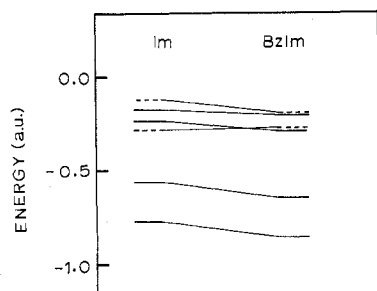
Figure 10. Highest energy occupied σ CNDO/2 molecular orbitals for imidazolate (Im⁻) and benzimidazolate (BzIm⁻). The solid lines are for σ orbitals which interact with the "bonding" combination of copper(II) d_{z^2} orbitals.

weaker interaction. On the basis of a consideration of the energy of the bridge orbitals, it is also expected that the BzIm⁻ dimer would have a weaker antiferromagnetic interaction. The added π conjugation in benzimidazolate compared with imidazolate could lead to a stabilization of the σ framework, increasing its energy gap with the metal d_{z^2} orbitals and, thus, decreasing the J value. To test this possibility, CNDO/2 molecular orbital calculations were carried out for the imidazolate and benzimidazolate ions assuming C_s symmetry and using the dimensions in ref 9 and 37, respectively. In Figure 10 are summarized the relative energies of the highest occupied σ imidazolate orbitals correlated with the appropriate orbitals of the benzimidazolate bridge. The orbitals that are identified with solid lines are σ orbitals which can interact with a bonding combination of d_{z^2} orbitals. Dashed lines are used for σ orbitals which can interact with an antibonding combination of d_{z^2} orbitals. It is apparent that on going from the imidazolate to the benzimidazolate bridge, a net stabilization of the σ orbitals occurs and this would attenuate the antiferromagnetic interaction.

The very weak interaction observed for [Cu₂(tren)₂-(BiIm)](BPh₄)₂ is most likely ascribable to the fact that the Cu(II) ions are now six-coordinate and the single unpaired electron is located in an orbital which is perpendicular to the plane of the BiIm²⁻ bridge. This type of explanation was used for [Cu₂(tren)₂(Ox)](BPh₄)₂, a compound which also does *not* show any signs of an interaction in the susceptibility taken to 4.2 K.

Changing the nonbridging ligand to phenanthroline in the imidazolate series to give [Cu₂(phen)₄(Im)](ClO₄)₃·3H₂O leads to a weaker antiferromagnetic interaction ($J = -24$ cm⁻¹) while changing to 2,2'-bipyridine leads, surprisingly, to a J value (–35 cm⁻¹) comparable to that of the tren compound. Previously,[17] it was observed that a weaker exchange interaction occurs on going from [Cu₂(tren)₂(CN)](PF₆)₃, where $J = -88$ cm⁻¹, to [Cu₂(phen)₄(CN)](PF₆)₃, where $J = -29$ cm⁻¹; the weakest interaction was found for [Cu₂(bpy)₄(CN)](PF₆)₃, where $J = -9.4$ cm⁻¹. The weaker antiferromagnetic interactions in the phen and bpy compounds were explained in terms of a dimer structure approaching structure I. The dimer Cu₂-

I   II
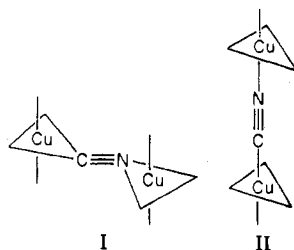
(tren)₂(CN)³⁺ is believed to have structure II. The cyanide bridge orbitals in dimer structure I are not properly oriented

for an effective overlap with the Cu(II) d_{z^2} orbitals, whereas, they are in structure II. The ratio of exchange parameters for Cu₂(tren)₂(CN)³⁺ and Cu₂(phen)₂(CN)³⁺ is $J_{phen}/J_{tren} = 0.33$. The reduction in antiferromagnetic interaction in Im⁻ dimers is most likely due to the fact that the phen–Im dimer has structure I. It is a certainty that the tren–Im dimer has structure II.

If the same trend occurred that was observed for the CN⁻-bridged dimers, the Cu₂(bpy)₄(Im)³⁺ species should have the weakest interaction. Instead, we find that the bpy–Im dimer has an interaction that is greater than the phen–Im dimer. Two possible explanations come to mind: (1) there is a structural distortion giving a different ground state, probably $d_{x^2-y^2}$, where an improved overlap with a bridge orbital leads to the unexpected increase in antiferromagnetic interaction; (2) the dimer does have a d_{z^2} ground state, but the structure is distorted enough to put the Im⁻ bridge into closer proximity to the main lobe of the d_{z^2} orbital. Phenanthroline and bipyridine are similar in their metal coordination tendencies, and it is known that both prefer trigonal-bipyramidal geometries where they are bonded in a cis–cis fashion.[38] Both are incapable of participating in square-planar coordination. The EPR spectra of [Cu₂(bpy)₄(Im)](PF₆)₃·H₂O were discussed above; the appearance of apparently zero-field splitting effects in the spectra makes it difficult to decide the Cu(II) ion ground state from the spectra.

An X-ray crystal structure determination[39] of the compound "[Cu(bpy)₂(ClO₄)]ClO₄" showed that in this complex the Cu(II) ion is at the center of a tetragonally distorted octahedron where the four nitrogen atoms of the bipyridine ligands are arranged in a flattened tetrahedral manner opening two axial coordination sites for two oxygen atoms of the perchlorate anions. This is the only authentic example in the literature of a Cu–bpy complex distorted from structure I. Due to the steric interference between the hydrogen atoms on the 6 and 6' carbon atoms of the two bpy molecules, square-planar bipyridine complexes of the general formula M(bpy)₂²⁺ do not exist, which is taken as a general rule. However, Carty and Chieh[40] isolated the stable compound [Pd(bpy)₂](NO₃)₂·H₂O and characterized the compound crystallographically. It is well-known that Pd(II) favors square-planar coordination; however, the crystal structure of this compound showed that the Pd(II) coordination geometry is distorted from square planar with the four nitrogen atoms assuming a tetrahedral arrangement. These results indicate that two bipyridine ligands can distort from a trigonal-bipyramidal geometry. The steric requirements of the Im⁻ bridge in Cu₂(bpy)₄(Im)³⁺ could be providing some of the impetus.

Whereas [Cu₂(dien)₂(Ox)](BPh₄)₂, [Cu₂(Me₅dien)₂-(Ox)](BPh₄)₂, and [Ni₂(tren)₂(Ox)](BPh₄)₂ exhibit J values of –7.3, –3.4, and –15.6 cm⁻¹, respectively, the biimidazolate-bridged analogues of the Cu(II) dien and Me₅dien complexes do not show any measurable interaction in the susceptibility data to 4.2 K and the Ni(II) dimer exhibits a very weak interaction with $J = -2.9$ cm⁻¹. On the basis of the similarity of the EPR spectra of the biimidazolate bridged "dien" complexes to the spectra of [Cu₂(Me₅dien)₂(Ox)]-(BPh₄)₂ (vide supra), it is reasonable to consider that these complexes have the same local ground state, namely, the $d_{x^2-y^2}$ orbital ground state. The J value will be inversely proportional to the energy difference between the bridge molecule's orbital and the metal $d_{x^2-y^2}$ orbital. The decreased viability of biimidazolate to propagate a magnetic exchange interaction, compared to the oxalate bridge, is probably a consequence of the greater crystal field strength of the biimidazolate ligand. This greater crystal field strength raises the energy of the metal $d_{x^2-y^2}$ orbital, increasing the energy gap between the biimidazolate molecular orbitals and the metal $d_{x^2-y^2}$ orbital. The

same argument explains the weaker interaction exhibited by $[Cu_2(dpt)_2(BiIm)](BPh_4)_2 \cdot 2CH_3CN$ where $J = -1.9$ cm^{-1} compared with $[Cu_2(dpt)_2(Ox)](BPh_4)_2$ where $J = -5.7$ cm^{-1}.

Finally, it should be pointed out that the BiIm^{2-} bridge is most likely not totally equivalent to two Im$^-$ bridges. The relatively short C(2)–C(2') distances noted in $M_2(COD)_2$-(BiIm)[13] and $M_4(CO)_8(BiIm)_2$[14] indicate the presence of some conjugation between the two imidazolate moieties in BiIm^{2-}. CNDO/2 calculations on BiIm^{2-} do show considerable π-orbital interactions and also small changes in the σ framework. X-ray structural work is in progress on $[Cu_2(Me_5dien)_2$-(BiIm)](BPh_4)_2$.[41]

Registry No. $[Cu_2(tren)_2(Im)](PF_6)_3$, 66900-41-2; $[Cu_2(tren)_2$-(Im)](ClO_4)_3$, 66900-40-1; $[Cu_2(tren)_2(Im)](BPh_4)_2(ClO_4)$, 66842-05-5; $[Cu_2(tren)_2(BzIm)](ClO_4)_3$, 66842-03-3; $[Cu_2(tren)_2$-(2-MeIm)](PF_6)_3$, 66900-39-8; $[Cu_2(tren)_2(2-MeIm)](ClO_4)_3$, 66842-01-1; $[Cu_2(bpy)_4(Im)](PF_6)_3$, 66810-44-4; $[Cu_2(phen)_4$-(Im)](ClO_4)_3$, 66810-46-6; $[Cu_2(tren)_2(BiIm)](BPh_4)_2$, 66842-07-7; $[Ni_2(tren)_2(BiIm)](BPh_4)_2$, 66842-09-9; $[Cu_2(dpt)_2(BiIm)](BPh_4)_2$, 66810-48-8; $[Cu_2(Me_5dien)_2(BiIm)](BPh_4)_2$, 66810-56-8; $[Cu_2$-(dien)_2(BiIm)](BPh_4)_2$, 66810-54-6; $[Cu_2(Me_5dien)_2(BiBzIm)](BPh_4)_2$, 66810-52-4; $[Cu_2(dien)_2(BiBzIm)](BPh_4)_2$, 66810-50-2.

Supplementary Material Available: Tables I (analytical data) and II–XVI (calculated and observed magnetic susceptibility data (28 pages). Ordering information is given on any current masthead page.

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Magnetic Exchange Interactions in Binuclear Transition-Metal Complexes. 16. Binuclear Ferric Complexes from the Reaction of Fe(II)(salen) with p-Quinones[1]

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The molecule Fe(II)(salen) reacts with p-quinones (four different 1,4-benzoquinones, 1,4-naphthoquinone, and bianthrone) to give a compound with the composition [Fe(salen)]$_2$Q, where Q is the quinone moiety. It is shown with IR, variable-temperature magnetic susceptibility, EPR, and ^{57}Fe Mössbauer measurements that the compounds consist of high-spin ferric ions bridged by the dianion of a hydroquinone. *Intra*molecular antiferromagnetic exchange interactions are present in these binuclear iron(III) complexes, where the exchange parameter varies from −5.8 to −0.21 cm^{-1}. Several of the complexes exhibit asymmetric quadrupole-split doublets in their ^{57}Fe Mössbauer spectra. The asymmetries are found to be temperature dependent with a relatively symmetric doublet seen at low temperatures. Only two of the compounds give EPR signals, consisting of broad isotropic derivatives at $g = $ ca. 2.0.

Introduction

In photosynthesis and respiration, energy in the form of a redox potential gradient is transduced into metabolically useful energy. A series of coupled redox reactions, frequently referred to as an electron transport chain, is utilized to discharge this gradient and synthesize adenosine triphosphate (ATP) from adenosine diphosphate (ADP) and inorganic phosphate. Several types of lipid-soluble quinones have been found to be