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Exchange Coupling in Triplet Ground State Dimeric Molecules with Specific Reference to Bis(μ-pyridine *N*-oxide)bis[bis(nitrato)(pyridine *N*-oxide)copper(II)] and Bis(diethyldithiocarbamato)copper(II)

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Some time ago Carlin and co-workers[1] questioned the existence of exchange coupling in the sulfur-bridged bimetallic complex bis(diethyldithiocarbamato)copper(II), $[Cu(dedtc)_2]_2$. Later, they[2] reported ferromagnetic intrapair exchange in $[Cu(dedtc)_2]_2$, in agreement with the original report by Gregson and Mitra,[3] which we verified.[4-6] Now, Carlin and co-workers[7] conclude that the copper(II) ions in bis(μ-pyridine *N*-oxide)bis[bis(nitrato)(pyridine *N*-oxide)copper(II)] exhibit doublet-state magnetism, and they state that the existence of ferromagnetically aligned pairs of copper(II) ions remains an open question.

Here, I will describe the theoretical results for exchange coupling, review the structural, magnetic, and EPR data available for these and analogous complexes, and show that an exchange-coupled description is required for a precise description of the electronic states in these complexes. In the next two sections a brief review of the theoretical basis for exchange coupling will be given with use of the symbols and terms as defined by Martin[8] for the localized description and by Hay, Thibeault, and Hoffmann[9] for the molecular orbital approach. (Note that J and K are defined differently in these two treatments; the traditional designations are retained here.)

Localized Description of Exchange Coupling

Martin[8] has shown for the case in which the unpaired electrons are localized on identical interacting paramagnetic centers, using Heitler–London wave functions, that the energies of the singlet (symmetric orbital combination, eq 1) and triplet (antisymmetric orbital combination, eq 2) states

$$\psi_{\mathrm{sym}}(1,2) = (1/2^{1/2})[(\phi_a(1))(\phi_b(2)) + (\phi_a(2))(\phi_b(1))] \quad (1)$$

$$\psi_{\mathrm{anti}}(1,2) = (1/2^{1/2})[(\phi_a(1))(\phi_b(2)) - (\phi_a(2))(\phi_b(1))] \quad (2)$$

are given by

$$E_{\mathrm{sym}} = 2E_0 + (K + J)/(1 + S^2) \quad (3a)$$

and

$$E_{\mathrm{anti}} = 2E_0 + (K - J)/(1 - S) \quad (3b)$$

where E_0 values are the energies of the degenerate states in the absence of electron interchange and S is the overlap integral. If the interacting paramagnetic centers are not identical, then E_0 will take on appropriate, nonequal values. K, the Coulomb integral, and J, the exchange integral, are defined as

$$K = \int\int (\phi_a(1))(\phi_b(2))[H'](\phi_a(1))(\phi_b(2))\, d\tau_1\, d\tau_2 = \int\int (\phi_a(2))(\phi_b(1))[H'](\phi_a(2))(\phi_b(1))\, d\tau_1\, d\tau_2$$

and

$$J = \int\int (\phi_a(1))(\phi_b(2))[H'](\phi_a(2))(\phi_b(1))\, d\tau_1\, d\tau_2$$

where

$$H' = e^2/r_{ab} + e^2/r_{12} - e^2/r_{b1} - e^2/r_{a2}$$

In these equation the subscripts a and b refer to the interacting magnetic centers, and the subscripts 1 and 2 refer to the two electrons. The $\phi_i(k)$ values are the one-electron wave functions with the electron k in orbital i.

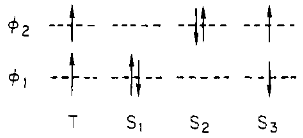
These results show that the singlet–triplet splitting, that is, $E_{ST} = E_{\mathrm{sym}} - E_{\mathrm{anti}}$, in exchange-coupled systems involving localized electrons, is not a straightforward measure of the modulus of the exchange coupling. One may deduce the singlet–triplet splitting from temperature-dependent magnetic measurements, but the *strength* of the exchange coupling requires detailed theoretical calculations.

Molecular Orbital Treatment

Hay, Thibeault, and Hoffmann[9] have provided a treatment of exchange coupling in copper(II) complexes with electronic configuration d^9 and the unpaired electrons in predominantly $d_{x^2-y^2}$ orbitals. They write the linear combinations

$$\phi_1 \approx (d_{x^2-y^2})^a + (d_{x^2-y^2})^b \qquad \phi_2 \approx (d_{x^2-y^2})^a - (d_{x^2-y^2})^b$$

and show the following electronic configurations that arise from these orbitals



These lead to the functions

$$\mathrm{T}{:}\ |\phi_1\alpha\phi_2\alpha| \qquad S_1{:}\ |\phi_1\alpha\phi_1\beta| \qquad S_2{:}\ |\phi_2\alpha\phi_2\beta|$$

$$S_3{:}\ (1/2^{1/2})(|\phi_1\alpha\phi_2\beta| - |\phi_1\beta\phi_2\alpha|)$$

with the lowest singlet state of the system being an approximately equal mixture of S_1 and S_2, viz.

$$\psi_S = \lambda_1(\psi(S_1)) + \lambda_2(\psi(S_2))$$

S_3 can be neglected since it will be high in energy and in some cases have a different symmetry. The energies of the singlet and triplet states are given by

$$E_T = h_1 + h_2 + J_{12} - K_{12} \qquad E_S = h_1 + h_2 + \tfrac{1}{2}(J_{11} + J_{22})$$

where

$$h_i = \int (\phi_i^*(1))[h(1)](\phi_i(1))\, d\tau_1$$

$$J_{ij} = \int\int (\phi_i^*(1))(\phi_j^*(2))[1/r_{12}](\phi_i(1))(\phi_j(2))\, d\tau_1\, d\tau_2$$

$$K_{ij} = \int\int (\phi_i^*(1))(\phi_j^*(2))[1/r_{12}](\phi_j(1))(\phi_i(1))\, d\tau_1\, d\tau_2$$

Hoffmann and co-workers[9] calculated the singlet–triplet splitting to be

$$E_T - E_S = J_{12} - K_{12} - \tfrac{1}{2}(J_{11} + J_{22}) + \tfrac{1}{2}[(2h_1 + J_{11} - 2h_2 - J_{22})^2 + 4K_{12}^2]^{1/2} \quad (4)$$

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It is clear that the singlet–triplet splitting is composed of many terms which arise from exchange coupling and, furthermore, that strongly exchange-coupled systems may exhibit vanishingly small singlet–triplet splittings. This fact, which is emphasized by eq 3a and 3b for the localized model and by eq 4 for the molecular orbital approach, has been pointed out.[10]

Hoffmann and co-workers[9] have defined orthogonal localized molecular orbitals of the form

$$\phi_a = (1/2^{1/2})[\phi_1 + \phi_2] \qquad \phi_b = (1/2^{1/2})[\phi_1 - \phi_2]$$

where $\langle\phi_a|\phi_b\rangle = 0$. ϕ_a contains both metal and ligand character but is largely a d orbital situated on metal A, and ϕ_b is largely a d orbital on metal B. From an analysis of the various terms in the exchange-coupling process, they find that the singlet–triplet splitting is given approximately by

$$E_T - E_S = -2K_{ab} + (\epsilon_1 - \epsilon_2)^2/(J_{aa} - J_{ab}) \qquad (5)$$

where K_{ab} is the exchange integral, J_{aa} and J_{ab} are the one- and two-center Coulomb repulsion integrals, and ϵ_1 and ϵ_2 are the energies of the molecular orbitals ϕ_1 and ϕ_2. Equation 5 is very useful. It emphasizes several important points for this discussion: (1) The ground state will be a triplet when the energies of the exchange-coupled molecular orbitals are equal. (2) The triplet state will be destabilized with respect to the singlet state when the energies of the symmetric and antisymmetric combinations become different. (3) The energy difference between the singlet and triplet states can become vanishingly small for certain values of the integrals and energies that describe the exchange-coupling process, but in each cases the paramagnetic centers remain exchange coupled. (4) For certain values of the integrals and energies the singlet state will become the ground state. Furthermore, Hoffmann and co-workers[9] argue that the exchange and Coulomb integrals are insensitive to small changes in structure as found in compounds in a related series, and they conclude that variations in singlet–triplet splittings in such series arise from differences in the energies of the molecular orbitals.

There are several series of compounds that reflect the trends suggested by these general points.[11]

Equation 5 may be generalized for the multielectron case in which there will be ferromagnetic and antiferromagnetic contributions. The ferromagnetic terms are given by

$$J_F = (1/m^2)\sum_{i\in A}\sum_{j\in B} K_{ij}$$

and the antiferromagnetic contributions are

$$J_{AF} = -(1/m^2)\sum_{i=1}^{m} \tfrac{1}{2}(\epsilon_{2i} - \epsilon_{2i-1})^2/(J_{ai,ai} - J_{ai,bi})$$

where the sum in the antiferromagnetic contribution is over pairs of molecular orbitals. This theory has been applied for the description of the magnetic properties of hydroxo- and alkoxo-bridged chromium(III) bimetallic complexes, which also show ground-state spin-multiplicity crossovers.[12,13]

Data Analysis

Magnetic susceptibility and magnetization data for one triplet state or for two doublet states do not differ much in the low-temperature range, and complications in interpretation arise from low-lying singlet states, interdimer interactions, and zero-field splittings. The most useful collaborative evidence comes from EPR studies. Once the triplet state is detected by EPR, it is necessary to analyze magnetic susceptibility and magnetization data in terms of the proper spin multiplicity and array of spin states.

Van Vleck Equation. The temperature dependence of the magnetic susceptibility of exchange-coupled $S = {}^1/_2$ ions may be described by the Van Vleck equation

$$\chi_M = [g^2N\mu_B{}^2/3k_BT][1 + \tfrac{1}{3}\exp(-E_{ST}/k_BT)]^{-1} + N\alpha \qquad (6)$$

where E_{ST}, the singlet–triplet splitting, is positive for a triplet ground state. In practice the equation is fit to temperature-dependent magnetic susceptibility data and magnetic parameters are obtained from best fit calculations.

In some instances eq 6 fails to provide an accurate description of magnetic data, presumably because of the complications mentioned above as well as the breakdown of assumptions that are inherent in the derivation of the Van Vleck equation, and magnetization expressions must be used. So that these complicating factors can be accounted for, it has become common place (although not strictly correct theoretically) to modify eq 1 by substituting the term $T - \Theta$ for T, yielding

$$\chi_M = [g^2N\mu_B{}^2/3k_B(T - \Theta)][1 + \tfrac{1}{3}\exp(-E_{ST}/k_BT)]^{-1} + N\alpha \qquad (7)$$

Curie–Weiss Law. The justification for the substitution of the term $T - \Theta$ for T in eq 7 is provided by the observation that eq 7 reduces to the Curie–Weiss law, eq 8, at sufficiently

$$\chi_M = C/(T - \Theta) = [Ng^2\mu_B{}^2S(S + 1)/3k_B]/(T - \Theta) \qquad (8)$$

high temperatures, that is, when $T >> |E_{ST}|$. The two Θ terms, one from eq 7 and the second from the Curie–Weiss law are different, and the Θ term from eq 7 is not the Weiss constant except in the high-temperature limit. Typically eq 7 is applied to data collected over wide ranges of temperature, and the Θ term is only a fitting parameter that contains information about other magnetic interactions.[14]

Magnetization. A Θ term is also frequently evaluated from magnetization data. Here, $\langle\mu\rangle = gS'(B_{S'}(X))$, where $B_{S'}(X)$ is the Brillioun function[15]

$$B_{S'}(X) = [(2S' + 1)/2S'] \coth [(2S' + 1)X/2S'] + (1/2S') \coth (X/2S')$$

In the Brillioun function S' is the effective spin of the dimeric molecule and $X = (H/T)(S'g\mu_B/k_B)$. The magnetic field is taken to be the sum of the applied field and the molecular field;[15,16] that is, $H = H_{applied} + H_{molecular}$. The molecular field is assumed to be proportional to the magnetization, $H_{molecular} = N_wM = N_wN\mu_B\langle\mu\rangle$, and N_w is given by

$$N_w = 3k_B\Theta/[Ng^2\mu_B{}^2S'(S' + 1)] \qquad (9)$$

The Θ term in eq 9 is once again taken to be an adjustable parameter to be determined by best fit calculations. The relationship of the Θ terms from magnetization studies and from the Van Vleck equation has been discussed.[17]

The magnetization per mole of sample M_0 of an exchange-coupled pair of $S = {}^1/_2$ ions is given by

$$M_0 = [Ng\mu_B \sinh (g\mu_BH_0)] \times [\exp(-E_{ST}/k_BT) + 2 \cosh (g\mu_BH_0/k_BT) + 1]^{-1} \qquad (10)$$

Interdimer interactions may be taken into consideration as above by replacing the applied field with an effective field which is the sum of the applied and molecular fields. In this

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manner a Θ term may be defined and evaluated from best fit calculations. In view of the approximate nature of the theory, identical values for these parameters should not be expected.

Review of Experimental Results

In this section a brief review of structural and magnetic data that are available for several related series of exchange-coupled copper(II) bimetallic compounds will be presented. These data show that exchange coupling varies in a rational way with the changes in chemical and structural features of the molecules in each series.

Variation of Singlet–Triplet Splitting with Bridge Angle. Systematic studies of the structural and magnetic properties of a series of bis(μ-hydroxo)bis[(diamine)copper(II)] complexes have established that the singlet–triplet splitting in this series of compounds is a function of the angle at the bridging oxygen atom.[18–20] Data for these compounds are collected in Table I (supplementary material). The $N_2CuO_2CuN_2$ units are largely planar with copper–oxygen bond distances of 1.92 ± 0.03 Å and copper–nitrogen bond distances of 2.00 ± 0.003 Å, and there are water molecules or counterions coordinated to copper in some, but not all, of the compounds.[18,20–44] The Cu–O–Cu angle ranges from 95.6 (1)° in $[Cu(bpy)OH]_2(NO_3)_2$[25] to 104.1 (2)° in $[Cu(tmen)OH]_2Br_2$,[43] and the singlet–triplet splitting varies linearly from +172 cm^{-1} (triplet ground state)[10] in the former compound to −509 cm^{-1} (singlet ground state)[44] in the latter compound. Except for α-$[Cu(dmaep)OH]_2(ClO_4)_2$,[29] $[Cu(bpy)OH]_2(ClO_4)_2$,[23] and $[Cu(2miz)OH]_2(ClO_4)_2{\cdot}2H_2O$,[35] which have two symmetrical perchlorato bridges positioned above and below the $N_2CuO_2CuN_2$ plane in addition to the two hydroxo bridges, the singlet–triplet splitting varies linearly with the angle at the bridging oxygen according to the relationship

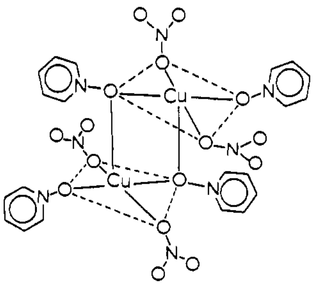

Figure 1. Structure of the parallel-planar dimeric molecule $[Cu(pyNO)_2(NO_3)_2]_2$ as determined by Ščavničar and Matković.

$$E_{ST} = -74.53\ \text{cm}^{-1}\ \text{deg}^{-1}\ (\phi\ \text{deg}) + 7270\ \text{cm}^{-1} \qquad (11)$$

Equation 11 predicts that the singlet–triplet splitting will vanish for a bridge angle near 97.5°. This does not mean that the copper ions in a (yet to be synthesized) bis(μ-hydroxo)-bridged copper compound with this angle will not be exchange coupled, it means that the terms in eq 4 and 5 sum to zero.

If two copper(II) ions were present in a dimeric complex bridged by magnetically insulating ligands with a large copper–copper separation on the order of 10 Å), exchange coupling would be nonexistent, each copper ion would exhibit doublet-state magnetism, and $2J$ would be zero.

Variation of Singlet–Triplet Splitting with Bridge Angle and with Length of Superexchange Pathway. It has now been established that the singlet–triplet splitting varies linearly with the bridge angle in the series of bis(μ-hydroxo)-bridged copper(II) complexes. The other structural features in the $N_2CuO_2CuN_2$ unit remain constant while the bridge angle changes in the series. The two compounds that are the primary subject of this note have parallel-planar rather than coplanar structures. The parallel-planar structure is shown in Figure 1.

Several series of compounds with this general structure, or structures that result from distortions of this structure toward trigonal-bipyramidal geometry, are known. For documentation of the variation of singlet–triplet splittings in compounds with this structure, attention will be focused initially on a series of bis(μ-chloro)-bridged copper(II) dimers. Structural and magnetic data[45–62] for seven such compounds are collected in

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Table II (supplementary material). The short, in-plane copper(II)–chloride bond distance is nearly constant at 2.28 ± 0.05 Å, while the long copper–chloride bond distance varies from 2.45 Å in $[Cu(Guan)Cl_3]_2{\cdot}2H_2O$[57–59] to 3.37 Å in $[Cu(\alpha\text{-pic})_2Cl_2]_2$.[47,48] (The long copper–chloride bond is the out-of-plane bond in compounds with strictly parallel-planar structures, while the long bond is in the quasi-equatorial plane in structures derived from edge-shared trigonal bipyramids.) The angle at the bridging chloride ligand varies from 86.1° in $[Cu(Me_2en)Cl_2]_2$[51] to over 100° in $[Cu(\alpha\text{-pic})_2Cl_2]_2$.[47,48] Yet, the singlet–triplet splitting in these seven compounds varies in a very regular way with the quotient ϕ/R_0, where ϕ is the angle at the bridging chloride ligand and R_0 is the long, out-of-plane copper(II)–chloride bond distance. These data show that the singlet–triplet splitting is dependent on the magnitude of the angle at the bridge as well as the bond length in the superexchange pathway. From orbital-overlap considerations alone it is clear that an increase in bond distance will be accompanied by a decrease in exchange coupling.

Singlet ground state molecules with large $|E_{ST}|$ values exhibit characteristic magnetic susceptibility and triplet-state EPR spectra. There are characteristic deviations from the Curie–Weiss law and maxima in the magnetic susceptibility for $[Cu(tmen)Cl_2]_2$ and $[Cu(Me_2en)_2Cl_2]_2$,[50] thereby establishing exchange coupling in these two members of the series with relatively smaller $|E_{ST}|$ values.

Magnetic susceptibility and magnetization data for $[Cu(dmg)Cl_2]_2$[17] are characteristic of a triplet ground state for this molecule, and exchange coupling has been verified independently.[53] This compound has structural features that place it in the middle of the ϕ/R_0 range, and the trend of E_{ST} with ϕ/R_0 predicts a small, positive value for E_{ST}, as observed.

The chemical periodicity arguments presented here demonstrate that the presence of exchange-coupling phenomena can be verified in systematic studies on structurally and chemically related series of compounds. Furthermore, it is now possible to predict, from structural features, the sign and magnitude of E_{ST} for members of such structurally and chemically related compounds.

Exchange Coupling in Sulfur-Bridged Bimetallic Copper(II) Compounds. Structural and magnetic data exist for only three sulfur-bridged bimetallic copper(II) complexes, those being $[Cu(TCH)Cl_2]_2Cl_2$ (TCH is 1-thiocarbonylhydrazidium(1+)),[63] $[Cu(dedtc)_2]_2$,[64] and α-$[Cu(dbdtc)_2]_2$ (dbdtc is di-*n*-butyldithiocarbamate).[65] These data are collected in Table III (supplementary material), along with data for $[Cu(dmdtc)_2]_2$,[66] which has a uniformly spaced, infinite chain structure. However, before the magnetic data are considered, it is important to establish the existence of exchange coupling in this series of compounds. All except $[Cu(dedtc)_2]_2$ have singlet ground states and characteristic temperature dependencies of magnetic susceptibilities.

The power of EPR spectroscopy in determining spin-state multiplicity is well-known. However, at room temperature and at 77 K the EPR spectra of all of these compounds consist only of broad lines as a result of dipolar broadening. The technique that has been used widely for the study of the EPR spectra of these compounds involves production of crystals of doped materials with either nickel or zinc ions as the major diamagnetic constituent. In the case of the diethyldithiocarbamate compound, the zinc analogue is suitable for these studies, since the zinc analogue has a dimeric structure similar to that of $[Cu(dedtc)_2]_2$.[68] Thus, if crystals of the mixed-metal system $[Cu_xZn_y(dedtc)_2]_2$ (with $x + y = 1$ and $y >> x$) form, there will be a large concentration of $[Zn_2(dedtc)_2]_2$ forming the diamagnetic host with the predominant paramagnetic species being the doublet-state molecule $[CuZn(dedtc)_4]$. Finally, there will be a finite concentration of $[Cu(dedtc)_2]_2$. These molecules will be in a magnetically dilute environment, and portions of their EPR spectra that are not obscured by the doublet-state resonances may be observed and studied. The presence of other chemical species is unlikely. Boyd et al.[65] note that the $[Cu(dedtc)_2]_2$ molecules present in the predominantly $[Zn_2(dedtc)_2]_2$ matrix will probably have different structural features, that is, bond angles and bond distances, than are present in pure $[Cu(dedtc)_2]_2$.

The data presented above show that the singlet–triplet splitting varies in a regular, predictable manner as structural features vary in closely related series of compounds. The theory asserts that many terms that contribute to exchange coupling (see eq 5) do not change appreciably with subtle differences such as those observed in the structures of $[Cu(dedtc)_2]_2$[64] and $[Zn(dedtc)_2]_2$.[68] Thus, if triplet-state EPR spectra are observed in $[Cu_xZn_y(dedtc)_2]_2$, the resonances arise from exchange-coupled copper ions in $[Cu(dedtc)_2]_2$.

Triplet-state EPR spectra of $[CuZn(dedtc)_4]$ have been extensively studied by a number of research groups. In recent work, Manjunath, Santosh, and Srinivasan[69] have used anomalous hyperfine structure in the fine structure of the triplet state to determine the sign of the zero-field splitting tensor, and Al'tshuler, Kirmse, and Solov'ev[70] have determined the singlet–triplet splitting (triplet ground state) from studies of the temperature dependence of the Orbach–Aminov process.

Now consider the periodicity of exchange coupling in the series of sulfur-bridged copper(II) compounds listed above. Three of the compounds exhibit antiferromagnetic exchange-coupling interactions and show characteristic maxima in plots of magnetic susceptibility vs. temperature. The variation of the singlet–triplet splitting with the structural parameter ϕ/R_0 follows the trend established for chloro-bridged complexes.

There are a number of important points: (1) The out-of-plane copper–sulfur bond distance in $[Cu(dedtc)_2]_2$ is the shortest bond distance yet observed for sulfur-bridged copper dimers.[63,65,66] (2) All other structurally characterized sulfur-bridged copper dimers exhibit exchange coupling.[10,65,67] (3) The terms that define exchange coupling do not change appreciably with subtle structural changes.[9] (4) Triplet-state EPR spectra are well characterized for $[Cu(dedtc)_2]_2$ in host lattices.[69,70] These facts lead to the conclusion that the copper(II) ions are exchange coupled in the dimeric sulfur-bridged compound $[Cu(dedtc)_2]_2$.

There is one final point concerning exchange-coupled copper ions in $[Cu(dedtc)_2]_2$, and that concerns the magnitude of the singlet–triplet splitting. Al'tshuler, et al.[70] deduced a value of 13 (1) cm^{-1}, while we obtained a value of 24 cm^{-1} from magnetic susceptibility data.[4] In view of the structural differences expected for $[Cu(dedtc)_2]_2$ in the mixed crystal $[CuZn(dedtc)_4]$ and in the pure compound, and the known variations of the singlet–triplet splitting with molecule structural changes, this is not a disturbing difference. Furthermore,

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singlet–triplet splittings from magnetic susceptibility and magnetization studies on triplet-state systems have large ranges of uncertainties.

I have remeasured the magnetic susceptibility of a powdered sample of $[Cu(dedtc)_2]_2$ in the temperature range 4.2–27.3 K and have compared the data obtained for this study with data reported in 1971 by Villa and Hatfield.[5] Data in this temperature range should be most sensitive to changes in state populations. There is very good agreement between the data obtained earlier in my laboratory and the new data with the expected field dependence being observed.[6]

Exchange Coupling in the Triplet Ground State Molecule Bis(μ-pyridine *N*-oxide)bis[bis(nitrato)(pyridine *N*-oxide)copper(II)]. Pyridine *N*-oxide complexes of copper(II) salts have long been of interest.[71–73] A structural determination of the parent member of the series, $[Cu(pyNO)Cl_2]_2$,[74] revealed that the copper(II) ions were bridged by pyridine *N*-oxide ligands. Watson and co-workers[75,76] reviewed the structure and magnetic data available in 1969 for pyridine *N*-oxide complexes of copper(II) salts and commented on the existence of dimeric complexes with normal magnetic moments.

The compound of immediate interest here is $[Cu(pyNO)_2(NO_3)_2]_2$, which is known from single-crystal X-ray diffraction structural studies to have the dimeric, parallel-planar structure shown in Figure 1.[77] Each plane consists of mutually trans-coordinated pyridine *N*-oxide and nitrato ligands with short copper–oxygen bonds (1.94–1.98 Å) with the long out-of-plane bond being 2.439 Å, and the Cu–O–Cu′ bridge angle is 102.9°.[77]

Subsequently, crystals of the mixed-metal system $[Cu_xZn_y(4\text{-R-pyNO})_4(NO_3)_4]$ (R = H, CH_3, OCH_3) were studied by EPR spectroscopy,[14] and triplet-state lines were observed in the half-field region, in the low-field parallel region (near 2260 G), and in a high-field region near 3500 G). Hyperfine structure was observed on the half-field and fine-structure lines of $[Cu(pyNO)_2(NO_3)_2]_2$ present in a matrix of predominantly diamagnetic $[Zn(pyNO)_2(NO_3)_2]_2$. Relatively intense lines from $[CuZn(pyNO)_4(NO_3)_4]$ obscured a portion of the triplet-state spectrum, but careful manipulation of rotation spectra of single crystals permitted an examination of important features of the triplet spectra. The triplet-state spectra were analyzd in terms of the spin Hamiltonian

$$\mathcal{H}_{S'} = g_{\parallel}\mu_B H_z S_z' + g_{\perp}\mu_B(S_x'H_x + S_y'H_y) + D(S_z'^2 - 2/3) + A(S_{1z}I_{1z} + S_{2z}I_{2z}) + B(S_{1x}I_{1x} + S_{1y}I_{1y} + S_{2x}I_{2x} + S_{2y}I_{2y})$$

with the spin Hamiltonian parameters $g_{\parallel} = 2.275$ (5), $g_{\perp} = 2.07$ (1), $|D| = 0.073$ (1) cm^{-1}, $|A| = 0.0130$ (2) cm^{-1}, and $|B| = 0.0040$ (4) cm^{-1}. Comparable spectra and spin Hamiltonian parameters were obtained for the 4-methylpyridine *N*-oxide analogue. Although the EPR spectra for the 4-methoxypyridine *N*-oxide analogue were less well resolved, the half-field line at about 1600 G was clearly visible.[14]

Magnetic susceptibility and magnetization studies have been carried out on $[Cu(4\text{-R-pyNO})_2(NO_3)_2]_2$, where R = H, CH_3, and OCH_3.[14] Since the triplet state and exchange coupling were known from EPR studies to be extant in these complexes, the magnetic susceptibility and magnetization data were analyzed in terms of singlet and triplet states. The data for $[Cu(pyNO)_2(NO_3)_2]_2$ and $[Cu(4\text{-MepyNO})_2(NO_3)_2]_2$ revealed positive exchange-coupling constants and triplet ground states, while the data for the methoxypyridine *N*-oxide analogue were consistent with a single ground state.

There is additional experimental evidence for the continuum in exchange coupling from positive to negative exchange-coupling constants as measured by singlet–triplet splittings. Kahn and co-workers[78,79] have shown that it is possible to design systems with $J_{AF} = 0$ (see eq 5) and in this manner have measured $J = J_F = J_{max}$.

The various terms that contribute to the singlet–triplet splitting in dimeric copper(II) acetate monohydrate as a result of exchange coupling have been considered recently in an ab initio calculation by de Loth et al.[80] These authors present a development of superexchange interactions introduced by Anderson[81] as well as higher order contributions including polarization of the ligands and closed shells. Summation of the various terms involved in the exchange process leads to a singlet–triplet splitting consistent with that which is experimentally observed. An examination of the rigorous ab initio development provides further support for the thesis of this note.

Experimental Section

Magnetic susceptibility data were collected on a powdered sample of $[Cu(dedtc)_2]_2$ with use of a Princeton Applied Research Model 155 vibrating-sample magnetometer and procedures that have been described elsewhere.[82]

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Registry No. $[C_4(pyNO)_2(NO_3)_2]_2$, 26507-58-4; $[Cu(dedtc)_2]_2$, 33939-19-4.

Supplementary Material Available: Listings of structural and magnetic properties of bis(μ-hydroxo)- (Table I), bis(μ-chloro)- (Table II), and sulfur-bridged copper(II) compounds (Table III) (4 pages). Ordering information is given on any current masthead page.

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Kinetics and Mechanism of the Complex Formation between Aluminum(III) and Some (Salicylato)pentaamminecobalt(III) Ions

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Previous studies have dealt with the kinetics of the reversible formation of the binuclear species of Fe(III) with (oxalato)pentaamminecobalt(III)[1] ($(NH_3)_5CoO_2CCO_2Fe^{4+}$) and (salicylato)pentaamminecobalt(III)[2] ions ($N_5CoO_2CC_6H_4OFe^{4+}$; N_5 = 5 NH_3, $(en)_2(NH_3)$, and tetraethylenepentamine). Evidence has been presented that supports our earlier views that Fe^{3+} is chelated by the oxalate and salicylate

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