

liquid just above its melting point, it is likely that many of the nickel atoms are already present in the form of small molecular clusters (2-10 or more atoms) prior to melting. These may form because of surface diffusion of the metal atoms during codeposition or bulk diffusion on matrix warm-up. Ozin and co-workers have extensively investigated these factors in the formation of dimers and higher oligomers of transition metals in inert matrices.^{24,25} Vanadium, for example, shows evidence of appreciable dimerization due to surface diffusion in CH₄ matrices during deposition at 10-12 K under conditions of

quite high dilution²⁵ (V:CH₄ = 1.5:1000). In general, it was found that bulk diffusion becomes important at temperatures around one-third of the matrix melting point.²⁵ On the basis of this criterion, a large fraction of the nickel atoms must be present in oligomeric form at the melting point of toluene. Since matrix decomposition becomes important only in the liquid phase, and on heating to room temperature, some degree of control of cluster and microcrystallite size might be possible by appropriate choice of solvent to enhance both surface and bulk diffusion rates in the solid during codeposition and subsequent warm-up of the metal/matrix phase.

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Exchange Coupling in Copper Dimers with Purine Ligands

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The EPR spectra of a series of dimeric copper complexes with purine ligands have been investigated to determine dipolar splittings and exchange energies. The copper atoms in these complexes are coordinated to the nitrogen atoms in the purine rings in each case but have different axial ligands. The metal-metal separations and dipolar couplings are similar in this group of molecules, but there are large differences in the exchange energies. The variation in exchange energy with the nature of the axial ligand can be explained by a mechanism involving mixing of the d_{z^2} and $d_{x^2-y^2}$ orbitals with overlap of the d_{z^2} orbitals of the two copper atoms.

Introduction

There are a variety of biologically important transition-metal complexes which contain more than one metal atom per molecule. The magnetic properties of such complexes depend on the exchange coupling of the metal atoms. The exchange interaction varies with the separation of the metal atoms, with the relative orientation of the orbitals of the metal atoms, and with the nature of the ligands surrounding the metal atoms.¹ If one considers complexes in which each metal atom has a single electron spin, the Hamiltonian operator describing the Zeeman, hyperfine, dipolar, and exchange interactions is given by eq 1. In this expression the A_i 's are the electron-nuclei

$$\mathcal{H} = g\beta HS_z + \sum_i A_i S_{iz} I_{iz} + D[S_z^2 - \frac{1}{3}S^2] + E[S_x^2 - S_y^2] + JS_1 \cdot S_2 + S_1 D_e S_2 \quad (1)$$

hyperfine coupling constants, D and E are constants describing the dipolar interaction, J is the isotropic exchange energy, and D_e is the anisotropic exchange energy.^{2,3} The anisotropic exchange term arises from spin-orbit coupling, and the magnitude of this term is dependent on the symmetry of the

crystal. If the two metal atoms in a copper dimer are located at points A and B, respectively, and the point bisecting the line AB is denoted by C, the anisotropic term is zero when C is a center of inversion for the complex.² Point C was a center of inversion for all of the complexes reported in this study, and the observed anisotropic splitting of the EPR spectra arises entirely from the dipolar interaction. If the electron spins are considered to be point dipoles, one can obtain an estimate of the separation of metal atoms (r) from the dipolar splitting in the EPR spectrum as in eq 2. The point-dipole approxi-

$$D = \frac{3}{2}(\mu/r^3) \quad (2)$$

mation is an oversimplification for copper complexes and should not give exact distances but does provide a reasonable comparison of changes in electron-electron separations within a series of similar complexes.

The exchange interaction for complexes of this type splits the energy level into singlet and triplet states. The Hamiltonian for the exchange interaction is given by eq 3. The

$$J = \iint (\psi_a(1))(\psi_b(2)) |H_{ex}| (\psi_b(1))(\psi_a(2)) d\tau_1 d\tau_2$$

$$H_{ex} = \frac{e^2}{r_{12}} + \frac{Z_a^* Z_b^* e^2}{R} - \frac{Z_b^* e^2}{r_{1b}} - \frac{Z_a^* e^2}{r_{2a}} \quad (3)$$

exchange interaction may result from direct overlap of the metal atoms' d orbitals or may involve orbitals in the coordinated ligands. In cases in which direct overlap of the d orbitals dominates the exchange interaction, the magnitude of this interaction will vary with the separation and orbital orientation of the metal atoms and with the crystal field

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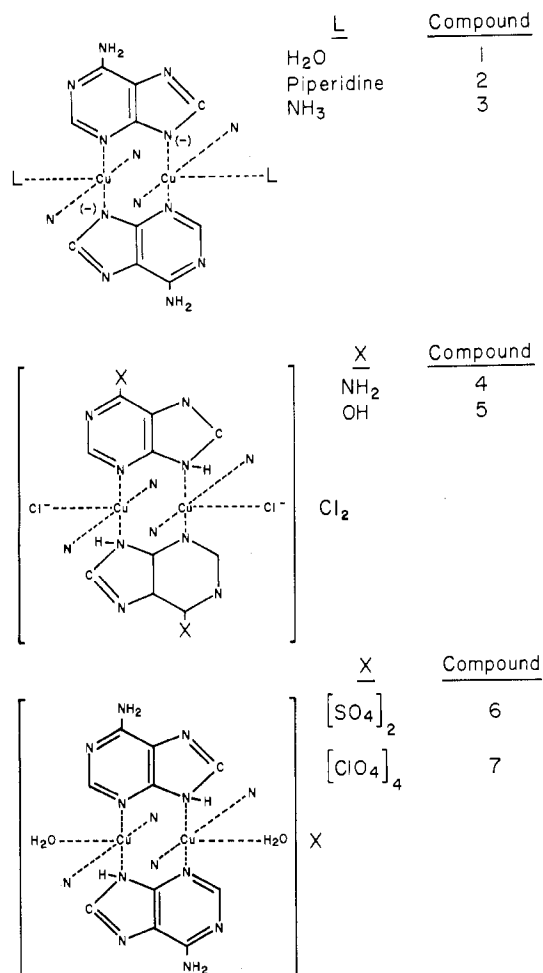


Figure 1. Structures of compounds investigated.

splitting of the energy levels. Exchange coupling through bonded ligands is a longer range process involving orbitals on both the metals and the ligands. For this process to be efficient the metal and ligand orbitals must have the correct symmetries and relative orientations.

The separation of the singlet and triplet states in an exchange-coupled metal dimer is given by $2J$. If $2J \gg kT$, all of the molecules may be in either the ground singlet or triplet states depending on the sign of J . When $2J \approx kT$, the magnetic susceptibility of the complex reflects the Boltzmann population of the states. When this is the case, the temperature dependence of the susceptibility (χ_m) is given by eq 4.⁴ For

$$\chi_m = \frac{2g^2\beta^2N}{3kT} \left[\frac{1}{1 + \frac{1}{3} \exp(-2J/kT)} \right] \quad (4)$$

cases in which the complex is a ground-state singlet with a thermally accessible triplet state, the susceptibility passes through a maximum as the temperature is lowered and decreases to zero as the population in the triplet state goes to zero. The magnitude of the exchange energy may be determined from a fit of experimental data to eq 4 or may be estimated from the position of the maximum (T_{\max}) in a plot of the temperature dependence of the susceptibility as $J = 1.6kT_{\max}$.

We have studied a series of copper complexes in which two copper atoms are held relatively close to one another through coordination to the nitrogen atoms in purine rings. The

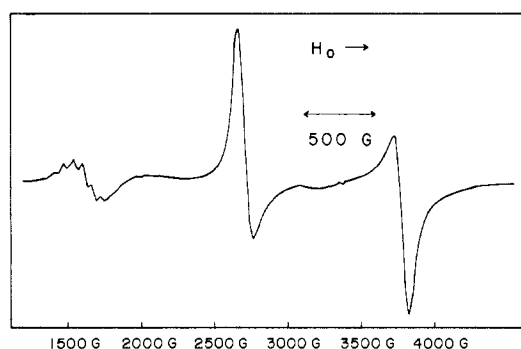


Figure 2. EPR spectrum of compound 7 ($[\text{Cu}_2(\text{Aden})_4(\text{H}_2\text{O})_2] \cdot (\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$) at -147°C .

structures of these complexes are shown in Figure 1. Two types of complexes have been investigated. In the first series of complexes, a proton has been removed from the 9-position to yield a charged adenine (Aden) ring. Axial ligands in this series include water, ammonia, and piperidine (Pip). In the second series of compounds, the purine ring is neutral and the axial ligand is either water or chloride. Both adenine and hypoxanthine (Hypox) complexes were studied with chloride as the axial ligand. Two adenine complexes with water as the axial ligand with outer-sphere sulfate or perchlorate ions were also investigated. Electron paramagnetic resonance studies of this group of complexes allowed us to obtain values for dipolar splittings, electron–electron separations, and exchange energies. This series of complexes was selected to allow us to determine the effect of small changes in the coordination on the exchange energies. The changes in exchange energies which are observed can be accounted for by perturbations of the ligand field splitting on variation of the ligands surrounding the copper atoms.

Experimental Section

(a) **Complexes.** All of the complexes except compounds 2 and 3 have previously been synthesized.⁵ Compounds 2 and 3 were made by a technique similar to that used to synthesize complex 1. A basic solution of adenine and CuSO_4 was added to a large excess of the appropriate base to make these complexes. All of the complexes precipitated directly from the reaction mixture and were filtered, washed, dried, and used without further purification. The complexes are extremely insoluble in most solvents, and attempts at recrystallization resulted in exchange of the axial ligands. Polycrystalline solids were used for all of the EPR studies. The EPR spectra of all of the complexes were similar (Figure 2), showing the characteristic dipolar splitting characteristic of triplet-state molecules. A signal at $g = 2$ from a doublet-state impurity was observed from some of the complexes. The appearances of all of the spectra were identical except for the relative intensities of the $\Delta m = 1$ transitions of the triplet-state molecules to that of the doublet-state impurity.

(b) **EPR Measurements.** The EPR spectra were taken with a JEOL 3BSX EPR spectrometer utilizing 100-kHz field modulation. The frequency of the instrument (~ 9.05 GHz) was measured with a Hewlett-Packard 5345 A frequency meter with a 5255 A 3–12-GHz plug-in. A Varian X-13 klystron was used in the spectrometer and run at a beam voltage of about 500 V. We were unable to saturate the EPR signals of any of the complexes with the power available from this klystron. We estimated the power at the sample to be about 20 mW, but power measurements were not made. The magnetic field scan was calibrated by measuring the separation of the lines in a solution of vanadyl acetylacetonate.⁶ DPPH was used as a reference for g -value determinations. The temperature was varied by blowing a stream of heated or cooled nitrogen gas over the sample. The temperature was monitored with a copper–constantan thermocouple placed directly below the sample which was calibrated against a

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Table I. Values for Exchange Energies, Dipolar Constants, and Distances

no.	compd	$2J,^a \text{ cm}^{-1}$	$2J(\text{estd}),^b \text{ cm}^{-1}$	$D,^a \text{ G}$	$r, \text{ \AA}$	$r(\text{Lit.}), \text{ \AA}$	g
1	$[\text{Cu}_2(\text{Aden}^-)_4(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$	-179	-178 ^c	1383	2.75	2.949 ^d	2.073
2	$[\text{Cu}_2(\text{Aden}^-)_4(\text{Pip})_2] \cdot 6\text{H}_2\text{O}$	-246	-233	1499	2.68		
3	$[\text{Cu}_2(\text{Aden}^-)_4(\text{NH}_3)_2] \cdot 6\text{H}_2\text{O}$		-247	1401	2.74		
4	$[\text{Cu}_2(\text{Aden})_4(\text{Cl}_2)] \text{Cl} \cdot 6\text{H}_2\text{O}$	-285	-279	1307	2.81	3.066 ^e	2.081
5	$[\text{Cu}_2(\text{Hypox})_4(\text{Cl}_2)] \text{Cl}_2 \cdot 6\text{H}_2\text{O}$	-211	-236	1111	2.96	3.024 ^e	2.068
6	$[\text{Cu}_2(\text{Aden})_4(\text{H}_2\text{O})_2] (\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	-305	-281	1272	2.83		2.075
7	$[\text{Cu}_2(\text{Aden})_4(\text{H}_2\text{O})_2] (\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	-312	-270 ^c	1299	2.86	2.951 ^f	2.173

^a The errors in $2J$ from nonlinear least-squares fits are $\pm 7 \text{ cm}^{-1}$. The errors in D are $\pm 5 \text{ G}$. ^b Values of $2J(\text{estd})$ were obtained from the maximum in the susceptibility curves and $2J(\text{estd}) = 1.6kT_{\text{max}}$. ^c Values of $2J$ for compound 1 previously reported are -210 cm^{-1} ¹⁵ and -160 cm^{-1} .¹⁶ A value of -300 cm^{-1} has previously been reported for compound 7.¹⁶

thermocouple placed in the sample cavity. Ten to fifteen minutes was allowed for the samples to equilibrate at each temperature.

The areas of the EPR signals are proportional to the magnetic susceptibilities of these complexes, and the areas were used to monitor the temperature dependence of the susceptibilities. The area of the EPR is proportional to the product of intensity of the signal and the line width squared. Both the intensity and the width of these complexes varied with changes in temperature (the lines became narrower at lower temperature), and both terms had to be measured to determine the temperature dependence of the area. A series of theoretical spectra with varying dipolar constants and line width were calculated with a Digital Equipment Corp. PDP-10 computer to determine the effect of line-width changes on spectral appearance. The spectra were calculated with a dipolar Hamiltonian and a powder distribution for the angular dependence. A Lorentzian line shape was assumed. The theoretical spectra were double integrated to confirm the intensity \times (line width)² dependence of the areas. The line widths were found to be proportional to the half-width of the $\Delta m = 1$ transitions at half-height. Small changes in instrumental conditions can affect the areas of the signals over the period of time necessary to obtain spectra at a series of different temperatures. The EPR spectrum of a sample of $\text{Cu}(\text{Gly})_2 \cdot \text{H}_2\text{O}$, whose susceptibility is known to follow the Curie-Weiss law over the temperature range investigated, was taken at each temperature. Instrumental variations with temperature were accounted for by using the area of this sample to standardize the areas of the signals from the other metal complexes. We estimate about a 5% error in our area measurements by using these procedures.

The dipolar splittings reported in Table I were determined by measuring the separation of the $\Delta m = 1$ transitions. The values of the exchange energies were determined with a nonlinear least-squares fit of the temperature dependence of the areas to eq 4. These fits yield an error limit for the exchange energies of about $\pm 7 \text{ cm}^{-1}$.

Results and Discussion

The EPR spectra of all of the complexes showed the $\Delta m = 1$ and $\Delta m = 2$ transitions characteristic of triplet states with nearly axial symmetry ($E \approx 0$) (Figure 2). The anisotropic exchange term vanishes because of the symmetry of these complexes, and the spectra can be accounted for by the dipolar interaction between the two electron spins. Values for the dipolar splitting (D) and distances calculated with the point-dipole approximation are listed in Table I. The structures of most of the complexes have been determined by X-ray crystallography.⁷⁻¹⁰ Copper-copper separations from the crystal structure determinations are also listed in Table I. The distances from the crystal structure determinations differ from those determined from the EPR spectra by between 0.06 and 0.26 \AA . The EPR measurements give the average separation of the spins while X-ray determinations give the distance between the metal nuclei. The differences in distances measured by EPR and by X-ray crystallography probably reflect the difference between the average position of the spin in a d orbital and the metal nucleus as well as some error in the EPR measurement. Average g values were measured for most of the complexes and are listed in Table I. The g anisotropy

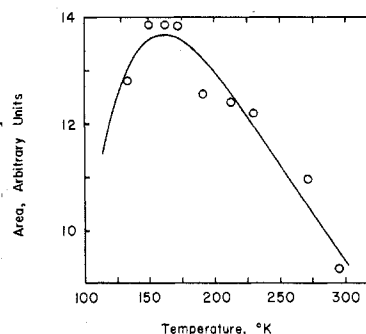


Figure 3. Temperature dependence of the EPR signal area of compound 1 ($[\text{Cu}_2(\text{Aden}^-)_4(\text{H}_2\text{O})_2] \cdot 6\text{H}_2\text{O}$). The solid line is the least-squares fit to the experimental data.

for these complexes is less than the width of the $\Delta m = 1$ transitions, and we were unable to measure the magnitude of the g tensor's components. The averaged g values which were determined varied slightly with the nature of the complex in most cases. The only complex which showed a significantly different g value was 7, which has perchlorate ligands. This g variation may indicate some contribution of the perchlorate ligands to the orbital angular momentum of the complex.

The X-ray structures of these complexes show that the nitrogen atoms in the purine ligands form nearly a square plane (very small orthorhombic distortion) with the axial ligands above to form a tetragonal pyramid. The copper atom is above the plane formed by the purine nitrogens by about 0.3 \AA . The second copper atom in the complex can be thought of as occupying the sixth coordination site. The unpaired spin is in the $d_{x^2-y^2}$ orbital which points toward the nitrogen atoms in the purine ligands while the d_z orbital points toward the axial ligand and the second copper atom.

The temperature dependence of the magnetic susceptibility was monitored through measurements of changes in the area of the ESR signal with temperature. A plot of signal area vs. temperature for compound 1 is shown in Figure 3. Values for exchange energies were determined by nonlinear least-squares fits of eq 4 to the experimental data and by measurement of the position of the maxima in the susceptibility curves. The data obtained from compound 3 were rather poor because of overlap of the signal from the complex with a doublet-state impurity. We were unable to obtain a good least-squares fit for this complex, and as a consequence, only the exchange energy from the susceptibility maximum is reported. All of the complexes were found to be ground singlet states with thermally accessible triplet states. The complexes with the charged adenine ligands are found to have the lowest exchange energies while the complexes with axial chlorides have intermediate values, and the complexes with axial waters have the highest values for the exchange energy.

The exchange interaction may result from a direct interaction of the metal atoms' d orbitals or may involve atoms in the ligands. Both models have been used to explain the results from earlier studies of copper dimers with carboxylic acid

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ligands.¹¹⁻¹³ The unpaired electron spin in the complexes we have studied and in the carboxylic acid dimers is in the $d_{x^2-y^2}$ orbital. The exchange interaction depends on overlap of orbitals, and the $d_{x^2-y^2}$ orbitals which lie in the plane formed by the ligand atoms do not overlap efficiently. The d_{z^2} orbitals of these complexes overlap more efficiently but are doubly occupied and must be mixed with the $d_{x^2-y^2}$ orbital to provide a mechanism for the exchange interaction. If ligand orbitals are involved in the exchange mechanism, the $d_{x^2-y^2}$ orbital of the first copper atom must initially mix with an orbital from a ligand atom, this ligand atom orbital must mix with an orbital on a ligand atom bound to the second copper, and this ligand orbital must mix with the $d_{x^2-y^2}$ orbital on the second copper atom.

The results from our studies of the copper-purine complexes can be adequately explained by interactions involving the d orbitals of the metal atoms. The observed exchange energies vary systematically with the axial ligands and the charge of the purine rings in these complexes. Variation of the axial ligands should have little effect on a mechanism involving exchange through the ligands but should affect the relative energy separations of the $d_{x^2-y^2}$ and d_{z^2} orbitals of the metals. The magnitude of the exchange interaction will depend on both the overlap of the d_{z^2} orbitals, which is a function of the separation of the metal atoms, and the mixing of the d_{z^2} and $d_{x^2-y^2}$ orbitals, which is a function of the energy separation of these orbitals. Variations in the crystal field surrounding the copper atoms will affect the relative energy separation of the $d_{x^2-y^2}$ and d_{z^2} orbitals and thereby affect the magnitude of the exchange interaction. The separation of the copper atoms is relatively constant in this series of complexes, and variations in the exchange energies appear to result mainly from changes in the relative energy separation of the $d_{x^2-y^2}$ and d_{z^2} orbitals.

The adenine complexes in which a proton has been removed from the nitrogen atom (compounds 1-3) show systematic variations in the exchange energy as a function of the axial ligand. Complex 1 has water as an axial ligand and is expected to have the maximum tetragonal distortion and the largest separation between the d_{z^2} and $d_{x^2-y^2}$ levels. This compound has the smallest exchange energy. In compounds 2 and 3 the axial water is replaced by piperidine and by ammonia. The tetragonal distortion is less in these complexes, and one observes an increase in the magnitude of the exchange energy in proportion to the strength of the axial ligand. The second series of compounds (complexes 4 and 5) have neutral adenines and chloride as an axial ligand. The adenine complex (compound 4) has a larger exchange energy than compound 2 or

3, indicating less tetragonal distortion. One predicts less distortion in this complex as the adenine rings are neutral. The hypoxanthine complex (compound 5) has a smaller exchange energy than compound 4. This decrease in exchange energy can be accounted for by the 0.15-Å increase in the separation of the spins. The final group of complexes (compounds 6 and 7) have neutral adenine ligands with water as the axial ligand while the anions are in an outer sphere. These complexes have the largest exchange energies, indicating the smallest tetragonal distortion and most efficient mixing of the $d_{x^2-y^2}$ and d_{z^2} orbitals. A similar dependence of exchange energy on the nature of the axial ligand has been observed from dimeric copper complexes with carboxylic acid ligands,¹¹ and these results might be explained by a similar mechanism for exchange.

The copper atoms in the carboxylic acid dimers are about 0.4 Å closer than in the complexes we have studied, but the exchange energies cover about the same range of values. If exchange in these complexes is through a mechanism involving the d_{z^2} and $d_{x^2-y^2}$ orbitals, the mixing of the orbitals must be less efficient than that of the copper-purine complexes. In a more recent study of a chloride-bridged dimer of copper-guanine an exchange energy of -99 cm^{-1} and a copper-copper separation of 3.6 Å have been reported.¹⁴ Exchange through the chloride-bridging ligands appears to be inefficient in this complex, and the small value of $2J$ is explained by the relatively large separation of the copper atoms.

Conclusions

Electron paramagnetic resonance studies of a series of copper-purine complexes with various axial ligands have allowed us to determine dipolar couplings, average spin separations, and exchange energies. The exchange energies are found to vary systematically with the nature of the axial ligands and the charge of the purine nitrogens. The variation of the exchange energy with changes in the axial ligand is explained by a mechanism involving overlap of the d_{z^2} orbitals and mixing of this orbital with the $d_{x^2-y^2}$ orbital. The mixing of these levels depends on their energy separation which varies with the nature of the ligand. The observed changes in the exchange energies with structure can be explained by variations in the separation and mixing of these levels in cases in which the spin separation is relatively constant.

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