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Magnetic Properties of a Pyrazine-Bridged Dinuclear Copper(II) Compound. X-ray Structure of $\{\mu\text{-}2,5\text{-Bis}[(\text{dimethylamino})\text{methyl}]\text{pyrazine}\}\text{bis}[(\text{diethylenetriamine})\text{copper(II)}]\text{Perchlorate}$

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The crystal structure and magnetic properties of $[\text{Cu}_2(\text{dapz})(\text{dien})_2](\text{ClO}_4)_4$, where dapz is 2,5-bis[(dimethylamino)methyl]pyrazine and dien is diethylenetriamine, are described. The compound crystallizes in the monoclinic space group $P2_1/a$ with $a = 15.441(3)$ Å, $b = 14.519(2)$ Å, $c = 7.954(2)$ Å, $\beta = 100.15(2)^\circ$, $V = 1755.4(6)$ Å³, and $\rho_{\text{calcd}} = 1.751$ g/cm³ for $Z = 2$. The structure was solved by a heavy-atom technique and refined by least-squares methods to give conventional discrepancy factors of $R = 0.039$ and $R_w = 0.042$ for 3197 observed ($|F_o| > 3\sigma|F_o|$) reflections. The compound is a ClO_4^- salt of a pyrazine-bridged, centrosymmetric Cu(II) dimeric cation. The copper atom is coordinated by five nitrogen atoms, forming a distorted trigonal-bipyramidal geometry. An antiferromagnetic interaction was deduced from magnetic susceptibility and EPR measurements that show the $\Delta m = 2$ transition at 1600 G, and the interaction is weak ($J = -1.7$ cm⁻¹ and $g = 2.106$) in spite of the fact that the unpaired electron, which resides in the d_{z^2} orbital, is almost directed at the nitrogen atom of bridged pyrazine ligand. From the extended Hückel MO studies for pyrazine- and triazole-bridged copper (II) complexes, in which the latter complex shows a substantial antiferromagnetic interaction (-112 cm⁻¹),¹ it is suggested that direct or through-ligand charge-transfer interaction between metal ions plays an important role in the propagation of an magnetic superexchange interaction in addition to the σ -orbital pathway.

Introduction

In the past few decades, metal-metal interactions through single or polyatomic bridging units have been the subject of many investigations.

Dinuclear copper(II) complexes bridged by hydroxo²⁻⁶ or alkoxo⁷⁻⁹ groups show antiferromagnetic or ferromagnetic interactions depending on the bridging structures. Hoffmann et al.¹⁰ interpreted the superexchange mechanism to be related to the bridging angle (Cu-O-Cu) by extended Hückel MO calculations. The metal-metal interaction through an imidazolite bridge has been extensively studied due to the interest of this bridging site in the enzyme superoxide dismutase.¹¹⁻¹⁸ Hendrickson et al.¹¹ suggested that both the extent of overlap and energy difference of metal d_{z^2} orbitals with the σ orbitals of bridging atoms determine the magnitude (the J value) of the magnetic interaction. Lippard et al.¹⁵ also suggested the importance of overlap of the d_{z^2} and σ orbitals of the nitrogen atom of the imidazolite and concluded that the difference in angle between the Cu-N(imidazolite) vectors is the important factor in determining the J value. Kolks et al.¹⁶ pointed out that the magnitude of the coupling constant

is proportional to the pK_a 's of the imidazolite groups when the exchange interaction is mediated by a ligand σ -electron pathway; that is, a decrease in energy separation between the d and σ orbitals, which results from the coordination of the ligand with the higher pK_a , leads to an increase in J .

Since Creutz and Taube¹⁹ first reported the mixed-valence complex $[(\text{NH}_3)_5\text{Ru}(\text{pyrazine})\text{Ru}(\text{NH}_3)_5]^{5+}$, metal-metal interactions through a bridging ligand have been our main focus. It is evident that electronic interaction between the two metal centers through the pyrazine ligand does exist, and this interaction was interpreted as a π back-donation of metal $d\pi$ electrons to an antibonding orbital of the bridging pyrazine ligand. Magnetic interactions through the bridging pyrazine ligand were also studied in dinuclear and polynuclear copper(II) complexes,²⁰⁻²² and these complexes showed very weak antiferromagnetic interactions. Hendrickson²⁰ concluded that the direction of magnetic orbitals to the bridging pyrazine ligand is important in both π and σ type exchange pathways.

Recently, Chaudhuri²³ reported a dinuclear complex bridged by a terephthalato group, which showed substantial antiferromagnetic interaction ($J = -70$ cm⁻¹) in spite of the Cu...Cu intermolecular separation of 11.252 Å. It is necessary to know the mechanism of magnetic and electronic interactions between metal centers through an organic ligand. We decided to clarify why the magnetic or electronic interaction is weak in the case of the copper(II) dinuclear complexes with pyrazine as the bridging ligand, which helps to account for the magnetic superexchange mechanism through the organic ligand. This paper describes the synthesis, crystal structure, magnetic properties, and extended Hückel MO (EHMO) calculations for dinuclear copper(II) complexes with pyrazine as the bridging ligand.

Experimental Section

Compound Preparation. The ligand 2,5-bis[(dimethylamino)methyl]pyrazine (dapz) was synthesized by refluxing a mixture of dimethylamine hydrochloride (Wako) (0.2 g, 0.51 mmol) and Na_2CO_3 (0.53 g, 5 mmol) in freshly distilled acetonitrile (300 mL) with an addition of 2,5-bis(bromomethyl)pyrazine²⁴ in acetonitrile (100 mL) for 2 h under stirring. After the mixture was cooled to room temperature, the

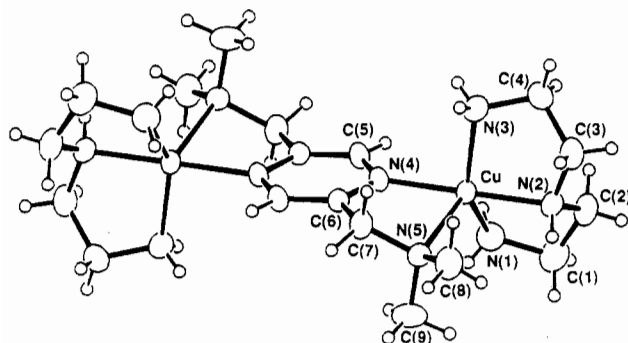
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Table I. Crystallographic Data for $[\text{Cu}_2(\text{dapz})(\text{dien})_2](\text{ClO}_4)_4$

$\text{C}_{18}\text{H}_{44}\text{Cl}_4\text{Cu}_2\text{N}_{10}\text{O}_{16}$	space group: $P2_1/a$ (No. 14)
$\text{fw} = 925.507$	$T = 20^\circ\text{C}$
$a = 15.441(3) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 14.519(2) \text{ \AA}$	$\rho = 1.751 \text{ g cm}^{-3}$
$c = 7.954(2) \text{ \AA}$	$\mu = 16.46 \text{ cm}^{-1}$
$\beta = 100.15(2)^\circ$	transm coeff = 0.909–0.898
$V = 1755.4(6) \text{ \AA}^3$	$R^a = 0.039$
$Z = 2$	$R_w^b = 0.042$

$^a R = \sum(|F_o| - |F_c|) / \sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

**Figure 1.** ORTEP diagram of $[\text{Cu}_2(\text{dapz})(\text{dien})_2]^{4+}$ with 50% probability ellipsoids.

insoluble solid was filtered off and the filtrate was evaporated to dryness. The crude product was redissolved in CHCl_3 and purified by alumina column chromatography with $\text{CHCl}_3/\text{MeOH}$.

The coordination compound was prepared by adding 1 mmol of dapz in methanol to a mixture of copper chloride (2 mmol) and dien (Wako) (2 mmol) in methanol followed by addition of sodium perchlorate. The blue crystals were filtered off, washed with methanol, and recrystallized in an acetonitrile and methanol mixture.

Magnetic Measurements. EPR spectra of a powdered sample were obtained with a JEOL FE2XG X-band (100-kHz field modulation) spectrometer. The microwave frequency was measured with a Takeda Riken 5201 frequency counter, and the magnetic field values of the signals were measured with an Echo Denshi EFM 2000 instrument. Variable-temperature dependence of magnetic susceptibilities on powdered samples was measured by an Oxford Faraday-type magnetic balance system equipped with a superconducting magnet. Temperature readings were calibrated with a magnetic thermometer by the use of $\text{Cr}(\text{NH}_3)_6\text{Cl}_3$. All data were corrected for diamagnetism²⁵ and TIP (120×10^{-6} cgsu per dinuclear complex). Least-squares fitting of the magnetic susceptibility to a Bleaney–Bowers equation²⁶ was performed with the least-squares computer program SALS.²⁷

Molecular Orbital Calculations. Calculations for dinuclear copper(II) complexes were carried out with the extended Hückel method.^{28,29} The basis set parameters were taken from refs 10 and 30. The geometries used for calculation will be mentioned in the text. Molecular orbital calculations for organic molecules were performed by using the MNDO method.^{31–33}

Data Collection and Processing. Crystals of $[\text{Cu}_2(\text{dapz})(\text{dien})_2](\text{ClO}_4)_4$ were grown by slow evaporation of an acetonitrile solution. A blue crystal ($0.34 \times 0.07 \times 0.1$ mm) was attached to the end of a glass fiber and mounted on a Rigaku AFC-5R four-circle diffractometer. Crystallographic data and data collection parameters are summarized in Table I. Intensity data were obtained by use of an ω - 2θ scan using graphite-monochromated Mo $K\alpha$ radiation: 11 031 reflections ($2^\circ < 2\theta < 65^\circ$; $-21 < h < 21$, $-20 < k < 20$, $0 < l < 11$) were measured, of which 3197

Table II. Positional ($\times 10^5$ for Copper; $\times 10^4$ for Other Atoms) and Equivalent Isotropic Thermal Parameters (\AA^2) for $[\text{Cu}_2(\text{dapz})(\text{dien})_2](\text{ClO}_4)_4$

	x	y	z	B_{eq}^a
Cu	44263 (2)	21995 (2)	9079 (5)	2.2
N(1)	3734 (2)	2459 (2)	-1484 (4)	3.3
N(2)	4043 (2)	3474 (2)	1435 (4)	2.8
N(3)	5579 (2)	2555 (2)	2453 (4)	3.0
N(4)	4820 (2)	907 (2)	318 (3)	2.3
N(5)	3645 (2)	1330 (2)	2431 (3)	2.3
C(1)	3310 (2)	3379 (3)	-1476 (5)	4.2
C(2)	3883 (2)	3971 (2)	-186 (5)	3.7
C(3)	4713 (2)	3898 (2)	2800 (5)	3.5
C(4)	5605 (2)	3566 (2)	2579 (4)	3.2
C(5)	5205 (2)	671 (2)	-1001 (4)	2.5
C(6)	4619 (2)	240 (2)	1336 (4)	2.2
C(7)	4224 (2)	524 (2)	2857 (4)	2.7
C(8)	3459 (2)	1758 (2)	4007 (4)	3.5
C(9)	2812 (2)	1031 (3)	1373 (5)	3.9
Cl(1)	2081 (1)	4436 (1)	3349 (1)	3.2
Cl(2)	6028 (1)	3012 (1)	-2544 (1)	3.3
O(1)	2156 (2)	3767 (2)	2052 (4)	5.7
O(2)	1770 (2)	5281 (2)	2559 (4)	6.8
O(3)	1444 (2)	4122 (2)	4307 (4)	6.5
O(4)	2899 (2)	4568 (3)	4425 (4)	7.2
O(5)	6769 (2)	3052 (2)	-3376 (4)	6.1
O(6)	5358 (2)	2492 (3)	-3591 (4)	6.7
O(7)	6237 (2)	2547 (2)	-947 (3)	6.6
O(8)	5746 (3)	3891 (2)	-2254 (7)	11.4

a The equivalent isotropic temperature factor is calculated from the expression $B_{\text{eq}} = (4/3) \sum_i \sum_j a_i a_j \beta_{ij}$, where a_i 's are the unit cell edges in direct space.

Table III. Selected Interatomic Distances (\AA) and Angles (deg) for $[\text{Cu}_2(\text{dapz})(\text{dien})_2]^{4+}$

Cu–N(1)	2.046 (3)	Cu–N(2)	2.009 (3)
Cu–N(3)	2.044 (3)	Cu–N(4)	2.052 (5)
Cu–N(5)	2.243 (3)	N(1)–C(1)	1.488 (5)
N(2)–C(2)	1.460 (5)	N(2)–C(3)	1.494 (4)
N(3)–C(4)	1.472 (4)	N(4)–C(5)	1.338 (4)
N(4)–C(6)	1.334 (4)	N(5)–C(7)	1.476 (4)
N(5)–C(8)	1.472 (5)	N(5)–C(9)	1.473 (4)
C(1)–C(2)	1.501 (5)	C(3)–C(4)	1.499 (5)
C(5)–C(6) ^a	1.386 (4)	C(6)–C(7)	1.505 (5)
N(1)–Cu–N(2)	84.3 (1)	N(1)–Cu–N(3)	140.3 (1)
N(1)–Cu–N(4)	94.8 (1)	N(1)–Cu–N(5)	111.3 (1)
N(2)–Cu–N(3)	84.2 (1)	N(2)–Cu–N(4)	178.8 (1)
N(2)–Cu–N(5)	101.5 (1)	N(3)–Cu–N(4)	96.1 (1)
N(3)–Cu–N(5)	108.2 (1)	N(4)–Cu–N(5)	79.5 (1)
Cu–N(1)–C(1)	108.6 (2)	Cu–N(2)–C(2)	106.3 (2)
Cu–N(2)–C(3)	109.9 (2)	Cu–N(3)–C(4)	107.7 (2)
Cu–N(4)–C(5)	127.2 (2)	Cu–N(4)–C(6)	114.5 (2)
Cu–N(5)–C(7)	102.0 (2)	Cu–N(5)–C(8)	115.3 (2)
Cu–N(5)–C(9)	110.9 (2)	C(2)–N(2)–C(3)	115.2 (3)
C(5)–N(4)–C(6)	118.2 (3)	C(7)–N(5)–C(8)	109.9 (2)
C(7)–N(5)–C(9)	109.3 (3)	C(8)–N(5)–C(9)	109.2 (3)
N(1)–C(1)–C(2)	108.1 (3)	N(2)–C(2)–C(3)	107.9 (3)
N(2)–C(3)–C(4)	108.4 (3)	N(3)–C(4)–C(5)	108.3 (3)
N(4)–C(5)–C(6) ^a	121.7 (3)	N(4)–C(6)–C(5) ^a	120.1 (3)
N(4)–C(6)–C(7)	117.4 (3)	N(5)–C(7)–C(6)	110.3 (2)
C(5) ^a –C(6)–C(7)	122.5 (3)		

a Key to symmetry operation: $1 - x, -y, -z$.

were considered observed [$|F_o| > 3\sigma(F_o)$]. The intensities were corrected for Lorentz–polarization and absorption effects, but not for extinction. Lattice constants were determined by a least-squares refinement based on 42 reflections ($12^\circ < \theta < 15^\circ$) measured on the diffractometer.

Structure Analysis and Refinement. The structures were solved by the conventional heavy-atom method and refined by a block-diagonal least-squares technique with anisotropic thermal parameters for non-H atoms and isotropic for H atoms. Atomic scattering factors and anomalous scattering corrections were taken from ref 34. The weighting scheme

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chosen was $w = [\sigma_c^2 + (0.015|F_o|)^2]^{-1}$ where σ_c^2 was the standard deviation of $|F_o|$ calculated from counting statistics. The final R and R_w values were 0.0386 and 0.0419. Final atomic parameters and equivalent isotropic thermal factors for non-hydrogen atoms are listed in Table II.

All the calculations were carried out on an HITAC M680 computer at the Computer Center of the Institute for Molecular Science with the Universal Crystallographic Computation Program System UNICS-III.³⁵

Results and Discussion

Description of the Structure. The blue crystals consist of $[\text{Cu}_2(\text{dapz})(\text{dien})_2]^{4+}$ and ClO_4^- ions. The ORTEP drawing of the molecular structure is presented in Figure 1, together with the atomic labeling system; the ClO_4^- anions are omitted for clarity. Selected bond lengths and angles are listed in Table III.

In the crystal, the complex cation $[\text{Cu}_2(\text{dapz})(\text{dien})_2]^{4+}$ contains two five-coordinate CuN_5 chromophores that are related by crystallographic centers of symmetry. Each of the Cu atoms is coordinated by five N atoms of the ligand: three N atoms of diethylenetriamine and two N atoms of 2,5-(dimethylamino)methylpyrazine. All bond lengths between Cu and coordinating N atoms show similar values (2.009–2.052 Å) except for Cu–N(5) (2.243 Å). The N(2)–Cu–N(4) angle is nearly linear (178.8 (1)°). The coordination angles about the Cu atoms in the plane defined by Cu, N(1), N(3), and N(5) atoms show values closer to 120°. This suggests a trigonal-bipyramidal geometry around the copper atom. The deviations of the copper atoms from the basal planes (N(1)–N(3)–N(5)) are 0.053 (2) Å. The dihedral angle between the pyrazine plane and these basal planes is 97.2 (3)°. In order to understand the electronic structure of the five-coordinate Cu complex, it is necessary to analyze quantitatively the trigonality of the coordination geometry around the Cu atom. The distortion of the five-coordinate complex from the trigonal-bipyramidal or square-pyramidal can be well expressed by using an index τ introduced by Addison et al.,³⁶ which is defined as $(\text{N}(2)\text{--Cu--N}(4) - \text{N}(1)\text{--Cu--N}(3))/60^\circ$ in this complex. The index τ is unity for perfect trigonal-bipyramidal geometry and zero for square-pyramidal geometry. The calculated τ value for $[\text{Cu}_2(\text{dapz})(\text{dien})](\text{ClO}_4)_4$ is 0.64. From this value, the bond angles between Cu, N(1), N(3), and N(5), and the value of N(2)–Cu–N(4), it is concluded that the stereochemistry of CuN_5 chromophores in this complex is closer to a trigonal bipyramid, in which N(2)–Cu–N(4) is regarded as the principal axis. However, the distortion toward the square-pyramidal geometry results in a longer Cu–N(5) bond compared to other equatorial Cu–N(1) and Cu–N(3) bonds. It can be expected that the unpaired electron resides mainly in the d_{z^2} orbital, which is directed at the nitrogen atom of the bridging pyrazine.

Magnetic Properties. ESR spectra of a powdered sample were recorded at 290 and 77 K. No hyperfine structure was resolved. The spectra were typical for copper(II) dimers; that is, both $\Delta m = 1$ and $\Delta m = 2$ absorptions were observed. Observation of the half-field band ($\Delta m = 2$) around 1600 G proves the formation of the triplet state by the magnetic interaction between the metal centers.

The temperature dependence of the magnetic susceptibility was measured from 253 down to 2.7 K. The data were fit to the Bleaney–Bowers equation²⁶ as shown in eq 1, where the symbols

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

have their usual meaning and the temperature-independent paramagnetism, $N\alpha$, was taken as 120×10^{-6} emu/mol for the dimer. Experimental data corrected for diamagnetism were fitted to this equation by a least-squares method in which both the g value and the exchange parameter J were fitting parameters. The J and g values were evaluated to be -1.7 cm^{-1} and 2.106, respectively. Experimental data and calculated curves are shown

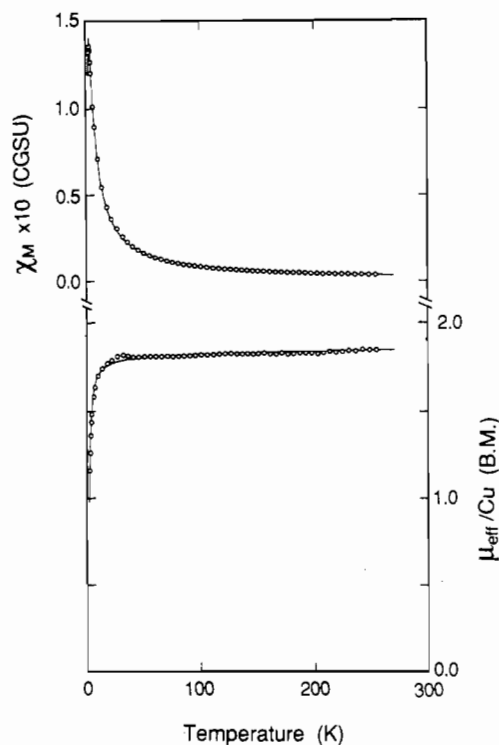


Figure 2. Temperature dependences of molar paramagnetic susceptibility and effective magnetic moment per copper ion of $[\text{Cu}_2(\text{dapz})(\text{dien})_2](\text{ClO}_4)_4$. The experimental data are represented as circles, and the solid lines result from a least-squares fit using the parameters and equation described in the text.

in Figure 2. The obtained J value is smaller than the value (-3.2 cm^{-1}) for the similar pyrazine-bridged dinuclear system $[\text{Cu}_2(\text{tren})_2(\text{pyz})](\text{ClO}_4)_4$ ($\text{tren} = \text{tris}(2\text{-aminoethyl})\text{amine}$).²⁰

Magnetic Interaction through the Organic Bridging Ligand. Several arguments have been made for the magnetic exchange interaction between metal centers through an organic bridging ligand. In a series of dinuclear copper(II) systems bridged by an imidazolato group, the variation of the magnitude of the anti-ferromagnetic interaction through σ orbitals was explained by the extent of overlap between the magnetic orbitals and the σ orbitals of the nitrogen atoms of the bridging group^{11,15} and by the different pK_a values in the bridging ligands, that is, the energy separation of the magnetic orbitals and nitrogen σ orbitals.¹⁶ It is evident that the magnetic interaction in the pyrazine-bridged dinuclear copper(II) system is much weaker than that in other organic bridging systems such as imidazolato,^{11–18} triazolato,³⁷ and triazole groups.¹ A direct overlap of the two magnetic orbitals cannot be expected because of the large separation of the two copper atoms; therefore, a magnetic superexchange mechanism through the bridging ligand should be taken into consideration. We decided to perform extended Hückel molecular orbital (EHMO) calculations in order to clarify the mechanism of magnetic superexchange interaction through the organic bridging ligand.

The systems we selected are $[\text{Cu}_2(\text{dapz})(\text{dien})_2]^{4+}$ and $[\text{Cu}(\text{aamt})\text{Br}(\text{H}_2\text{O})_2]_2^{2+}$ ($\text{aamt} = 4\text{-amino-3,5-bis(aminomethyl)-1,2,4-triazole}$),¹ which shows a substantial antiferromagnetic interaction ($J = -112 \text{ cm}^{-1}$). These systems seem to be appropriate to compare MO characteristics because both complexes are centrosymmetric and neither bridging ligand has a negative charge. The geometries of the two complexes, which were taken from the X-ray structural data, were modified to those of $[\text{Cu}_2(\text{pyrazine})(\text{NH}_3)_8]^{4+}$ and $[\text{Cu}_2(\text{triazole})_2(\text{NH}_3)_4(\text{OH})_2(\text{H}_2\text{O})_2]^{2+}$, maintaining the symmetry around the copper atoms, and were used in the calculation. The EHMO results are shown in Figure 3. If the magnetic orbitals on each of the copper atoms are

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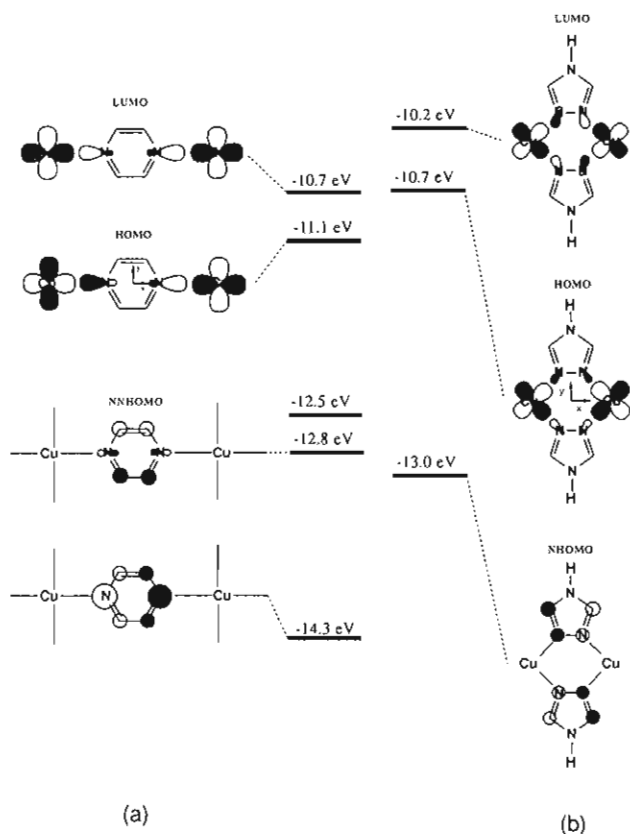


Figure 3. Extended Hückel MO diagrams of (a) $[\text{Cu}_2(\text{pyrazine})(\text{NH}_3)_8]^{4+}$ and (b) $[\text{Cu}_2(\text{triazole})_2(\text{NH}_3)_4(\text{OH})_2(\text{H}_2\text{O})_2]^{2+}$.

assigned to $d_{z^2}^A(d_{x^2-y^2}^A)$ and $d_{z^2}^B(d_{x^2-y^2}^B)$, the bonding and antibonding combinations form the two molecular orbitals $\phi_1 = d_{z^2}^A + d_{z^2}^B$ (or $d_{x^2-y^2}^A + d_{x^2-y^2}^B$) and $\phi_2 = d_{z^2}^A - d_{z^2}^B$ (or $d_{x^2-y^2}^A - d_{x^2-y^2}^B$). The triplet-singlet energy difference ($E_T - E_S$) is defined as¹⁰

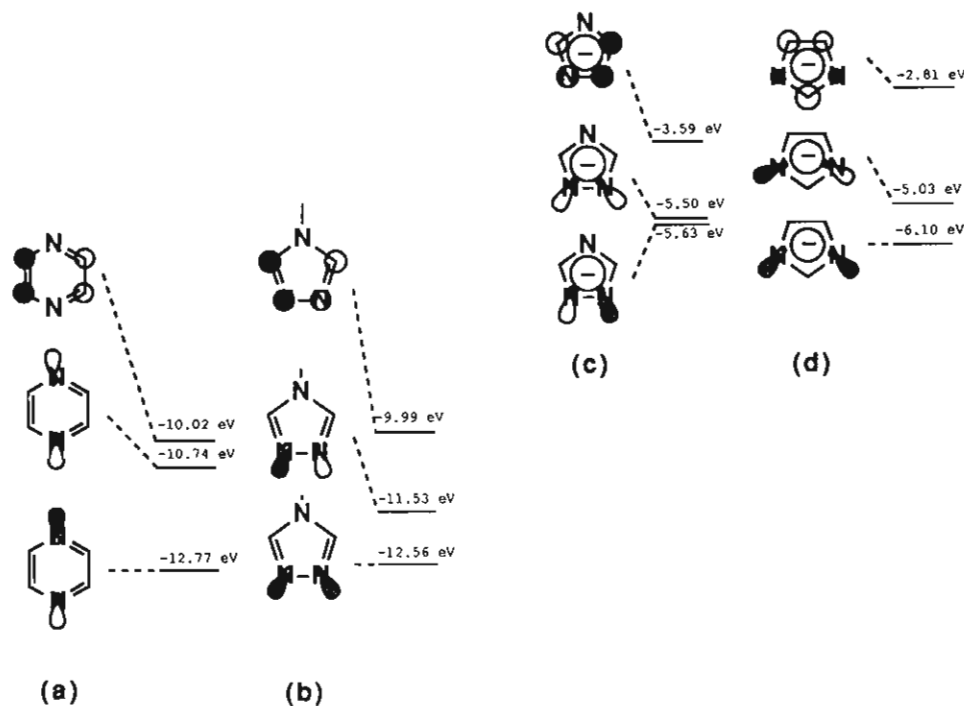
$$E_T - E_S = -2K_{ab} + \frac{2(\epsilon_1 - \epsilon_2)^2}{J_{aa} - J_{ab}} \quad (2)$$

Table IV. Coupling Constants of Some Dinuclear Complexes

complex ^a	bridging ligand	-J, cm ⁻¹	ref
$[\text{Cu}_2(\text{dapz})(\text{dien})_2]^{4+}$	pyrazine	1.7	this work
$[\text{Cu}(\text{aamt})\text{Br}(\text{H}_2\text{O})_2]^{2+}$	triazole	110	1
$[\text{Cu}(\text{bpt})(\text{CF}_3\text{SO}_3)(\text{H}_2\text{O})_2]$	triazolate	118	36
$[\text{Cu}(\text{tren})_2(\text{im})]$	imidazolate	38-40	10

^a Abbreviations for ligands: aamt = 4-amino-3,5-bis(amino-methyl)-1,2,4-triazole; bpt = 3,5-bis(pyridine-2-yl)-1,2,4-triazole; im = imidazole.

where K_{ab} , J_{aa} , and J_{ab} are the exchange integral and one-center and two-center Coulomb repulsion integrals, respectively, and ϵ_1 and ϵ_2 are the energy levels of the two molecular orbitals. If the denominator of the second term in (2) is constant, the energy difference between the two molecular orbitals ($\Delta\epsilon = |\epsilon_1 - \epsilon_2|$), which corresponds to the HOMO-LUMO energy gap, determines the magnitudes of the antiferromagnetic interaction.¹⁰ The larger HOMO-LUMO energy gap results in the stronger antiferromagnetic interaction. The calculated HOMO and LUMO energy levels are -11.1 and -10.7 eV for $[\text{Cu}_2(\text{pyrazine})(\text{NH}_3)_8]^{4+}$ (Figure 3a) and -10.7 and -10.2 eV for $[\text{Cu}_2(\text{triazole})_2(\text{NH}_3)_4(\text{OH})_2(\text{H}_2\text{O})_2]^{2+}$ (Figure 3b). The energy differences $\Delta\epsilon$ for $[\text{Cu}_2(\text{pyrazine})(\text{NH}_3)_8]^{4+}$ and $[\text{Cu}_2(\text{triazole})_2(\text{NH}_3)_4(\text{OH})_2(\text{H}_2\text{O})_2]^{2+}$ show similar values, 0.4 and 0.5 eV, respectively, in spite of the quite different magnitudes of antiferromagnetic interaction in the two complexes. This disagreement between experimental and EHMO calculation results might be interpreted as follows. The antiferromagnetic interaction is related to $2(\epsilon_1 - \epsilon_2)^2 / (J_{aa} - J_{ab})$ as described above. The EHMO calculations show similar $\epsilon_1 - \epsilon_2$ values for both complexes, and this might mean different $J_{aa} - J_{ab}$ values for the two complexes. The J_{aa} values for both complexes are considered to be same because J_{aa} is the one-center Coulomb repulsion integral, while the longer metal-metal distance for the pyrazine-bridged complex causes a smaller J_{ab} value. This results in a larger $J_{aa} - J_{ab}$ value for the pyrazine-bridged complex, hence, a weaker antiferromagnetic interaction. On the other hand, the $J_{aa} - J_{ab}$ term corresponds to a U value which is the energy associated with the electron transfer (that is, the charge-transfer property) between the two copper centers.³⁸⁻⁴⁰ According to the



This work

Figure 4. MNDO diagrams of (a) pyrazine, (b) triazole, (c) triazolate, and (d) imidazolate.

above arguments, the U value for the pyrazine-bridged complex is larger than that for the triazole-bridged complex. It can be suggested that a direct or through-ligand charge-transfer interaction is important in the propagation of the antiferromagnetic interaction.

It is important to know the molecular orbitals of the bridging ligands in order to predict whether a substantial magnetic interaction exists between the metal centers. MNDO calculations for the organic bridging ligands, which can form dinuclear copper(II) complexes with antiferromagnetic interactions (Table IV), were performed, and the HOMO and related σ orbitals are shown in Figure 4. In the case of the bridging ligands with a negative charge, the energy levels of the $p\sigma$ orbital, which can coordinate to the copper atoms, are closer in energy to the copper d orbital than that of the bridging ligand without a negative charge. This closer energy difference can cause more mixing of the copper d orbital and nitrogen $p\sigma$ orbitals, meaning a stronger magnetic interaction in the dinuclear complexes with an anion as the bridging ligand. This character of the molecular orbitals in the bridging ligand is reflected in the magnetic properties; that is, the pyrazine-bridged dinuclear complexes show weaker antiferromagnetic interaction than those with imidazolate and triazolate.

It is also interesting to compare the magnetic interactions of triazole-bridged and triazolato-bridged complexes. The magnetic exchange interactions in dinuclear copper(II) complexes bridged by the triazolate group, $[\text{Cu}(\text{bpt})(\text{CF}_3\text{SO}_3)(\text{H}_2\text{O})_2]_2$ (bpt = 3,5-bis(pyridin-2-yl)-1,2,4-triazolate),³⁷ and the triazole group, $[\text{Cu}(\text{aamt})\text{Br}(\text{H}_2\text{O})_2]_2\text{Br}_2(\text{H}_2\text{O})_2$,¹ are comparable ($J = -102$ to -118 cm^{-1} and $J = -100$ to -110 cm^{-1} , respectively) in spite of the fact that the HOMO and other levels of the triazolate are higher in energy than those of triazole because of the negative charges on the ligand molecule. The stronger antiferromagnetic interaction in the triazolato-bridged complex compared with that in the triazole-bridged one is expected because of the smaller energy difference between copper d and ligand orbitals in the former complex. The conflict of theoretical expectations with the experimental results suggests the importance of geometrical factors of copper and the bridging ligand with respect to the magnetic superexchange interaction.

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Supplementary Material Available: Tables listing crystallographic parameters, fractional atomic coordinates for H atoms, anisotropic thermal parameters for non-H atoms, and complete bond lengths and angles, figures showing a packing diagram of the crystal and ESR spectra, and tables of experimental and calculated magnetic susceptibilities (9 pages); a table of structure factors (8 pages). Ordering information is given on any current masthead page.

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Magnetism of ACu^{II} Bimetallic Chain Compounds (A = Fe, Co, Ni): One- and Three-Dimensional Behaviors

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The $\text{ACu}(\text{pbaOH})(\text{H}_2\text{O})_3 \cdot n\text{H}_2\text{O}$ chain compounds, hereafter abbreviated as ACu, have been synthesized. A is Fe ($n = 3$), Co, Ni, or Zn ($n = 2$), and pbaOH is 2-hydroxy-1,3-propylenebis(oxamato). These compounds are isomorphous with $\text{MnCu}(\text{pbaOH})(\text{H}_2\text{O})_3$, of which the crystal structure was known. However, they contain two or three additional water molecules, located between the chains. The magnetic properties have been investigated in the 1.8–300 K temperature range. For A = Fe, Co, and Ni, the $\chi_{\text{M}}T$ versus T plot, χ_{M} being the molar magnetic susceptibility per ACu unit and T the temperature, shows the minimum characteristic of ferrimagnetic chains. This minimum appears at 95 K for FeCu, 53 K for CoCu, and 80 K for NiCu. At low temperature, the magnetic data are affected by three-dimensional effects. In all the cases, the interchain interactions are antiferromagnetic in nature. CoCu shows a long-range antiferromagnetic ordering at 3.4 K, and NiCu, at 2.9 K. For FeCu, the situation is more complex. The spins of the ferrimagnetic chains do not exactly cancel on the scale of the crystal lattice. There is a canting, which leads to a weak ferromagnetism and a remnant magnetization below the critical temperature $T_{\text{c}} = 10$ K. The magnetic data have been quantitatively interpreted in the temperature range where the three-dimensional effects may be ignored. For NiCu, a ring chain approach has been used, which leads to $J(\text{NiCu}) = -81.4 \text{ cm}^{-1}$; the interaction Hamiltonian is $-\sum_i S_{\text{Cu},i} S_{\text{Cu},i+1} + S_{\text{Cu},i-1}$. For CoCu and FeCu involving an orbitally degenerate ion A, a model of branch chain has been developed. The interaction between local spins S_{A} (A = Co, Fe) and S_{Cu} has been assumed to run along the chain axis while the branches have been related to the spin-orbit coupling for Co(II) or Fe(II) ions. In order to solve analytically this problem, it has been further assumed that only z components of spin and orbital momentums were coupled and that the applied field was along the quantization axis. In the frame of this model, the magnetic properties of CoCu and FeCu have been satisfactorily interpreted with $J(\text{CoCu}) = -18 \text{ cm}^{-1}$ and $J(\text{FeCu}) = -20 \text{ cm}^{-1}$.

Introduction

A new class of magnetic materials appeared a few years ago, namely the ferrimagnetic chain compounds, in which there is alternation of the magnetic centers A and B along the direction of the chains.^{2–6} A and B may be either both metal ions^{2–12} or

metal ion and organic radical,^{13,14} respectively. In other respects, the ferrimagnetic chains may be either regular, the magnetic

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