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Exchange Interaction through Extended Molecular Bridges: Magnetic Properties of μ -4,4'-Bipyridine and μ -Pyrazine Copper(II) Binuclear Complexes and Crystal Structures of (μ -4,4'-Bipyridine)bis[(diethylenetriamine)(perchlorato)copper(II)] Perchlorate and Aquo(4,4'-bipyridine)(diethylenetriamine)copper(II) Perchlorate

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Three complexes, $[\text{Cu}_2(\text{dien})_2(4,4'\text{-bpy})(\text{ClO}_4)_2](\text{ClO}_4)_2$ (1), $[\text{Cu}_2(\text{dien})_2(\text{pyz})(\text{ClO}_4)_4]$ (2), and $[\text{Cu}(\text{dien})(4,4'\text{-bpy})(\text{H}_2\text{O})(\text{ClO}_4)_2]$ (3), with dien = diethylenetriamine, 4,4'-bpy = 4,4'-bipyridine, and pyz = pyrazine, have been synthesized. The structures of 1 and 3 have been solved at room temperature. 1 crystallizes in the orthorhombic system, space group *Pbca*, with $a = 11.184$ (2) Å, $b = 14.414$ (2) Å, $c = 16.213$ (2) Å, and $Z = 4$ and 3 in the triclinic system, space group *P* $\bar{1}$, with $a = 16.221$ (4) Å, $b = 10.270$ (3) Å, $c = 6.975$ (8) Å, $\alpha = 105.53$ (5)°, $\beta = 97.96$ (5)°, $\gamma = 74.75$ (3)°, and $Z = 2$. The structure of 1 is made up of 4,4'-bipyridine-bridged copper(II) binuclear cations linked by two monodentate perchlorate anions. The copper(II) is six-coordinate with four N atoms having an almost planar configuration and two O atoms of two perchlorate anions occupying the axial positions. The structure of 3 consists of $[\text{Cu}(\text{dien})(4,4'\text{-bpy})(\text{H}_2\text{O})]^{2+}$ mononuclear cations with noncoordinated perchlorate anions. The copper(II) has a square-pyramidal coordination geometry with four N atoms building the basal plane (three from dien and one from 4,4'-bpy) and a water molecule occupying the apical position. For the three compounds, the magnetic susceptibility was investigated in the 50–4.2 K temperature range. For compounds 1 and 3 supplementary data were recorded down to 1.3 K. The decrease of the product $\chi_M T$ when the systems are cooled down from 50 to 1.3 K is attributed to intermolecular and/or intramolecular interactions. The EPR spectra of all three compounds show a half-field forbidden transition at 6.6 K not observed at room temperature. Magnetic experimental data are discussed in relation to the structures in the framework of a localized molecular orbital model.

Introduction

The problem of exchange interaction between transition-metal ions through extended molecular bridges, both in synthetic polynuclear compounds and in biological materials, has given rise to much interest among inorganic and bioinorganic chemists in the past few years.²

The importance of parameters such as the symmetry of magnetic orbitals³⁻⁵ and the energy of the molecular orbitals of the bridging ligand with suitable symmetry to combine with the magnetic orbitals⁵⁻⁷ is now better understood: the larger the overlap between nonorthogonal magnetic orbitals, the larger the antiferromagnetic exchange coupling between the metallic ions;⁷ the larger the overlap density between orthogonal magnetic orbitals, the larger the ferromagnetic coupling.³

One unresolved problem is the limit of interaction between two transition-metal ions:^{5,8-10} Is there a limit, and if so, what is it?

Clear-cut answers to these questions would imply (i) the ability to synthesize binuclear complexes with continuously increasing metal-metal distances with various magnetic orbital symmetries and (ii) the ability to be able to distinguish intramolecular interactions from intermolecular ones for long distances and weak interactions.

Up to now, most of the published results have been related to binuclear copper(II) complexes with one unpaired electron by metal center—and therefore a unique exchange pathway—with distances in the range 5–8 Å: relatively strong interactions were achieved with bridging ligands such as end-to-end azide,¹¹ oxalate,^{4,6,12} oxamate and oxamido,^{5,7,13,14} dithiooxamide,¹⁵⁻¹⁸ tetra-thiooxalate,¹⁹ and bromanilate.^{20a} Copper-copper distances larger than 7.5 Å are rare, as shown in Coffman and Buettner's review of the available structural and magnetic data.⁸ These authors proposed the relation

$$|J_{\text{lim}}| = 1.35 \times 10^7 \exp(-1.80R) \quad (1)$$

for the limiting value of J (cm^{-1}), the singlet-triplet gap in the binuclear complex, versus R (Å), the distance between the metallic ions. To the best of our knowledge, this limit has not been reached for clearly defined intramolecular interactions with $R > 8$ Å.

Bridging ligands such as terephthalic acid¹⁰ and 4,4'-bipyridine are suitable candidates to give R distances greater than 10 Å. Following our previous work on copper(II) binuclear complexes, where the interactions seem to be *inter-* rather than *intramolecular*,¹⁰ we decided to synthesize μ -4,4'-bipyridine copper(II) complexes with dien as terminal ligands and perchlorate counteranions. The choice of 4,4'-bipyridine (and pyrazine for comparison) was determined first by the guess that such bridges are capable of giving a strong intramolecular interaction,²¹ even if,

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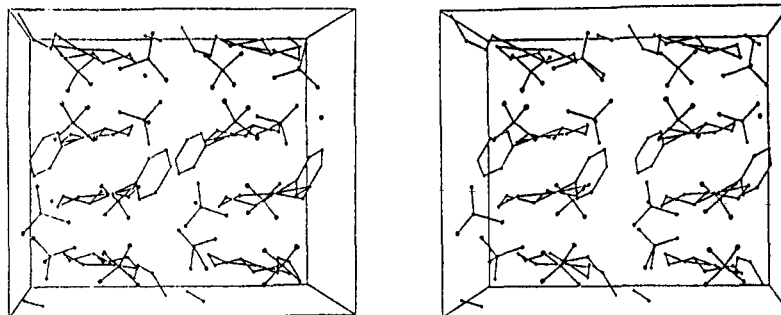


Figure 1. Stereoscopic view of the cell of complex **1** down the b axis (the c axis is vertical). Black circles represent noncoordinated perchlorate anions.

to date, experimental results do not support this supposition. Haddad et al. found no sign of interaction in $[\text{Cu}_2(\text{tren})_2(4,4'\text{-bpy})]^{4+}$, where tren is triethylenetetramine and the Cu(II) ions are in a d_{z^2} state²² (in contrast with what happened with a benzidine bridging ligand, where Felthouse et al.²³ found a J value of -7.4 cm^{-1}). Second, 4,4'-bpy is well-known to bridge transition-metal ions,²⁴ even if it is only recently, as far as we know, that crystallographic structures of μ -4,4'-bpy binuclear complexes²⁵ or chains²⁶ have been reported.

Dien was chosen as the terminal ligand to give a $d_{x^2-y^2}$ ground state since the d_{z^2} state appears to be inefficient.²² Perchlorate allows the growth of single crystals suitable for X-ray diffraction analyses, necessary for magnetic data discussion.

In this paper we report the synthesis and magnetic properties of three new compounds: two binuclear complexes, $[\text{Cu}_2(\text{dien})_2(4,4'\text{-bpy})(\text{ClO}_4)_2](\text{ClO}_4)_2$ (**1**) and $[\text{Cu}_2(\text{dien})_2(\text{pyz})](\text{ClO}_4)_4$ (**2**), and one mononuclear complex with a monodentate 4,4'-bpy ligand, $[\text{Cu}(\text{dien})(4,4'\text{-bpy})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (**3**). We present the crystal structures of **1** and **3**, which allow the discussion of the magnetic properties.

Experimental Section

Materials. Pyrazine, 4,4'-bipyridine, and diethylenetriamine were Merck reagents, whereas $[\text{Cu}(\text{H}_2\text{O})_6](\text{ClO}_4)_2$ was purchased from Aldrich. All reagents were used as received.

Synthesis. $[\text{Cu}_2(\text{dien})_2(4,4'\text{-bpy})(\text{ClO}_4)_2](\text{ClO}_4)_2$ (**1**). This compound was obtained as a purple crystalline solid after adding 156 mg (1 mmol) of 4,4'-bpy to a methanolic solution of 741 mg (2 mmol) of copper(II) perchlorate and 260 mg (2 mmol) of dien. The precipitate was washed with methanol and dried in vacuo over CaCl_2 . The yield is almost quantitative. Aqueous solutions of this complex yield compound **3** by evaporation. Single crystals of **1** suitable for X-ray investigation were grown by slow evaporation at room temperature of mixed aqueous solutions of **3** and $[\text{Cu}(\text{dien})](\text{ClO}_4)_2$ in a 1:8 molar ratio. Anal. Calcd for $\text{C}_{18}\text{H}_{34}\text{N}_8\text{O}_{16}\text{Cl}_4\text{Cu}_2$ (**1**): C, 24.37; H, 3.83; N, 12.63; Cl, 15.99; Cu, 14.33. Found: C, 24.20; H, 3.93; N, 12.28; Cl, 15.89; Cu, 14.11.

$[\text{Cu}_2(\text{dien})_2(\text{pyz})](\text{ClO}_4)_4$ (**2**). A methanolic solution of 80 mg (1 mmol) of pyrazine was added to a methanolic filtered solution of 741 mg (2 mmol) of copper(II) perchlorate and 206 mg (2 mmol) of dien. A pink precipitate of **2** separated when the mixture was cooled. It was filtered, washed with methanol, and dried in vacuo over P_2O_{10} . The compound can crystallize as an hydrate. All our attempts to grow single crystals were unsuccessful. Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{N}_8\text{O}_{16}\text{Cl}_4\text{Cu}_2$ (**2**): C, 17.76; H, 3.73; N, 13.81; Cl, 17.48; Cu, 15.66. Found: C, 17.64; H, 3.75; N, 13.25; Cl, 17.32; Cu, 15.44.

$[\text{Cu}(\text{dien})(4,4'\text{-bpy})(\text{H}_2\text{O})](\text{ClO}_4)_2$ (**3**). A 156-mg (1-mmol) amount of 4,4'-bpy dissolved in a minimum amount of methanol was added to an aqueous solution of 370 mg (1 mmol) of copper(II) perchlorate and 103 mg (1 mmol) of dien. Dark blue crystals of **3** were obtained from the resulting blue-violet solution by slow evaporation at room temperature. They were isolated, washed with cold water and methanol, and air-dried. Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{N}_5\text{O}_9\text{Cl}_2\text{Cu}$ (**3**): C, 31.16; H, 4.26; N, 12.97; Cu, 11.78. Found: C, 31.23; H, 4.25; N, 12.95; Cu, 11.81.

IR and Electronic Spectra. Infrared spectra were recorded on a Pye Unicam SP 200 spectrophotometer as KBr pellets. The diffuse-reflectance spectra of **1** and **3** were recorded with a Pye Unicam SP 100-8 UV-visible spectrophotometer, with magnesium oxide as the reference.

Magnetic Measurements. Magnetic measurements were carried out on polycrystalline samples in the 4.2–50 K temperature range with a previously described Faraday-type magnetometer,^{20a} equipped with a helium continuous-flow cryostat. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. The independence of the magnetic susceptibility upon the magnetic induction was checked at room temperature. A mutual inductance bridge^{20b} was used to measure the magnetic susceptibility of **1** and **2** in the 1.2–4.2 K temperature range. Corrections for the diamagnetism of the complexes were estimated from Pascal constants as -460×10^{-6} , -420×10^{-6} , and $-280 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ for **1**, **2**, and **3**, respectively.

EPR Spectra. X-Band EPR spectra were recorded, both at room temperature and at 7 K, with a Bruker ER 200 spectrometer equipped with a helium continuous-flow cryostat.

Crystal Structure Refinement. The data were collected with a Nonius CAD-4F diffractometer for both compounds **1** and **3**. Prismatic dark blue crystals were used, whose dimensions were $0.17 \times 0.07 \times 0.41 \text{ mm}$ for **1** and $0.2 \times 0.08 \times 0.40 \text{ mm}$ for **3**. Their densities were determined by flotation in a dibromoethane-hexane mixture. **1** crystallizes in the orthorhombic system, space group $Pbca$, with $a = 11.184$ (2) Å, $b = 14.414$ (2) Å, $c = 16.213$ (2) Å, $V = 3314.7$ (8) Å³, $Z = 4$, $\rho_{\text{calcd}} = 1.78 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$, $\rho_{\text{measd}} = 1.76 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$, and $F(000) = 1808$. **3** crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 16.221$ (4) Å, $b = 10.270$ (3) Å, $c = 6.975$ (8) Å, $\alpha = 105.53$ (5)°, $\beta = 97.96$ (5)°, $\gamma = 74.75$ (3)°, $V = 1049$ (1) Å³, $Z = 2$, $\rho_{\text{calcd}} = 1.71 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$, $\rho_{\text{measd}} = 1.64 \times 10^3 \text{ kg} \cdot \text{m}^{-3}$, and $F(000) = 554$. Unit cell constants were refined from least-squares fitting of the setting angles of 25 reflections.

Intensities of the reflections were measured at 295 K with monochromatic Mo $K\alpha$ radiation (0.71073 Å) in the $\omega/2\theta$ scan mode with $2 \leq \theta \leq 27^\circ$ (4777 reflections for **1** and 4576 reflections for **3**). Three reflections were monitored periodically, and they did not show any crystal decomposition. Intensities were corrected for Lorentz and polarization factors; 2249 for **1** and 3041 for **3** were considered as observed with $I > 3\sigma(I)$. Scattering factors for neutral atoms and anomalous dispersion corrections for Cu and Cl were taken from ref 27. The structures were solved by a three-dimensional Patterson map and Fourier synthesis, which allowed the location of all atoms other than hydrogen. An empirical absorption correction²⁸ was applied at the end of the isotropic refinement. The oxygen atoms of the perchlorate anions were refined isotropically because of some nonresolvable disorder from thermal motion.

For **1**, mixed full-matrix least-squares refinement with unit weights led to $R = 0.074$. Hydrogen atoms were fixed at calculated positions. In order to prevent bias on ΔF versus F_o or $(\sin \theta)/\lambda$, the last steps of the refinement were carried out with weight $w = w_1 w_2$, where $w_1 = 1/[A + B|F_o|^2]$ and $w_2 = 1/[C + D(\sin \theta)/\lambda]^2$. The coefficients A , B , C , and D were calculated by the PESOS program.²⁹ Final refinements with fixed isotropic temperature factors for oxygen atoms converged at $R = 0.07$ and $R_w = 0.062$.

For **3**, mixed full-matrix least-squares refinement with unit weights led to $R = 0.075$. Only the hydrogen atoms of the water molecule were located. No trend in ΔF versus F_o or $(\sin \theta)/\lambda$ was observed. Final

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Table I. Atomic Coordinates and Thermal Parameters^{a,b} for Non-Hydrogen Atoms of [Cu₂(dien)₂(4,4'-bpy)(ClO₄)₂](ClO₄)₂ (1)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	10 ³ <i>U</i> _{eq} , Å ²
Cu	0.604 47 (6)	0.203 71 (6)	0.801 12 (5)	31 (0)
N(1)	0.642 00 (45)	0.098 52 (44)	0.728 43 (45)	41 (2)
C(2)	0.600 66 (68)	0.013 37 (57)	0.731 60 (68)	53 (3)
C(3)	0.620 00 (66)	0.016 12 (61)	0.851 71 (66)	51 (3)
N(4)	0.583 70 (54)	0.104 54 (50)	0.886 22 (48)	48 (2)
C(5)	0.616 59 (65)	0.124 05 (68)	0.643 62 (55)	50 (3)
C(6)	0.649 51 (66)	0.222 64 (68)	0.630 12 (52)	49 (3)
N(7)	0.613 34 (49)	0.280 18 (46)	0.697 87 (44)	43 (2)
N(10)	0.565 26 (44)	0.310 63 (43)	0.872 76 (38)	35 (2)
C(11)	0.482 85 (53)	0.311 49 (54)	0.912 49 (61)	45 (2)
C(12)	0.455 31 (53)	0.384 14 (56)	0.962 85 (58)	45 (2)
C(13)	0.513 28 (48)	0.460 37 (48)	0.972 91 (41)	29 (2)
C(14)	0.596 85 (65)	0.459 77 (61)	0.929 49 (58)	48 (3)
C(15)	0.619 59 (63)	0.383 94 (69)	0.881 89 (62)	54 (3)
Cl(1)	0.355 90 (14)	0.228 18 (13)	0.682 35 (15)	47 (1)
O(1)	0.414 99 (53)	0.271 55 (54)	0.623 65 (52)	66 (0)
O(2)	0.415 30 (84)	0.179 23 (94)	0.741 03 (90)	111 (0)
O(3)	0.305 08 (94)	0.295 67 (106)	0.727 01 (95)	125 (0)
O(4)	0.279 97 (89)	0.179 00 (115)	0.645 38 (102)	129 (0)
Cl(2)	0.338 18 (13)	-0.008 59 (14)	0.907 68 (13)	45 (1)
O(5)	0.424 55 (56)	-0.055 87 (60)	0.920 66 (54)	70 (0)
O(6)	0.270 32 (73)	-0.047 23 (85)	0.961 25 (76)	99 (0)
O(7)	0.307 26 (61)	-0.023 32 (67)	0.824 93 (60)	78 (0)
O(8)	0.351 17 (74)	0.088 42 (83)	0.918 02 (74)	98 (0)

^a Estimated standard deviations in the last significant digits are given in parentheses. ^b $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

Table II. Atomic Coordinates and Thermal Parameters^{a,b} for Non-Hydrogen Atoms of [Cu₂(dien)₂(4,4'-bpy)(H₂O)](ClO₄)₂ (3)

atom	<i>z/a</i>	<i>y/b</i>	<i>z/c</i>	10 ⁴ <i>U</i> _{eq} , Å ²
Cu	0.218 14 (6)	0.228 00 (9)	0.110 45 (15)	303 (3)
O(9)	0.165 65 (36)	0.368 11 (61)	-0.123 39 (89)	474 (24)
N(1)	0.111 87 (40)	0.156 84 (65)	0.056 10 (105)	394 (25)
C(2)	0.132 76 (62)	0.008 79 (89)	-0.060 04 (154)	550 (38)
C(3)	0.191 60 (62)	-0.001 84 (91)	-0.217 79 (144)	539 (37)
N(4)	0.263 88 (44)	0.056 84 (68)	-0.113 65 (105)	436 (26)
C(5)	0.072 12 (58)	0.186 78 (101)	0.251 45 (151)	542 (38)
C(6)	0.074 39 (52)	0.333 01 (95)	0.361 92 (134)	473 (34)
N(7)	0.162 53 (40)	0.349 80 (67)	0.367 16 (94)	374 (24)
N(10)	0.326 56 (37)	0.297 65 (60)	0.170 78 (90)	308 (22)
C(11)	0.321 98 (45)	0.435 68 (73)	0.214 34 (107)	322 (25)
C(12)	0.391 99 (46)	0.489 71 (70)	0.238 67 (107)	313 (25)
C(13)	0.473 74 (43)	0.402 16 (66)	0.219 34 (95)	250 (23)
C(14)	0.478 36 (45)	0.260 32 (73)	0.182 16 (119)	339 (27)
C(15)	0.405 43 (50)	0.213 38 (74)	0.160 42 (127)	382 (29)
C(16)	0.551 58 (45)	0.456 58 (69)	0.239 56 (97)	267 (23)
C(17)	0.547 12 (48)	0.597 87 (73)	0.282 03 (111)	334 (26)
C(18)	0.621 31 (54)	0.642 57 (80)	0.296 10 (119)	390 (30)
N(11)	0.697 76 (45)	0.559 42 (73)	0.267 88 (99)	422 (27)
C(19)	0.702 57 (52)	0.420 80 (88)	0.224 85 (138)	450 (33)
C(20)	0.632 15 (49)	0.366 82 (78)	0.209 35 (124)	380 (29)
Cl(1)	0.088 01 (14)	0.716 46 (22)	0.253 03 (38)	501 (9)
O(1)	0.037 33 (67)	0.624 49 (110)	0.138 58 (161)	1163 (33)
O(2)	0.130 09 (53)	0.664 86 (86)	0.421 77 (128)	851 (24)
O(3)	0.036 47 (71)	0.848 35 (115)	0.306 71 (168)	1228 (35)
O(4)	0.148 19 (77)	0.708 08 (124)	0.118 98 (183)	1356 (39)
Cl(2)	0.349 66 (15)	-0.058 54 (21)	-0.616 64 (35)	484 (8)
O(5)	0.285 35 (51)	0.064 56 (83)	-0.600 22 (123)	804 (22)
O(6)	0.390 78 (50)	-0.096 99 (80)	-0.798 36 (121)	773 (21)
O(7)	0.334 75 (74)	-0.163 86 (120)	-0.554 68 (177)	1299 (37)
O(8)	0.409 26 (96)	-0.016 39 (155)	-0.441 76 (233)	1789 (56)

^a Estimated standard deviations in the last significant digits are given in parentheses. ^b $U_{eq} = 1/3 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$.

refinement with fixed isotropic temperature factors and coordinates for hydrogen atoms converged at *R* = 0.069.

Refined atomic coordinates are given in Table I for 1 and in Table II for 3. Structure factor amplitudes are supplied as supplementary material. Most of the calculations were carried out by using XRAY.³⁰

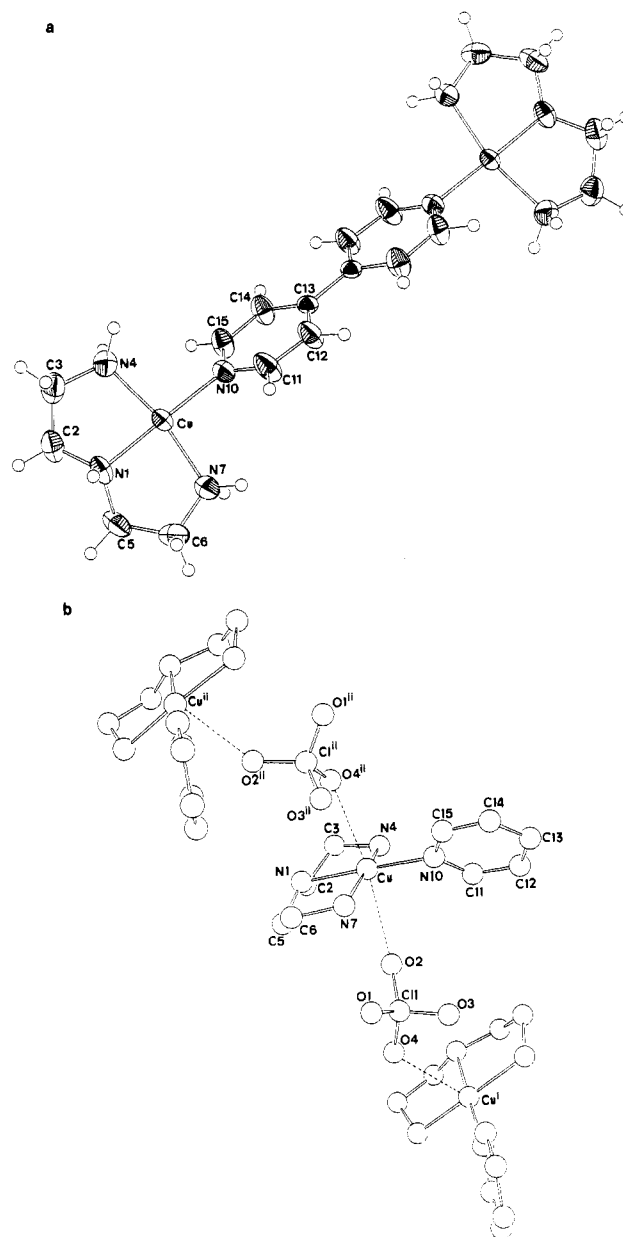


Figure 2. (a) Perspective view of the binuclear cation [Cu₂(dien)₂(4,4'-bpy)]²⁺ in 1, with 50% probability ellipsoids. (b) One-dimensional array of Cu(II) ions in 1, with bridging perchlorate anions. For the sake of clarity, only half of the binuclear cations are drawn. Atoms with roman numeral superscripts are generated by the following symmetry operations relative to *x*, *y*, *z*: (i) $-1/2 + x$, y , $3/2 - z$; (ii) $1/2 + x$, y , $3/2 - z$.

Results

Description of the Structures. [Cu₂(dien)₂(4,4'-bpy)(ClO₄)₂](ClO₄)₂ (1). The structure of 1 consists of μ -4,4'-bipyridine copper(II) binuclear cations and of perchlorate anions. A view of the cell down the *b* axis is depicted in Figure 1. Two of the perchlorate anions are noncoordinated, whereas the two others link the binuclear units in a bis(monodentate) way, building one-dimensional chains of Cu(II) linked by 4,4'-bipyridine to form ladders. They are arranged in a three-dimensional network. A perspective view of the μ -4,4'-bipyridine binuclear complex is shown in Figure 2a. A crystallographic inversion center stands at the middle of the C(13)–C(13)ⁱ bond in the 4,4'-bpy molecule. The μ -perchlorate array of copper(II) ions is displayed in Figure 2b. Main distances and angles are given in Table III.

The copper(II) ion is in a 4+2 surrounding. The four nearest neighbors, at about 2 Å, are the four nitrogen atoms N(1), N(4), and N(7) from dien and N(10) from 4,4'-bpy. The two apical positions are occupied by oxygen atoms of two perchlorate anions

(30) Stewart, J. M.; Kundell, F. A.; Baldwin, J. C. "The X-RAY System"; Computer Science Center, University of Maryland: College Park, MD, 1970.

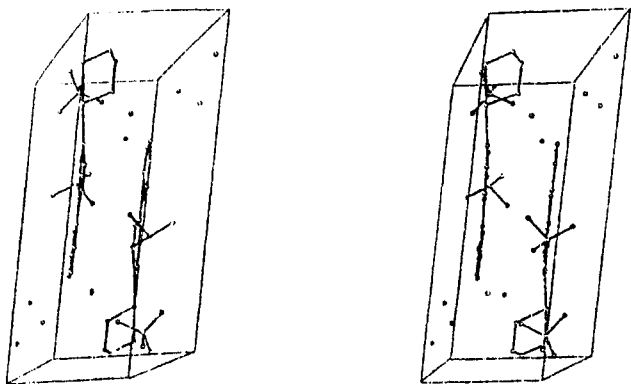


Figure 3. Stereoscopic view of the cell of complex 3 down the b axis (the a axis is vertical).

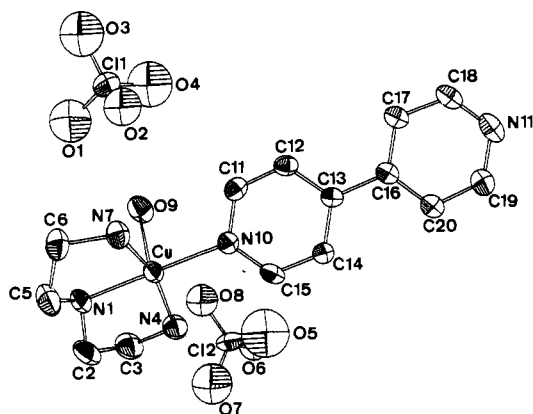


Figure 4. Perspective view of the mononuclear complex 3, with 50% probability ellipsoids. The two noncoordinated perchlorate anions are also shown.

at greater distances: $\text{Cu}-\text{O}(2) = 2.88 \text{ \AA}$ and $\text{Cu}-\text{O}(4)^{\text{ii}} = 2.66 \text{ \AA}$. The four nitrogen atoms of the basal plane are almost planar; the deviation of the copper(II) from the mean basal plane is $0.0677 (9) \text{ \AA}$. The dihedral angle between the mean basal plane and the aromatic rings of 4,4'-bpy—which coplanarity is imposed by the inversion center—is $56.4 (2)^\circ$. The copper-copper distance through the 4,4'-bipyridine molecule, within a binuclear unit, is $11.106 (2) \text{ \AA}$, much longer than the copper-copper distance through a perchlorate anion between two binuclear units, which is $7.283 (2) \text{ \AA}$.

[Cu(dien)(4,4'-bpy)(H₂O)](ClO₄)₂ (3). The triclinic cell contains two of the mononuclear dication $[\text{Cu}(\text{dien})(4,4'\text{-bpy})(\text{H}_2\text{O})]^{2+}$ and four noncoordinated perchlorate anions. A view of the cell down the b axis is shown in Figure 3. The main distances and angles of 3 are compared to those of 1 in Table III. A perspective view of the complex is shown in Figure 4. The main point is that only one nitrogen atom of the 4,4'-bpy, N(10), binds to the copper(II) ion, giving rise to a mononuclear complex. The surroundings of copper(II) are best described by a square-planar pyramid in a 4+1 coordination: the basal plane is built by the N(1), N(4), and N(7) nitrogen atoms of dien and N(10) of 4,4'-bpy whereas the apical position is occupied by the O(9) oxygen atom of the water molecule. The average deviation of N(1), N(4), and N(10) from the main basal plane is $0.115 (7) \text{ \AA}$, and the Cu(II) ion is displaced by $0.133 (2) \text{ \AA}$ from this plane toward the apex. The copper(II)-nitrogen bond lengths range from 1.995 to 2.038 \AA . They are shorter than the apical distance $\text{Cu}-\text{O}(9) = 2.35 \text{ \AA}$, but except for Cu(II)-N(1), they are longer than in complex 1. The dihedral angle between the mean basal plane around copper(II) and the vicinal ring of 4,4'-bpy is $43.9 (2)^\circ$. The two rings of 4,4'-bpy show no significant deviation from planarity, but they display a small dihedral angle of $3.7 (3)^\circ$ in contrast to the case for complex 1.

The O(9) oxygen atom of the water molecule is hydrogen-bonded to the noncoordinated nitrogen atom N(11)' of the 4,4'-bpy

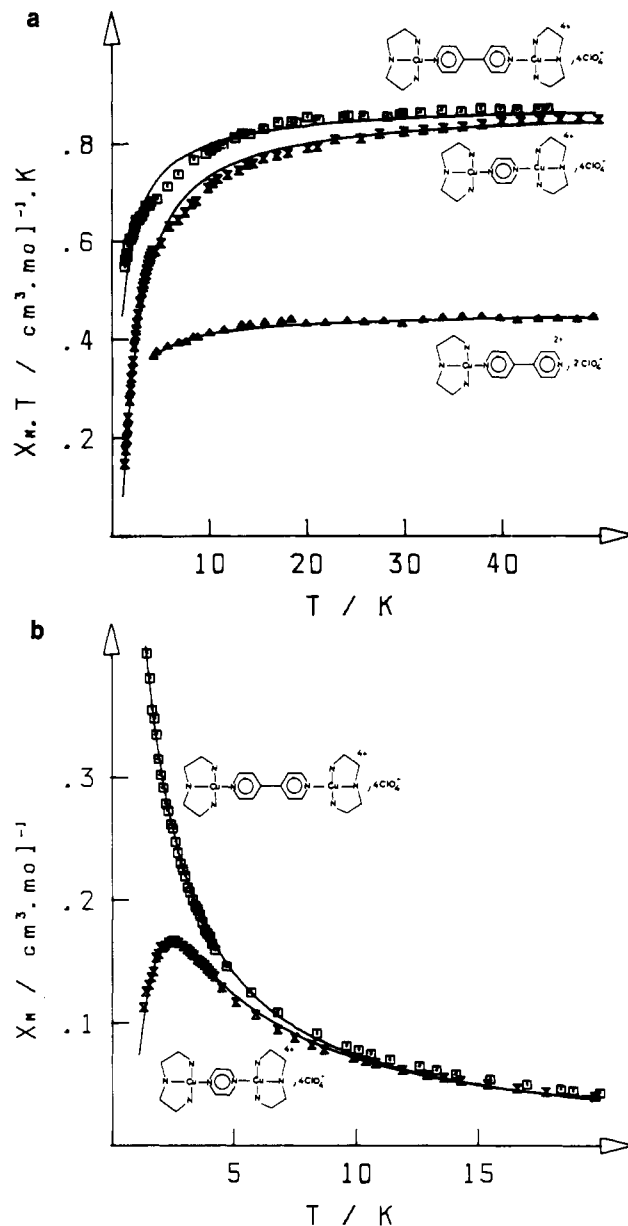


Figure 5. (a) Thermal variation of the molar susceptibility for complexes 1, 2, and 3 in the form $\chi_M T$ versus T : (open points) experimental results; (solid line) best theoretical fits (see text). (b) Thermal variation of the molar susceptibility for complexes 1 and 2 in the 20–1.3 K temperature range in the form χ_M versus T .

group of another unit: the distances $\text{O}(9)-\text{N}(11)'$ and $\text{H}(91)-\text{N}(11)'$ are $2.878 (11)$ and $1.995 (8) \text{ \AA}$, respectively; the $\text{O}(9)-\text{H}(91)-\text{N}(11)'$ angle is $160.7 (6)^\circ$. The hydrogen bonds expected between the oxygen atoms of the perchlorate and the NH groups of dien were not characterized due to the disorder of the oxygen atoms of the perchlorate.

Electronic and IR Spectra. The three compounds display similar electronic spectra consisting of intense charge-transfer bands at 320 nm for 1 and 3 and at 265 nm for 2, a shoulder at 380 nm for 1 and 3, and a broad d-d band of weak intensity centered at 550 nm for 1, 560 nm for 2, and 600 nm for 3. The shift toward lower energy from 1 to 3 can be related to a lower ligand field in 3, as confirmed by the longer copper-nitrogen distances in this latter complex.

The main IR absorptions agree with the proposed formulas for all the complexes.³¹⁻³³ The essential differences between the

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Table III. Main Interatomic Distances (Å) and Bond Angles (deg)^{a,b} for Complexes and **1** and **3**

	1	3		1	3
Copper Surroundings					
Cu-N(1)	1.993 (7)	1.995 (7)	Cu-O(2)	2.876 (12)	
Cu-N(4)	2.008 (8)	2.038 (6)	Cu-O(4) ⁱⁱ	2.660 (13)	
Cu-N(7)	2.008 (7)	2.023 (6)	Cu-Cu (intra)	11.106 (2)	
Cu-N(10)	2.008 (6)	2.021 (7)	Cu-Cu (inter)	7.283 (2)	6.795 (8)
Cu-O(9)		2.351 (7)			
N(1)-Cu-N(4)	84.5 (3)	84.0 (3)	N(4)-Cu-O(9)		92.9 (3)
N(1)-Cu-N(7)	84.7 (3)	83.8 (3)	N(7)-Cu-N(10)	94.5 (3)	95.8 (3)
N(1)-Cu-N(10)	179.0 (3)	178.7 (3)	N(7)-Cu-O(2)	81.0 (3)	
N(1)-Cu-O(2)	87.4 (3)		N(7)-Cu-O(4) ⁱⁱ	106.7 (4)	
N(1)-Cu-O(4) ⁱⁱ	80.8 (4)		N(7)-Cu-O(9)		101.6 (3)
N(1)-Cu-O(9)		91.0 (3)	N(10)-Cu-O(2)	91.8 (3)	
N(4)-Cu-N(7)	166.5 (3)	161.1 (3)	N(10)-Cu-O(4) ⁱⁱ	100.0 (4)	
N(4)-Cu-N(10)	96.2 (3)	96.1 (3)	N(10)-Cu-O(9)		90.3 (2)
N(4)-Cu-O(2)	90.5 (3)		O(2)-Cu-O(4) ⁱⁱ	165.2 (4)	
N(4)-Cu-O(4) ⁱⁱ	79.5 (4)				
Diethylenetriamine					
N(1)-C(2)	1.463 (11)	1.468 (11)	N(7)-C(6)	1.469 (11)	1.478 (12)
N(1)-C(5)	1.468 (11)	1.479 (13)	C(2)-C(3)	1.487 (15)	1.497 (16)
N(4)-C(3)	1.484 (12)	1.465 (12)	C(5)-C(6)	1.512 (14)	1.496 (13)
Cu-N(1)-C(2)	108.3 (5)	109.0 (6)	N(1)-C(2)-C(3)	105.4 (7)	106.6 (7)
Cu-N(1)-C(5)	107.3 (5)	108.9 (5)	N(4)-C(3)-C(2)	109.2 (7)	108.2 (8)
C(2)-N(1)-C(5)	117.1 (7)	116.4 (7)	N(1)-C(5)-C(6)	107.2 (7)	107.0 (8)
Cu-N(4)-C(3)	107.5 (6)	108.2 (6)	N(7)-C(6)-C(5)	108.3 (7)	108.7 (8)
Cu-N(7)-C(6)	109.6 (5)	109.8 (5)			
4,4'-Bipyridine					
N(10)-C(11)	1.335 (10)	1.352 (10)	C(14)-C(15)		1.367 (12)
N(10)-C(15)	1.316 (11)	1.341 (9)	C(16)-C(17)		1.386 (10)
C(11)-C(12)	1.384 (12)	1.362 (11)	C(16)-C(20)		1.392 (9)
C(12)-C(13)	1.382 (10)	1.393 (9)	C(17)-C(18)		1.380 (13)
C(13)-C(14)	1.379 (11)	1.394 (10)	C(19)-C(20)		1.377 (13)
C(13)-C(13) ⁱ	1.489 (10)		N(11)-C(18)		1.314 (10)
C(13)-C(16)		1.487 (11)	N(11)-C(19)		1.357 (12)
Cu-N(10)-C(11)	121.9 (5)	120.0 (5)	C(13)-C(14)-C(15)	119.5 (8)	120.4 (7)
Cu-N(10)-C(15)	121.3 (6)	123.5 (5)	C(14)-C(15)-N(10)	124.3 (8)	123.3 (7)
C(11)-N(10)-C(15)	116.8 (7)	116.4 (7)	C(13)-C(16)-C(17)		121.8 (7)
N(10)-C(11)-C(12)	122.6 (7)	123.3 (7)	C(13)-C(16)-C(20)		121.1 (7)
C(11)-C(12)-C(13)	120.2 (7)	120.4 (7)	C(17)-C(16)-C(20)		117.1 (7)
C(12)-C(13)-C(13) ⁱ	121.9 (6)		C(16)-C(17)-C(18)		119.3 (7)
C(14)-C(13)-C(13) ⁱ	121.6 (7)		C(17)-C(18)-N(11)		124.3 (8)
C(12)-C(13)-C(14)	116.5 (7)	116.1 (7)	C(18)-N(11)-C(19)		116.6 (8)
C(12)-C(13)-C(16)		122.1 (6)	N(11)-C(19)-C(20)		123.0 (8)
C(14)-C(13)-C(16)		121.8 (6)	C(19)-C(20)-C(16)		119.5 (8)
Perchlorate Anions					
Cl(1)-O(1)	1.414 (8)	1.418 (11)	Cl(2)-O(5)	1.418 (8)	1.401 (7)
Cl(1)-O(2)	1.454 (14)	1.407 (9)	Cl(2)-O(6)	1.411 (12)	1.398 (9)
Cl(1)-O(3)	1.411 (15)	1.374 (10)	Cl(2)-O(7)	1.427 (10)	1.348 (14)
Cl(1)-O(4)	1.422 (15)	1.396 (14)	Cl(2)-O(8)	1.420 (12)	1.469 (15)
O(1)-Cl(1)-O(2)	108.1 (6)	108.2 (6)	O(5)-Cl(2)-O(6)	108.0 (6)	112.9 (5)
O(1)-Cl(1)-O(3)	110.1 (7)	109.0 (7)	O(5)-Cl(2)-O(7)	109.5 (5)	118.3 (7)
O(1)-Cl(1)-O(4)	112.7 (7)	104.2 (7)	O(5)-Cl(2)-O(8)	110.1 (6)	100.8 (7)
O(2)-Cl(1)-O(3)	107.8 (8)	113.6 (6)	O(6)-Cl(2)-O(7)	108.1 (3)	115.5 (6)
O(2)-Cl(1)-O(4)	118.2 (8)	109.5 (7)	O(6)-Cl(2)-O(8)	113.9 (7)	109.7 (8)
O(3)-Cl(1)-O(4)	100.0 (8)	111.8 (7)	O(7)-Cl(2)-O(8)	107.3 (6)	96.6 (8)

^a Esd's are given in parentheses. Abbreviations: intra, shortest intramolecular distance; inter, shortest intermolecular distance. ^b Roman numeral superscripts refer to the following equivalent positions relative to *x*, *y*, *z*: (i) 1 - *x*, 1 - *y*, 2 - *z*; (ii) 1/2 + *x*, *y*, 3/2 - *z*.

binuclear complex **1** and the mononuclear complex **3** are a strong band at 1588 cm⁻¹ present in **3** but not in **1** and bands at 3420 (strong), 1630 (shoulder), and 610 cm⁻¹ (medium) related to the existence of a copper(II)-coordinated water molecule in **3**.

Magnetic Results. The thermal variations of the molar susceptibilities of the three compounds are shown in Figure 5a as the product $\chi_M T$ versus *T*, whereas plots of χ_M versus *T* for compounds **1** and **2** are shown in Figure 5b. In the temperature range studied, the susceptibility exhibits a maximum for compound **2** at 2.55 K and no maximum for compounds **1** and **3**. The $\chi_M T$ product decreases slightly at low temperature; this indicates a weak antiferromagnetic exchange interaction between the copper(II) ions.

The data for complexes **1** and **2** were fitted in one of three ways. The first way was by the modified Bleaney-Blowers expression

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

for a binuclear copper(II) complex, where *J* is the singlet-triplet gap defined by the phenomenological Hamiltonian with quantum spin operators \hat{S}_1 and \hat{S}_2

$$H = -J\hat{S}_1 \cdot \hat{S}_2 \quad (3)$$

J expresses the intramolecular exchange interaction. In formula 2, *N*, *g*, β , *k*, and *T* have their usual meaning. *N* α is the tem-

Table IV. Best-Fit Results of Magnetic Data and Agreement Factors

model		compd						
		1		2		3		
Bleaney-Bowers	J , cm ⁻¹	-0.09	0	-0.3	-2.8	0	-2.4	0
	g	2.02	2.04	2.03	2.12	2.59	2.12	2.20
	Θ , K	0	-0.6	-0.4	0	-5.9	-0.4	-1.0
	$10^4 R$	7.8	2.9	3.4	14.2	223	4.2	0.7
Heisenberg $S = 1/2$ chain	J' , cm ⁻¹		-0.6			-2.2		-1.1
	g		2.03			2.16		2.19
	$10^4 R$		3.6			4.9		0.8
alternating chain	J , cm ⁻¹		-0.7			-2.3		
	g		2.01			2.09		
	α		0.29			0.32		
	$10^4 R$		4.8			2.9		

perature-independent paramagnetism ($120 \times 10^{-6} \text{ cm}^3 \cdot \text{mol}^{-1}$ for two copper(II) ions). The correction term $T/(T - \Theta)$ attempts to take into account the intermolecular interaction between the binuclear units in the crystal in a molecular field approach ($\Theta = zJ'$, z being the number of neighbors and J' the intermolecular interaction).

The second way was by the empirical expression of the magnetic susceptibility proposed by Estes et al.³⁴ to fit antiferromagnetic 1D Heisenberg $S = 1/2$ chains with

$$H = -J' \sum_{i=1}^{N-1} \hat{S}_i \hat{S}_{i+1} \quad (4)$$

The final way was by the empirical relation proposed by Hatfield et al.³⁵ for alternating chains with

$$H = -J \sum_{i=1}^{N/2-1} (\hat{S}_{2i-1} \hat{S}_{2i} + \alpha \hat{S}_{2i} \hat{S}_{2i+1}) \quad (5)$$

where α is the exchange alternating parameter.

Table IV summarizes the results. R is the agreement factor

$$R = \frac{\sum_i (\chi_{\text{exptl}}(i) - \chi_{\text{calcd}}(i))^2}{\sum_i \chi_{\text{exptl}}(i)^2}$$

As for the Bleaney-Bowers expression, for each compound, we present three fits. In the first fit we put $\Theta = 0$ and varied J : the obtained J value can be considered as the maximum possible magnitude of intramolecular exchange. In the second fit we put $J = 0$ and varied Θ : the calculated Θ value can be considered as the maximum possible magnitude for intermolecular exchange. In the third fit, J and Θ were varied. The theoretical curves in Figure 5 are drawn by using these results, including inter- and intramolecular exchange interaction. All the R agreement factors are good, around 4×10^{-4} for 61 experimental points. Nevertheless, when the initially introduced J and Θ values are varied, there is some correlation between J and Θ .

The results of the fits with the Heisenberg $S = 1/2$ chain and the alternating-chain models are also reported in Table IV. One can note here correlations between J and g , depending on the theoretical model used. Indeed, there is no computing evidence to choose the right physical model.

To try to evaluate directly the intermolecular interactions, we decided to synthesize and to measure the susceptibility of the mononuclear complex **3**, $[\text{Cu}(\text{dien})(4,4'\text{-bpy})(\text{H}_2\text{O})](\text{ClO}_4)_2$, where only intermolecular interactions are operating. The results are plotted in Figure 5a. The $\chi_M T$ value decreases from $0.44 \text{ mol}^{-1} \cdot \text{cm}^3 \cdot \text{K}$ at 50.6 K to $0.36 \text{ mol}^{-1} \cdot \text{cm}^3 \cdot \text{K}$ at 4.2 K, showing again an antiferromagnetic interaction between the copper(II) ions: in this case, the coupling is inevitably intermolecular since each complex contains only one copper(II) ion. The data fit the Curie-Weiss expression

$$\chi_M = \frac{Ng^2\beta^2}{4kT} \left[\frac{T}{T - \Theta} \right] + N\alpha \quad (6)$$

with $\Theta = -1 \text{ K}$ (-0.7 cm^{-1}) and $g = 2.20$ ($N\alpha = 60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) demonstrating a weak intermolecular interaction.

EPR Results. The X-band EPR spectra recorded on microcrystalline powders show absorption bands of axial symmetry ($g_{\parallel} = 2.24$ and $g_{\perp} = 2.09$ for **1**; $g_{\parallel} = 2.20$ and $g_{\perp} = 2.05$; for **2**; $g_{\parallel} = 2.24$ and $g_{\perp} = 2.06$; for **3**), with no significant variations from room temperature to 7 K. At low temperatures, there appears a very weak half-field transition not only in the binuclear complexes **1** and **2**, where it could be interpreted as the $\Delta M_s = 2$ forbidden transition in the triplet, but also in the structurally characterized mononuclear complex **3**, where this interpretation is no longer valid. We comment on this point further in the Discussion.

Discussion

This work was undertaken to answer the following questions: (i) Is it possible to demonstrate structurally the bridging ability of 4,4'-bipyridine between two copper(II) ions in a $d_{x^2-y^2}$ state separated by more than 11 Å? (ii) Is there a clearly defined intermolecular interaction at such a distance between the two paramagnetic ions through a molecule theoretically expected to allow exchange interaction? Our experimental results allow us to answer clearly yes to the first question and, unfortunately, no to the second one.

Although 4,4'-bpy has been used for a long time^{24,36,37} to study electronic interactions in solution between transition-metal ions with different oxidation states, its bridging ability in the solid state was demonstrated only recently, in a rare-earth binuclear complex of Nd(III)²⁵ and in 1D chains of Ni(II).²⁶ Complex **1** appears therefore, to the best of our knowledge, to be the first example of a μ -4,4'-bpy binuclear transition complex with a full structural characterization. It seems that the coordination ability of the nitrogen atoms of 4,4'-bpy is efficiently counterbalanced by the tendency to give protonated or hydrogen-bonded species on the second nitrogen atom when the first one is already bound to a transition-metal ion. For instance, in ref 25 4,4'-bpy molecules play three roles: monoprotonated cations, hydrogen-bonded neutral species, and, for only one-fourth of the molecules, bridges between rare-earth ions. In this work, we verify that the mononuclear complex **3** is the most stable species formed from water: it can be obtained from aqueous solutions of the binuclear complex **1**; it is stabilized in the solid state by a hydrogen bond between the noncoordinated nitrogen atom and a water molecule bound to a Cu(II) ion of another complex. This hydrogen bond allows the formation of pairs of mononuclear complexes shown in Figure 3. In contrast, it is necessary to displace solid-state solution and solution equilibria by a large excess of $[\text{Cu}(\text{dien})]^{2+}$ mixed with **1** (molar ratio 8:1, respectively) to obtain the binuclear complex **1** from aqueous solutions.

Crystal structures of compounds **1** and **3** allow the verification once more of the chameleon-³⁸ or the Janus-like¹² coordination behavior of Cu(II) due to Jahn-Teller distortion. With the same initial reagents in water (copper(II) perchlorate, dien, and 4,4'-

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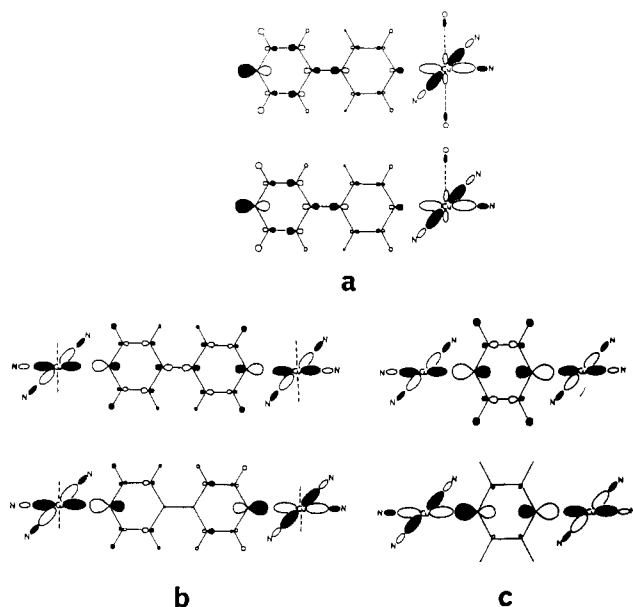


Figure 6. (a) Magnetic orbitals in compounds 1 and 3. (b) Singly occupied molecular orbitals in 1. (c) Singly occupied molecular orbitals in 2.

bpy), we obtain two very different complexes: **1** is binuclear with a 4+2 coordination and two coordinated perchlorate anions, whereas **3** is mononuclear with a 4+1 coordination and without coordinated perchlorate but with an axial water molecule instead. In both cases, however, we found, as is frequently the case,⁴ that the nearest neighbors of copper(II) are nitrogen rather than oxygen atoms. The copper–nitrogen bond lengths, close to 2 Å as usual, are longer in **3**: this is reflected by the bathochromic shift in the electronic spectra in going from **1** to **3**. Half of the perchlorate anions play a major role in the framework of the crystal structure of **1**: they bridge the copper(II) ions on each side of the binuclear units to give 1D alignments of metallic ions. This peculiar structural feature is probably one of the factors that stabilizes the crystal, allows the determination of the structure, and yields a positive answer to our first question. Unfortunately, it is also the feature that obliged us to answer the second question in the negative since our experimental data show weak interactions that cannot be safely attributed to intramolecular interaction only through 4,4'-bpy. We now discuss this point.

The results of Figure 5 and Table IV demonstrate that the magnitudes of the interaction in complexes **1–3** decrease in the order $2 \geq 1 \geq 3$, whatever the origin of the interaction (intra- or intermolecular) may be.

In compounds **1** and **3**, the unpaired electron of the copper(II) ion can be described by a magnetic orbital of $d_{x^2-y^2}$ symmetry partially delocalized on the ligands, shown in Figure 6a.³⁹ The presence of axial oxygen (one at 2.33 Å in **3**, two at 2.67 and 2.88 Å in **1**) leads to a small admixture of d_{z^2} in the magnetic orbital: the spin delocalization is large on the nitrogen atom nearest neighbors and much smaller on the axial oxygen atoms. We guess that in **2**, whose structure is unknown, the magnetic orbitals can be described as in **1** or as in the closely related $[\text{Cu}(\text{pyz})(\text{NO}_3)_2]$ chain,⁴⁰ where interaction through pyrazine was demonstrated with a J intrachain exchange strength equal to -7.4 cm^{-1} .⁴¹ We anticipate from this that the antiferromagnetic interaction found in **2** is probably mainly intramolecular: the two $d_{x^2-y^2}$ magnetic

orbitals overlap through the pyrazine bridge, building the two singly occupied molecular orbitals shown in Figure 6c. The energy gap Δ_2 between them as found by the extended Hückel calculations³⁹ on the binuclear cation is $\Delta_2 = 0.863 \text{ eV}$. In systems with similar geometries,²¹ Hay proposed that $J \propto \Delta^2$. In **3**, the interaction, which is the weakest of the three compounds, can be only intermolecular and the exchange pathway goes probably through space between nearest copper(II) atoms at 6.8 Å. The copper(II)–copper(II) interaction is sufficiently large to give rise to the EPR half-field transition, which is not therefore a signature of a binuclear unit. In **1**, the interaction is intermediate in magnitude between those in **2** and **3** but our present data give no means to determine the intra- or intermolecular character. In other terms, we have no way of knowing if the σ overlap between the two $d_{x^2-y^2}$ orbitals through a 4,4'-bpy group bridging copper(II) ions, at 11.1 Å, is significantly larger than the δ overlap of $d_{x^2-y^2}$ orbitals through a perchlorate group linking Cu(II) ions, at 7.3 Å.

From extended Hückel calculations performed on the binuclear cation, we can draw the singly occupied molecular orbitals shown in Figure 6b. The energy gap Δ_1 between them is $\Delta_1 = 0.406 \text{ eV}$, smaller than Δ_2 in **2** but still very important.⁴² Indeed, these calculations cannot solve our problem since they overemphasize the intramolecular overlap: the molecular orbitals of the bridge are higher in energy than the 3d atomic orbitals, and the gap between them is very large (0.7 eV). This gives rise to a large overlap with the d orbitals and to an important separation between the singly occupied molecular orbitals in the binuclear complex. Such problems in using simple semiempirical Hückel calculations have already been pointed out.^{5,7,21}

Therefore, we can give only an upper limit for a possible intramolecular antiferromagnetic interaction, -0.9 cm^{-1} in **1** and -2.8 cm^{-1} in **2**.

If we compare our values with the ones of Coffman and Buetner (CB), we can conclude that for compound **1**, if J is intramolecular, it would be beyond the CB limit (about $-3 \times 10^{-2} \text{ cm}^{-1}$ at 11 Å), while if J is intermolecular, it would be less than the CB value (about -30 cm^{-1} at 7.2 Å). For compound **2**, our J value is much less than the CB frontier (about -65 cm^{-1} at 6.8 Å, the estimated distance between the two copper(II) ions in **2**).

Conclusion

We demonstrated the bridging role of 4,4'-bipyridine between two copper(II) ions separated by 11.1 Å. Nevertheless, we could not attribute the observed antiferromagnetic coupling to intramolecular interaction only. We proposed an upper limit of J_{intra} at -0.9 cm^{-1} . A definite answer would imply further measurements: magnetization and specific heat measurements at lower temperatures. We are now planning such experiments. Measurements on a binuclear complex diluted in a diamagnetic host matrix would also be useful.

The discussion confirms that the determination of the limit of intramolecular exchange interaction through extended bridges is a difficult problem in concentrated magnetic materials: on one hand, the intermolecular distances become shorter than the intramolecular ones without the use of bulky counterions, and hydrogen-bonded or dipolar interactions can also be present; on the other hand, the comparison between couplings in related mononuclear and binuclear species is not very helpful since the crystallographic structures, and hence the intermolecular exchange pathways, are often very different.

Safety Note

Perchlorate salts of metal complexes with organic ligands are potentially explosive. We used in the syntheses here described only small amounts of material (the preparations were carried out at the millimole scale), and the starting perchlorate salt was an aquo complex. The dilute solutions were handled with great

(39) These results are from extended Hückel calculations performed with FORTICON 8 (QCPE, Program No. 344, Indiana University, Bloomington, IN). The geometries used were the averaged crystallographic ones. The semiempirical parameters were drawn from ref 21. We performed calculations with self-consistent charge iterations for all atoms.

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(42) For example, in ref 7, we computed an energy gap between the two singly occupied molecular orbitals of a μ -oxalato copper(II) binuclear complex as 0.257 eV for a J value of -385 cm^{-1} (to be compared here to 0.406 eV and -2.7 cm^{-1}).

caution and evaporated slowly at room temperature in an open hood (cf. ref 43).

Caution! Perchlorates are not only potentially explosive in the writing of safety notes but also actually explosive in the laboratory. We are sad to say that at the same time we were drawing up this paper, a chemist was killed on the campus at Orsay, due to an explosion of lithium perchlorate handled in tenths of grams in methanolic concentrated solutions within a metallic glovebox.

When noncoordinating agents are required, every attempt

(43) *J. Chem. Educ.* **1985**, *62*, 1001. *Chem. Eng. News* **1983**, *61* (Dec 5), 4; **1963**, *41* (July 8), 47. Please note that the reference in the notice to authors (*Inorg. Chem.* **1987**, *26*(1), 4A-6A) must read: *J. Chem. Educ.* **1973**, *50*, A335.

should be made to substitute anions such as the fluoro sulfonates for the perchlorates.

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Supplementary Material Available: Listings of atomic coordinates, thermal parameters, weighted least-squares planes, and bond distances and angles for both compounds 1 and 3 (67 pages); listings of structure factor amplitudes (63 pages). Ordering information is given on any current masthead page.

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Dinickel and Dicopper Complexes with N,N-Linked Bis(cyclam) Ligands. An Ideal System for the Investigation of Electrostatic Effects on the Redox Behavior of Pairs of Metal Ions

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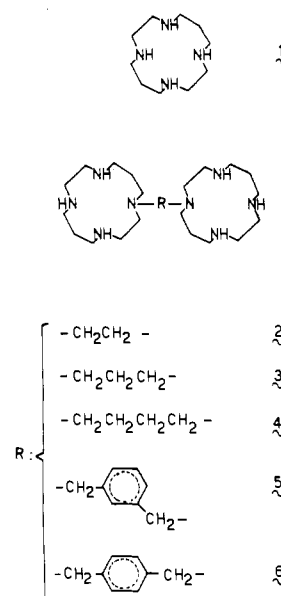
A novel family of bis(macrocycles) in which two cyclam subunits are linked through nitrogen atoms by a carbon chain R of varying length ($R = -(CH_2)_2-$, $-(CH_2)_3-$, $-(CH_2)_4-$, *m*-xylyl, *p*-xylyl) has been designed. Synthesis is based on the condensation of the readily available intermediate *N,N,N'*-tritosylcyclam (2 equiv) with an X-R-X fragment ($X = Br$ or OTs). Electrochemical investigation has shown that the corresponding dinickel(II) and dicopper(II) bis(macrocyclic) complexes undergo a two-electron-oxidation process, according to two reversible one-electron steps, whose redox potentials are separated by the quantity ΔE° . The value of ΔE is related to the comproportionation (or *valence scrambling*) equilibrium $[M^{III}M^{III}(L)]^{6+} + [M^{II}M^{II}(L)]^{4+} \rightleftharpoons 2[M^{III}M^{II}(L)]^{5+}$ and results from the combination of a statistical fixed contribution and a term that reflects the electrostatic repulsion between the metal centers of the dinuclear complex. It has been found that the electrostatic repulsion term decreases when the distance between the metal centers is increased, according to a hyperbolic mode, but does not show any definite dependence upon the macroscopic values of the dielectric constant of the explored media. Moreover, the electrostatic term significantly varies with the stereochemical features of each metal center in its oxidation state (II or III), which cannot be any longer considered as simple point charges.

Introduction

The preparation and properties of a large number of homodimetallic complexes have been described over the past two decades. Some of these dinuclear species display redox activity in solution disclosing two consecutive one-electron-redox steps. The separation of the potentials associated with each redox event, ΔE , may range from 36 mV (limiting case in which the two equivalent redox centers behave independently), to some hundreds of millivolts for complexes in which strong mutual interactions exist between metal centers. The communication between the two metals may occur through two main paths: (i) electronic (direct interaction or delocalization through a bridging coordinating unit) and/or (ii) electrostatic. The separation of the two contributions may not be straightforward.²

Recently a novel class of ligands capable of binding pairs of metal ions quite strongly has been introduced: the bis(macrocycles). In these ligating systems two cyclic polyaza subunits are linked together either through an aliphatic chain joining two nitrogen atoms (*N,N'*-bis(macrocycles))³⁻⁷ or by a covalent bond

Chart I



joining two carbon atoms (*C,C'*-bis(macrocycles)).⁸⁻¹² Each subunit may incorporate a transition-metal ion to give a very stable

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