Bonding Flexibility of 2,2′-Bipyrimidine (bpm): Symmetry and Magnetism of Three Copper(II) Complexes with Different Cu:bpm Ratios

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The study of exchange interactions between transition-metal ions has been an active field of research in the last 15 years.[2] The search to push back the upper limit for the magnitude of the interaction between two magnetic centers separated by polyatomic bridging groups,[3–10] the synthesis of models to mimic polynuclear biologically active centers,[11] and the design of new molecular materials[12] are among the driving forces of this interdisciplinary research field.

In this context, the possibilities of 2,2′-bipyrimidine (hereafter abbreviated bpm) as a bridging ligand were demonstrated by the first coupled structural and magnetic data on a series of bpm-bridged Ni(II), Co(II), and Mn(II) complexes.[13] In previous works, we have investigated the formation of complexes between copper(II) and 2,2′-bipyrimidine, characterized structurally the coordination modes of this polyatomic ligand, and checked its ability to transmit exchange coupling between metal ions separated by more than 5.5 Å.[14–18] Chelating and bischelating bpm-containing copper(II) complexes were characterized with different counterions. Strong antiferromagnetic coupling (about -200 cm^{-1} for the singlet–triplet energy gap) was observed in the bischelating systems.

In the present contribution, we show how it is possible to tune the singlet–triplet energy gap in bpm-bridged copper(II) complexes between zero and -200 cm^{-1}. This result is achieved by varying both the bpm:Cu(II) molar ratio and the nature of the counterion X. We report the structural and magnetic characterization of three complexes $[Cu(bpm)_2(H_2O)](ClO_4)_2\cdot 2H_2O$ (**1**) (mononuclear), $[Cu_2(bpm)_3(H_2O)_4](ClO_4)_4$ (**2**) (dinuclear), and $[Cu(bpm)(H_2O)_2](ClO_4)_2\cdot H_2O$ (**3**) (chain).[19] The magnetic properties of **2** and **3** provide another example of orbital reversal.[20]

Experimental Section

Materials. 2,2′-Bipyrimidine and copper(II) perchlorate hexahydrate were purchased from Janssen and used without purification. Copper content was determined by atomic absorption spectrophotometry. Elemental analysis (C, H, N) were performed by the Servicio de Análisis Elemental de la Universidad Autónoma de Madrid.

Synthesis. $[Cu(bpm)_2(H_2O)](ClO_4)_2\cdot 2H_2O$ (1). Parallelepiped blue-greenish crystals of **1** suitable for X-ray analysis were obtained from a

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[19] A preliminary communication of the structures of complexes **1**–**3** was presented at the 11th European Crystallographic Meeting at Vienna (Austria) which appeared published in *Z. Krystallogr.* **1988**, *185*, 323. During the preparation of the present paper, the crystal structures of **1** (Morgan, L. W.; Pennington, W. T.; Petersen, J. D.; Ruminski, R. R.; Bennett, D. W.; Rommel, J. S. *Acta Crystallogr.* **1992**, *C48*, 163) and **3** (Morgan, L. W.; Goodwin, K. V.; Pennington, W. T.; Petersen, J. D. *Inorg. Chem.* **1992**, *31*, 1103) were published.

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Table I. Crystallographic Data for Compound **2**

chem formula	$C_{24}H_{26}N_{12}Cl_4Cu_2O_{20}$	fw	1071.4
a, Å	9.228(2)	space group	$P\bar{1}$
b, Å	10.825(2)	T, K	298
c, Å	11.110(3)	λ, Å	0.710 69
α, deg	118.33(1)	ρ_{calcd}, g cm^{-3}	1.90
β, deg	103,86(1)	μ, cm^{-1}	15.2
γ, deg	91.20(1)	R^a	0.0412
Z	1	$R_w{}^b$	0.0481

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

mixed 1:1 water–ethanol solution containing $[Cu(H_2O)_6](ClO_4)_2$ (1 mmol, 10 mL of water) and 2,2′-bipyrimidine (2 mmol, 10 mL of ethanol) by slow evaporation at room temperature. They were filtered off, washed with cold water, and air-dried. Anal. Calcd for $C_{16}H_{18}N_8Cl_2CuO_{11}$ (**1**): C, 30.38; H, 2.85; N, 17.70; Cu, 10.04. Found: C, 30.55; H, 2.87; N, 17.75; Cu, 9.90.

$[Cu_2(bpm)_3(H_2O)_4](ClO_4)_4$ (2) and $[Cu(bpm)(H_2O)_2](ClO_4)_2 \cdot H_2O$ (3). Rhombohedral blue crystals of complex **2** and blue needles of complex **3** separated together from H_2O–EtOH mixtures containing copper(II) perchlorate (4 mmol dissolved in 10 mL of H_2O) and 2,2′-bipyrimidine (2 mmol dissolved in 10 mL of EtOH). They were separated by hand, washed with cold water and ethanol, and air-dried. Compound **3** is the only product obtained when aqueous ethanolic solutions containing copper(II) perchlorate and bpm in a 4:1 molar ratio are slowly evaporated. Anal. Calcd for $C_{24}H_{26}N_{12}Cl_4Cu_2O_{20}$ (**2**): C, 26.91; H, 2.43; N, 15.69; Cu, 11.86. Found: C, 26.47; H, 2.58; N, 15.42; Cu, 11.70. Calcd for $C_8H_{12}N_4Cl_2CuO_{11}$ (**3**): C, 20.25; H, 2.53; N, 11.80; Cu, 13.39. Found: C, 19.86; H, 2.48; N, 11.53; Cu, 13.27.

Physical Techniques. Magnetic susceptibility measurements were carried out on polycrystalline samples of **2** and **3** in the 4.2–300 K temperature range with a Faraday-type magnetometer, equipped with a helium flow cryostat. The apparatus was calibrated with mercury tetrakis(thiocyanato)cobaltate(II). The corrections for the diamagnetism using Pascal's constants are estimated at -514×10^{-6} and -218×10^{-6} cm^3 mol^{-1} for complexes **2** and **3**, respectively.

X-ray Data Collection and Structure Refinement. Diffraction data were collected at room temperature on a Siemens Stoe four-circle diffractometer (**1** and **2**) and on a CAD-4 Enraf-Nonius automatic diffractometer (**3**) by using graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation and an ω-2θ scan technique. Accurate unit cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 25 strong reflections in the $12 < 2\theta < 30°$ range. A summary of the crystallographic data for **2**[21] is given in Table I. A more complete list of crystallographic data is reported in Table S1.[22] All data were corrected for Lorentz and polarization effects, absorption and extinction corrections being ignored. After every 100 reflections, 3 were collected as an intensity and orientation control, and they showed no significant intensity decay.

The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares calculations, with $\sum w(|F_o| - |F_c|)^2$ being minimized. All non-hydrogen atoms were refined anisotropically, except perchlorate O atoms of compound **3**. On the difference map of this compound, several oxygen positions were localized for all perchlorate O atoms except O(3). This disorder was described by assigning population parameters of 0.7 and 0.3 to each pair of sites. The hydrogen atoms of the water molecules were located on a ΔF map and refined with constraints. All other hydrogen atoms were set in calculated positions and refined as riding atoms. A common thermal parameter was assigned to all hydrogen atoms.

Of the 2243 measured reflections for **1**, 3165 for **2**, and 3145 for **3**, 1591 and 2858 were unique ($I > 3\sigma(I)$) for **1** and **2**, respectively, whereas only 1434 were unique ($I > 3.5\sigma(I)$) for **3**. These data were used in the final refinement of the structural parameters to converge to final residuals R (R_w) of 0.039 (0.047) for **1**, 0.041 (0.048) for **2**, and 0.069 (0.075) for **3**, with goodness of fit of 0.99, 0.95, and 1.71 for **1**, **2**, and **3**, respectively. The weighting scheme used in the last refinement cycle was $w = 1.0000/(\sigma^2|F_o| + qF_c{}^2)$ with q = 0.003 388 (**1**), 0.003 592 (**2**), and 0.001 000 (**3**). In the final difference map, the values of the residual maxima and minima were 0.51 and −0.51 e Å^{-3} for **1**, 0.71 and −0.63 e Å^{-3} for **2**, and 0.93 and −0.62 e Å^{-3} for **3**. All calculations were performed with the SHELX-76[23] and PARST[24] sets of programs. Drawings were produced with the SHELXTL-PLUS system.[25] Final fractional coordinates for non-hydrogen atoms are listed in Tables II (**2**), S2 (**1**), and S3 (**3**). Main interatomic bond distances and angles for **2** are given in Table III. Complete lists of bond distances and angles (Tables S4–S6), anisotropic temperature factors (Tables S7–S9), hydrogen coordinates (Tables S10–S12), and least-squares planes (Tables S13–S15) for **1**–**3** are available as supplementary material.[22]

Table II. Final Atomic Fractional Coordinates and Equivalent Isotropic Displacement Parameters[a,b] for Non-Hydrogen Atoms of $[Cu_2(bpm)_3(H_2O)_4](ClO_4)_4$ (**2**)

atom	x/a	y/b	z/c	10^3U_{eq}, Å^3
Cu(1)	0.3309(1)	0.2255(1)	0.3046(1)	27(1)
Cl(1)	0.8517(1)	0.3173(1)	0.5908(1)	46(1)
Cl(2)	0.5056(1)	−0.2538(1)	0.1902(1)	51(1)
N(1)	0.5100(3)	0.3546(3)	0.3335(3)	27(1)
N(2)	0.1360(3)	0.1238(3)	0.2827(3)	28(1)
N(3)	0.1900(3)	0.2719(3)	0.1621(3)	27(1)
N(4)	−0.1233(2)	0.0634(3)	0.1544(3)	36(1)
N(5)	0.6562(3)	0.5833(3)	0.4806(3)	27(1)
N(6)	−0.0693(3)	0.2184(3)	0.0296(3)	36(1)
C(1)	0.2211(4)	0.3454(4)	0.1008(4)	34(2)
C(2)	0.1110(5)	0.3576(4)	0.0011(4)	39(2)
C(3)	−0.0338(5)	0.2931(5)	−0.0310(5)	42(2)
C(4)	0.0445(4)	0.2119(3)	0.1220(4)	28(1)
C(5)	0.0164(4)	0.1286(3)	0.1914(4)	28(1)
C(6)	−0.1436(5)	−0.0108(4)	0.2195(5)	40(2)
C(7)	−0.0275(5)	−0.0191(4)	0.3178(5)	41(2)
C(8)	0.1144(5)	0.0491(4)	0.3473(4)	36(2)
C(9)	0.5451(3)	0.4833(4)	0.4490(3)	24(1)
C(10)	0.5937(4)	0.3245(4)	0.2424(4)	34(2)
C(11)	0.7082(4)	0.4224(5)	0.2662(4)	38(2)
C(12)	0.7372(4)	0.5521(4)	0.3879(4)	34(2)
O(1)	0.3716(3)	0.0304(3)	0.1025(3)	45(1)
O(2)	0.4575(3)	0.1377(3)	0.4131(3)	48(1)
O(3)	0.8911(5)	0.3206(5)	0.4773(5)	80(2)
O(4)	0.7198(4)	0.3786(4)	0.6179(4)	70(2)
O(5)	0.9719(5)	0.3689(8)	0.7129(5)	118(4)
O(6)	0.8030(7)	0.1673(5)	0.5430(7)	112(4)
O(7)	0.5155(5)	−0.2114(6)	0.0898(5)	87(3)
O(8)	0.4250(7)	−0.1529(5)	0.2785(7)	112(4)
O(9)	0.6500(7)	−0.2454(10)	0.2668(9)	159(6)
O(10)	0.4234(9)	−0.3857(5)	0.1317(10)	166(5)

[a] Estimated standard deviations in the last significant digits are given in parentheses. [b] U values for anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

Table III. Bond Lengths (Å) and Interbond Angles (deg) for Complex **2**[a]

	Distances		
Cu(1)–N(1)	2.003(3)	Cu(1)–O(2)	2.045(4)
Cu(1)–N(2)	1.990(3)	Cu(1)–N(3)	2.060(4)
Cu(1)–O(1)	2.362(3)	Cu(1)–N(5a)	2.272(3)
	Angles		
N(1)–Cu(1)–O(2)	93.3(1)	N(1)–Cu(1)–N(2)	170.9(1)
N(1)–Cu(1)–N(3)	93.3(1)	N(1)–Cu(1)–O(1)	93.9(1)
N(1)–Cu(1)–N(5a)	78.2(1)	O(2)–Cu(1)–N(2)	93.5(1)
O(2)–Cu(1)–N(3)	168.3(1)	O(2)–Cu(1)–O(1)	83.9(1)
O(2)–Cu(1)–N(5a)	87.6(1)	N(2)–Cu(1)–N(3)	81.2(1)
N(2)–Cu(1)–O(1)	92.9(1)	N(2)–Cu(1)–N(5a)	96.0(1)
N(3)–Cu(1)–O(1)	86.1(1)	N(3)–Cu(1)–N(5a)	103.1(1)
O(1)–Cu(1)–N(5a)	168.1(1)	Cu(1)–N(1)–C(9)	117.7(3)
Cu(1)–N(1)–C(10)	125.2(2)		

[a] Symmetry code: (a) $1 - x$, $1 - y$, $1 - z$.

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(21) The structures of **1** and **3** were reported very recently (see ref 19), and consequently, only minor structural information concerning them is given in this paper.

(22) Supplementary material.

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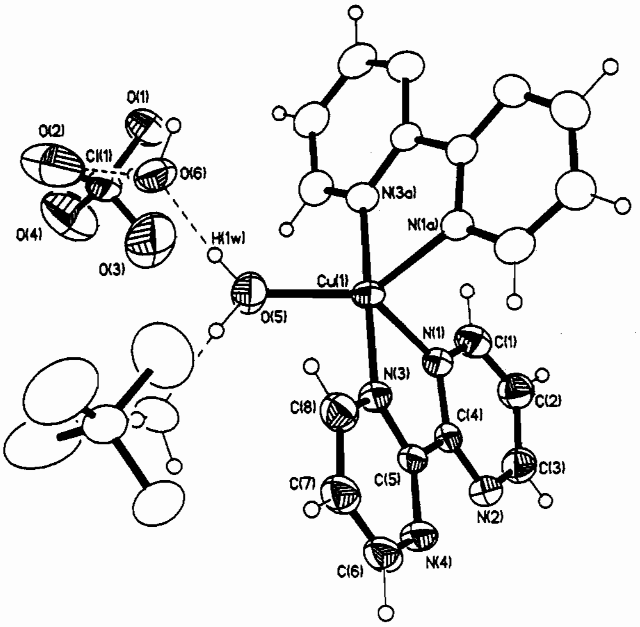

Figure 1. ORTEP view of the mononuclear $[Cu(bpm)_2(H_2O)](ClO_4)_2{\cdot}2H_2O$ complex (**1**) with the atom-numbering scheme. Thermal ellipsoids are plotted at the 50% probability level. Shaded ellipsoids represent the atoms of the asymmetric unit. All hydrogen atoms are drawn with uniform isotropic thermal parameters.

Results and Discussion

Description of the Structures. $[Cu(bpm)_2(H_2O)](ClO_4)_2{\cdot}2H_2O$ (1). The structure of complex **1** is made up of mononuclear $[Cu(bpm)_2(H_2O)]^{2+}$ cationic units, uncoordinated perchlorate anions, and water of crystallization molecules. The metal ion is in a pentacoordinate environment which is best described as distorted trigonal bipyramidal: two nitrogen atoms of a bpm ligand and the oxygen atom of a water molecule occupy the equatorial positions, whereas two nitrogen atoms of another bpm ligand fill the axial sites as shown in Figure 1. Bond distances and angles agree with those previously reported.[19] The molecular structure is similar to that of the complex $[Cu(bpm)_2(H_2O)](PF_6)_2{\cdot}2H_2O$.[16] Both compounds exhibit similar N(1)–Cu(1)–O(5) and N(1a)–Cu(1)–O(5) (130.0(1)° in **1** and 128.6(1)° in the hexafluorophosphate compound) and N(1a)–Cu(1)–N(1) angles (100.0(1)° in **1** and 102.8(1)° in the hexafluorophosphate derivative), and the Cu(1), N(1), N(1a), and O(5) atoms are in an exactly planar arrangement. The structure of **1** is also similar to those reported previously for the parent bis(2,2′-bipyridine)-containing copper(II) complexes,[26] noted hereafter Cu–bipy.

Bond distances and angles within the bpm ligand are practically identical to those previously reported for the $[Cu(bpm)_2(H_2O)](PF_6)_2{\cdot}2H_2O$,[16] $[Cu_2(bpm)_2(H_2O)_4(OH)_2](ClO_4)_2{\cdot}2H_2O$,[17] and $[Cu(bpm)(NCS)_2]_n$[18] complexes in which bpm acts as a terminal ligand. Some differences are observed, especially in the N(2)–C(4)–C(5) and N(3)–C(5)–C(4) bond angles, when terminal bpm is compared with bridging bpm in $Cu_2(bpm)X_4$ (X = NO_3, Cl, Br, NCO, NCS).[14,15,18] The N(1)···N(3) distance (2.603(4) Å) is smaller than the N(2)···N(4) one (2.751(4) Å) due to the bidentate coordination of bpm to Cu(II) through N(1) and N(3) nitrogen atoms. The bipyrimidine rings are planar, and they form a dihedral angle (6.2°), as in $[Cu(bpm)_2(H_2O)](PF_6)_2{\cdot}2H_2O$ (6.7°) and $[Cu_2(bpm)_2(H_2O)_4(OH)_2](ClO_4)_2{\cdot}2H_2O$ (7.1°).

Hydrogen bonding involves both coordinated water and water of crystallization molecules and one of the perchlorate oxygen atoms (2.37(4) Å and 165(3)° for O(2)···O(6) and O(2)···H(2w)–O(6), respectively; 2.68(1) Å and 176(5)° for O(6)···O(5) and O(6)···H(1w)–O(5), respectively). This scheme of hydrogen bonding involving coordinated and uncoordinated solvent molecules and a counterion has been observed in other five-coordinated copper(II) complexes.[27] The shortest intermolecular copper···copper separation is 7.558 Å for $Cu(1)\cdots Cu(1)^{i}$ (symmetry code: (i) *x*, 1 + *y*, *z*).

$[Cu_2(bpm)_3(H_2O)_4](ClO_4)_4$ (2). The structure of complex **2** consists of centrosymmetric cationic $[Cu_2(bpm)_3(H_2O)_4]^{4+}$ dinuclear units (Figure 2) and uncoordinated perchlorate anions. Two types of bpm molecules are present, terminal bidentate and asymmetrical bridging bis-bidentate. Each copper atom is in a distorted elongated octahedral environment: the equatorial positions are occupied by an oxygen atom (O(2)) from a water molecule, two nitrogen atoms (N(2) and N(3)) from the terminal bpm group, and one nitrogen atom (N(1)) from the bridging bpm, whereas the axial sites are filled by an oxygen atom (O(1)) from another water molecule and one nitrogen atom (N(5a)) from the bridging bpm ligand. The Cu–N equatorial distances (2.003(3), 1.990(3), and 2.060(4) Å for Cu(1)–N(1), Cu(1)–N(2), and Cu(1)–N(3), respectively) are in the range reported for other bpm-containing copper(II) complexes, and they are shorter than the axial ones (2.272(3) and 2.362(3) Å for Cu(1)–N(5a) and Cu(1)–O(1), respectively).

The slight differences between bond distances and angles of terminal and bridging bpm ligands are due to their different coordination modes. The N(2)···N(3) distance (2.635(6) Å) is shorter than the N(4)···N(6) one (2.737(7) Å) because of the bidentate coordination of the terminal bpm through N(2) and N(3) atoms. On the contrary, N(1)···N(5a) and N(1a)···N(5) distances in the bridging bpm ligand are identical (2.705(5) Å) (a symmetry center lies in the middle of the C(9)–C(9a) bond) and close to the N(4)···N(6) distance due to its asymmetrical bischelating mode. The pyrimidine rings are planar. The dihedral angle between the pyrimidine rings of the terminal bpm group (1.5(1)°) is smaller than that of **1** (6.2(1)°), whereas the pyrimidine rings are coplanar in the central bpm ligand.

Hydrogen bonding occurs between coordinated water molecules and some oxygen atoms of the perchlorate anions (3.05(1) Å and 137(3)° for O(4)···O(2) and O(4)···H(3w)–O(2), respectively; 2.74(1) Å and 152(5)° for O(8)···O(2) and O(8)···H(4w)–O(2), respectively; 2.92(1) Å and 131(5)° for O(7)···O(1) and O(7)···H(2w)–O(1), respectively). The intramolecular copper···copper separation is 5.670 Å, the largest observed for bpm-bridged copper(II) complexes, whereas the shortest intermolecular copper···copper separation is 7.348 Å for $Cu(1)\cdots Cu(1)^{ii}$ (symmetry code: (ii) −*x*, −*y*, −*z*).

$[Cu(bpm)(H_2O)_2](ClO_4)_2{\cdot}H_2O$ (3). The structure of complex **3** consists of cationic chains of bipyrimidine-bridged copper(II) ions (Figure 3), uncoordinated perchlorate anions, and water of crystallization molecules. Each copper atom is in a distorted octahedral environment as in compound **2**: two oxygen atoms from two water molecules occupying one axial and one equatorial position and four nitrogen atoms from two bpm ligands filling the remaining axial and equatorial sites create the octahedral environment around the metal ion. In compound **3**, all bpm molecules are equivalent, in contrast to compound **2**. In the present compound, bpm acts in an asymmetrically bischelating fashion with three Cu–N(bpm) short distances (Cu(1)–N(1), Cu(1)–N(2), and Cu(1)–N(4a)) and a longer one (Cu(1)–N(3a)). Bond distances and angles agree with those previously reported.[19]

As in compounds **1** and **2**, the pyrimidine rings of bpm are planar and they form a dihedral angle of 4.8(3)°. The arrange-

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(26) (a) Harrison, W. D.; Hathaway, B. J.; Kennedy, D. *Acta Crystallogr.* **1979**, *B35*, 2301. (b) Harrison, W. D.; Hathaway, B. J. *Acta Crystallogr.* **1979**, *B35*, 2910. (c) Harrison, W. D.; Kennedy, D. M.; Power, M.; Sheahan, R.; Hathaway, B. J. *J. Chem. Soc., Dalton Trans.* **1981**, 1556 and references therein.

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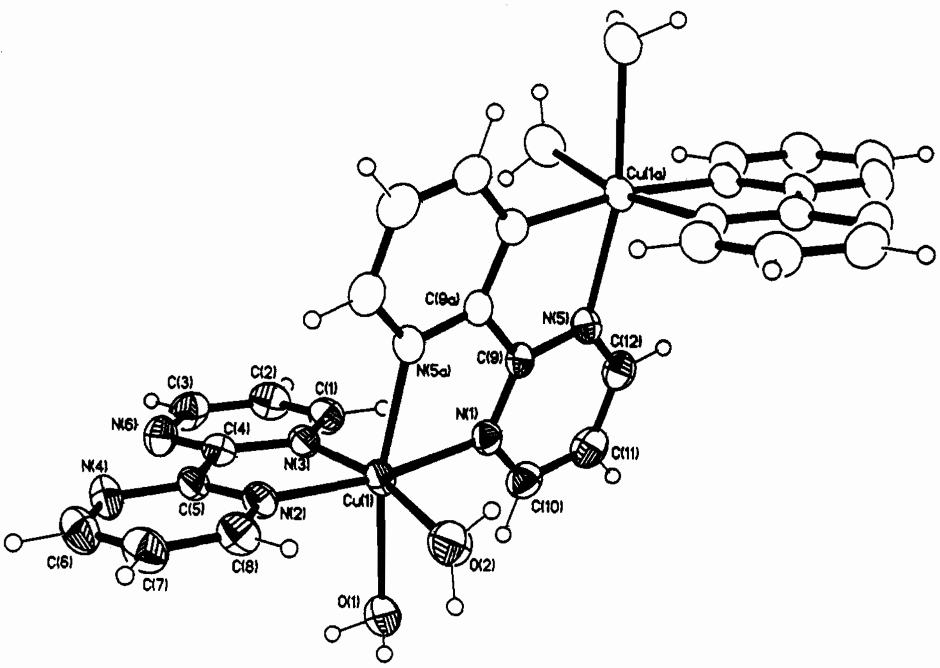

Figure 2. ORTEP view of the dinuclear $[Cu_2(bpm)_3(H_2O)_4]^{4+}$ unit of complex **2** with the atom-numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Shaded ellipsoids represent the atoms of the asymmetric unit. All hydrogen atoms are drawn with uniform isotropic thermal parameters.

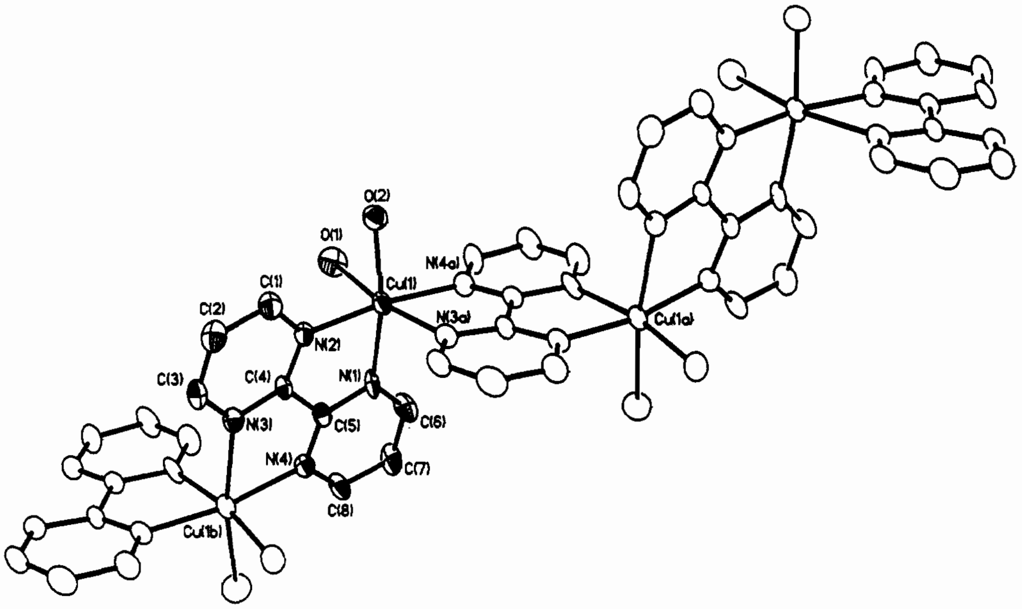

Figure 3. ORTEP view of one asymmetric unit (shaded ellipsoids) and three symmetry-related ones of the $[Cu(bpm)(H_2O)_2](ClO_4)_2{\cdot}H_2O$ complex (**3**) with the atom-numbering scheme. Thermal ellipsoids are plotted at the 50% probability level. All hydrogen atoms are drawn with uniform isotropic thermal parameters.

ment of the bridging bpm groups in **3** is similar to that of **2**. The substantial difference is that, in **2**, the equatorial planes in the dimeric unit are parallel as well as the mean plane of the terminal bpm. On the contrary, in **3**, the neighboring equatorial copper planes within the chain are mutually perpendicular and the bpm mean planes are parallel. The distances between these planes is 3.860(11) Å, larger than that found in compound **2** (3.780(4) Å). The interaction Cu(1)···Cu(1a) separation is 5.597(3) Å, whereas the shortest interchain Cu(1)···Cu(1)^{ii} distance is 7.379 Å.

Magnetic Properties. The thermal variations of the magnetic susceptibility (χ_M) per mole of copper(II) for complexes of **2** and **3** vs T are depicted in Figure 4. Both curves exhibit a behavior characteristic of antiferromagnetically coupled copper(II) ions with a rounded maximum in the susceptiblity occurring at about 18 K for **2** and 58 K for **3**. The data for complex **2** were fitted to a modified Bleaney–Bower expression

$$\chi_M = 2N\beta^2 g^2/kT(3 + \exp(-J/kT)) \qquad (1)$$

for a dinuclear copper(II) complex, where J is the single–triplet energy gap defined by the Hamiltonian

$$\hat{H} = -J\hat{S}_1{\cdot}\hat{S}_2 \qquad (2)$$

J expresses the intramolecular exchange interactions, S_1 and S_2 are quantum spin operators, and N, g, β, and T have their usual meaning. The magnetic data for complex **3** were fitted by the empirical expression of the magnetic susceptibility proposed by Estes et al.[28] to fit antiferromagnetic 1D Heisenberg $S = {}^1/_2$

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(28) Estes, W. E.; Gavel, D. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1978**, *17*, 1415.

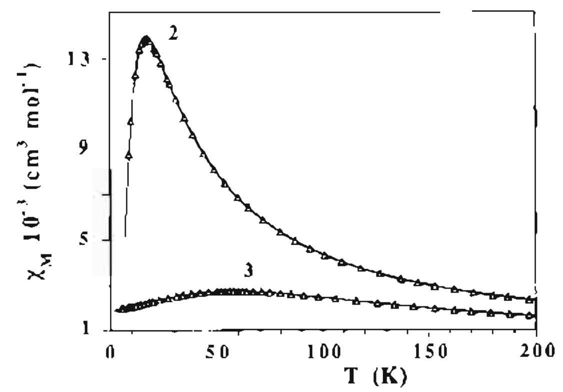


Figure 4. Thermal variation of the magnetic susceptibility per mole of copper(II) for complexes **2** and **3**: (Δ) experimental points; (—) theoretical best fit.

Table IV. Best fitted values for J, g, and ρ

compd	$-J$, cm^{-1}	g	10^5R^a	ref
2	19	2.21	3.2	this work
3	62	2.10	5.0	this work
4^b	199			18

^{a} R is the agreement factor defined as $R = \sum_i(\chi_{\text{exptl}}(i) - \chi_{\text{calcd}}(i))^2/\sum_i(\chi_{\text{exptl}}(i))^2$. ^{b} $[\text{Cu}_2(\text{bpm})(\text{NCO})_4]_n$.

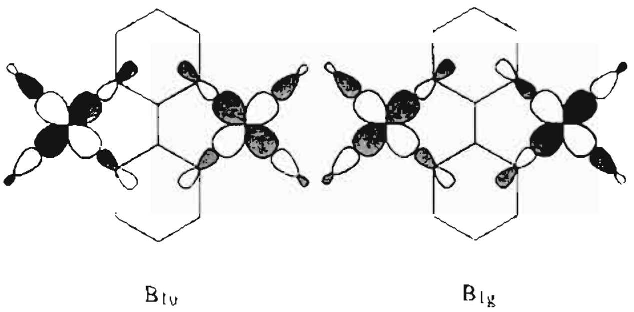
chains with

$$\hat{H} = -J\sum_{i=1}^{N-1}\hat{S}_i\cdot\hat{S}_{i+1} \tag{3}$$

The best fit results are given in Table IV. In **3**, the interaction is intermediate ($J = -62$ cm^{-1}) whereas, in **2**, it is weaker ($J = -19$ cm^{-1}).

This work was undertaken to analyze the influence of factors such as stoichiometry and bonding flexibility on the structure and magnetic properties of bipyrimidine-containing copper(II) complexes. Concerning this family of complexes, it has been shown that bpm can act as either a bidentate[16-18] or a bis-bidentate ligand.[14,15,18] When bidentate, it can be used to synthesize mononuclear compounds as in **1**, dinuclear ones as in $[\text{Cu}_2(\text{bpm})_2(\text{OH})_2(\text{H}_2\text{O})_4](\text{ClO}_4)_2\cdot2\text{H}_2\text{O}$,[17] or chain compounds as in $[\text{Cu}(\text{bpm})(\text{NCS})_2]_n$.[18] When bis-bidentate, it leads to complex 1D, 2D, or 3D arrangements of copper(II) ions of formula $[\text{Cu}_2(\text{bpm})\text{X}_4]_n$ (X = NO_3, Cl, Br, NCO, NCS).[14,15,18] For this series of complexes, the bpm bridge exhibits an inversion center at the middle of the inter-ring carbon–carbon bond. The structure of **3** introduces a new bridging scheme where no inversion center is present in the bis-bidentate bpm, leading to 1D arrangement of copper(II) ions. Finally, the combination of chelating and bischelating coordination modes allows the formation of dinuclear entities as shown by the structure of **2**. This complex can be considered formally as the precursor of **3** since it could be prepared by polymerization of **2** in the presence of copper(II) ions. Crystal structures of **1**–**3** illustrate the bonding flexibility of bpm and reveal once more the chamaleon-[29] or Janus-like[4d] coordination behavior of Cu(II) due to the Jahn–Teller effect. This flexibility is obtained through the Cu(II):bpm molar ratio.

We interpreted the coupling through the bpm bridge[15,18] using the model of interaction of localized nonorthogonal magnetic orbitals proposed by Kahn and Briat.[30] We showed that the large singlet–triplet energy ($|J| > 190$ cm^{-1} for copper(II) ions separated by more than 5.5 Å) is due to the overlap between the $d_{x^2-y^2}$ orbitals centered on each copper(II) ion through the bpm bridge, where they are partially delocalized. A schematic drawing of the two singly occupied molecular orbitals (MO) Ψ_g and Ψ_u in the dinuclear unit found in the $[\text{Cu}_2(\text{bpm})\text{X}_4]_n$ series (**4**) is depicted in I. The two MO's are built from the g and u combinations of the $d_{x^2-y^2}$ magnetic orbitals ϕ_A and ϕ_B centered on coppers A and B. We recall[31] that the approximated J value in such a dinuclear unit is given by eq 4, where S is the overlap



I

$$J = 2j + 4\beta S \tag{4}$$

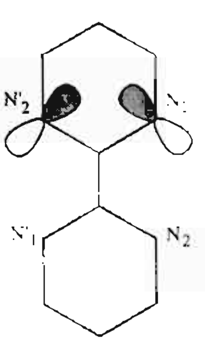
integral between the two magnetic orbitals centered on the two copper ions and β and j are their monoelectronic resonance (<0) and bielectronic exchange integrals, respectively.

For bpm ligands, the exchange integral j is sufficiently weak to be negligible compared to βS and

$$|J| \propto 4\beta S \propto S^2 \tag{5}$$

A large value of S favors the pairing and increases the coupling constant J. Diagram I illustrates the σ in-plane overlaps between the two magnetic orbitals in complexes **4**. In such a case[4b,5b] already encountered in oxalato-[4b,20] and oxamidato-bridged[5c] Cu(II) complexes, the magnitude of the integral overlap S_4 is governed by the integral overlap s between the $\sigma(\text{N}_1)$ and $\sigma(\text{N}_2)$ orbitals (eq 6) engaged in the magnetic orbitals (II) and by the

$$s = \langle\sigma(\text{N}_1)|\sigma(\text{N}_2)'\rangle \tag{6}$$



II

α mixing coefficient of N in the magnetic orbital. In compounds **4**, two such pathways are operating, one on each side of the bridge, and

$$S_4 = 2\alpha^2 s \qquad J_4 \propto 4\alpha^4 s^2 \tag{7}$$

In compound **2**, the magnetic orbitals are localized in a plane perpendicular to the bpm molecule, and due to the inversion center, no more overlap occurs. We get *orbital reversal or orbital switching* as shown in III. In compound **3**, the lack of an inversion center leads to an intermediate situation where the overlap occurs only on one side of the bridge, as shown in IV and eq 9. When these estimates are compared to the experimental results, retaining a value $J_4 = -199$ cm^{-1} in the cyanato compound where the

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(30) Kahn, O.; Briat, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 268.
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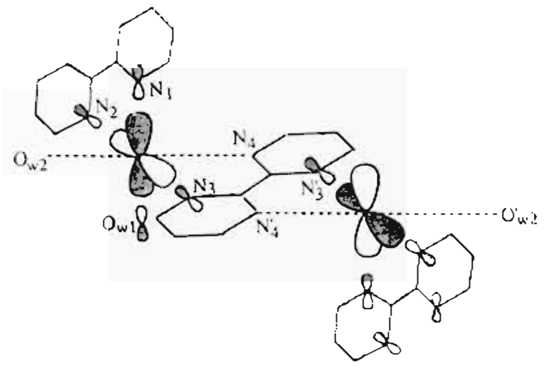
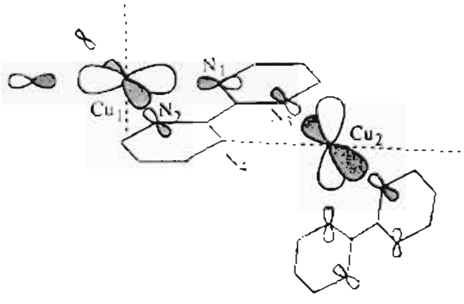


III

$$S_2 \sim 0 \qquad J_2 \propto S_2^2 \text{ (weak)} \tag{8}$$



IV

$$S_3 = \alpha^2 s \qquad J_3 \propto S_3^2 = \alpha^4 s^2 \sim J_4/4 \tag{9}$$

copper(II) environment is similar to the ones in **2** and **3**, it can be observed that $|J_2|$ is much weaker than $|J_4|$ and $J_3 \sim J_4/3$. J_2 is different from 0 because of some admixture of spin density in a d_{z^2} orbital (mean Cu–N(axial) = 2.272(3) Å) which leads to a nonzero overlap between the magnetic orbitals. The experimentally found ratio $J_4/J_3 = 3$ instead of 4 can be considered as satisfying, given the crude model used. This orbital approach allows therefore a semiquantitative prevision of the antiferromagnetic coupling between two copper(II) atoms through a bpm bridge, as in the case of oxalato and oxamidato bridges.

Conclusion

The present examples show that the bonding flexibility of bpm can be used to tune the coupling constant *J* between two copper(II) ions bridged by bpm, by varying the overall symmetry of the systems and the Cu(II):bpm stoichiometry.

Safety Note

Perchlorate salts of metal complexes with organic ligands are potentially explosive. In the syntheses described here, we used only small amounts of materials (the preparations were carried out at the millimole scale), and the starting perchlorate salt was an aqua complex. The dilute solutions were handled with great caution and evaporated slowly at room temperature in an open hood (cf. ref 32).

When noncoordinating agents are required, every attempt should be made to substitute anions such as the fluoro sulfonates for the perchlorates. Nevertheless, it should be noted that as counterions are often noninnocent and can introduce unexpected structural and magnetic effects, these substitutions could prevent one from obtaining meaningful results.

Acknowledgment. This work was partially supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica, the Programa de Acciones Integradas Hispano-Francesas, and the Comisión Interministerial de Ciencia y Tecnología (Project PB91-0490-C02-01). The authors are most grateful to Professor P. Dapporto, University of Firenze, for data collection for compound **3**.

Supplementary Material Available: Tables giving crystal data and details of the structure determinations (Table S1), atom coordinates (Tables S2 and S3), bond lengths and angles (Tables S4–S6), anisotropic thermal parameters (Tables S7–S9), hydrogen atom locations (Tables S10–S12), and least-squares planes (Tables S13–S15) and figures showing a stereoview of **1**, a view of the unit cell of **2**, and a stereoview of **3** (Figures S1–S3) (21 pages). Ordering information is given on any current masthead page.

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