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Magneto–Structural Effects of the Jahn–Teller Distortions on 2,2′-Bipyrimidine- (bpm-) Bridged Dinuclear Copper(II) Complexes: Crystal Structures and Magnetic Properties of $[Cu_2(bpm)(H_2O)_4(SO_4)_2]\cdot 3H_2O$ and $[Cu_2(bpm)(H_2O)_8](SO_4)_2\cdot 2H_2O$

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Two new copper(II) compounds of formula $[Cu_2(bpm)(H_2O)_4(SO_4)_2]\cdot 3H_2O$ (**1**) and $[Cu_2(bpm)(H_2O)_8](SO_4)_2\cdot 2H_2O$ (**2**) (bpm = 2,2′-bipyrimidine) have been synthesized and structurally characterized by X-ray diffraction. Compound **1** crystallizes in the monoclinic system, space group $P2_1/n$, with $a = 7.651(1)$ Å, $b = 25.119(3)$ Å, $c = 11.050(1)$ Å, $\beta = 108.80(1)°$, $Z = 4$ and $V = 2010.4(4)$ Å^3, whereas compound **2** is orthorhombic, space group *Pbcn*, with $a = 13.401(2)$ Å, $b = 12.116(2)$ Å, $c = 14.178(4)$ Å, $Z = 4$, and $V = 2302.0(6)$ Å^3. The structure of **1** consists of a 2D-array of copper(II) ions bridged by bis-bidentate bpm groups and bis-unidentate sulfate. Each copper atom in **1** is in an elongated octahedral CuO_6 surrounded by two water molecules and two nitrogen atoms from bpm building the basal plane and two sulfate oxygens in the axial positions. The structure of **2** is made up of noncentrosymmetric dinuclear $[Cu_2(bpm)(H_2O)_8]^{4+}$ cationic units, uncoordinated sulfate anions, and water of crystallization. Both copper(II) ions in **2** have distorted octahedral CuO_6 surroundings, one being compressed and the other elongated. Compounds **1** and **2** exhibit antiferromagnetic coupling, which is relatively strong in the former (J(singlet–triplet energy gap) $= -159$ cm^{-1}) and weak in the latter ($J = -24$ cm^{-1}). The influence of the distortions (elongation or compression) of the copper environment on the exchange coupling in **1** and **2** is analyzed by extended Hückel calculations in the framework of a simple orbital model.

Introduction

A lot of work has been carried out on polynuclear complexes containing oxalato-type ligands as bridges in molecular magnetism.[2–5] The versatility of this kind of ligands and their well-known remarkable ability to transmit exchange coupling between metal ions separated by more than 5 Å are the main reasons. They have played a key role in the investigation of the factors that control the exchange interaction between metal centers. Restricting ourselves to copper(II) complexes for simplicity, several groups have used the nature of the terminal ligands[2a,b,3b] and the electronegativity of the atoms of the bridge[3a,4f] as useful tools to tune the magnitude of the exchange coupling in a wide range. As far as the peripheral ligand is concerned, the great plasticity of the coordination sphere of copper(II) makes very easy the modification of the symmetry of its magnetic orbital in a controlled fashion, the orbital reversal[5d,6] being a direct consequence from this feature. On the other hand, the comprehension of the role of the electronegativity of the donor atoms of the bridge together with the great stability of mononuclear oxamidato-containing copper(II) complexes[3n] are at the origin of the vast amount of work which has been carried out with ferrimagnetic chains.[7] At this regards, it is worthwhile noting that ferrimagnetism is one of the known strategies used to design molecular-based magnets.[8]

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(1) (a) Università della Calabria. (b) Universitat de València. (c) Università di Firenze.

(2) (a) Felthouse, T. R.; Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 1077. (b) Julve, M.; Verdaguer, M.; Kahn, O.; Gleizes, A.; Philoche-Levisalles, M. *Inorg. Chem.* **1983**, *22*, 368; **1984**, *23*, 3808. (c) Verdaguer, M.; Julve, M.; Michalowicz, A.; Kahn, O. *Inorg. Chem.* **1983**, *22*, 2624. (d) Pei, Y.; Journaux, Y.; Kahn, O. *Inorg. Chem.* **1989**, *28*, 100. (e) Alvarez, S.; Julve, M.; Verdaguer, M. *Inorg. Chem.* **1990**, *29*, 4500. (e) Gleizes, A.; Julve, M.; Verdaguer, M.; Real, J. A.; Faus, J.; Solans, X. *J. Chem. Soc., Dalton Trans.* **1992**, 3209. (f) Tamaki, H.; Zhong, Z. J.; Matsumoto, N.; Kida, S.; Koikawa, M.; Achiva, N.; Hashimoto, Y.; Okawa, H. *J. Am. Chem. Soc.* **1992**, *114*, 6974. (g) Ohba, M.; Tamaki, H.; Matsumoto, N.; Okawa, H. *Inorg. Chem.* **1993**, *32*, 5385.

(3) (a) Verdaguer, M.; Kahn, O.; Julve, M.; Gleizes, A. *Nouv. J. Chim.* **1985**, *9*, 325. (b) Journaux, Y.; Sletten, J.; Kahn, O. *Inorg. Chem.* **1985**, *24*, 4063. (c) Bencini, A.; Benelli, C.; Fabretti, A. C.; Franchini, G.; Gatteschi, D. *Inorg. Chem.* **1986**, *25*, 1063. (d) Journaux, Y.; Sletten, J.; Kahn, O. *Inorg. Chem.* **1986**, *25*, 439. (e) Pei, Y.; Journaux, Y.; Kahn, O.; Dei, A.; Gatteschi, D. *J. Chem. Soc., Chem. Commun.* **1986**, 1300. (f) Lloret, F.; Journaux, Y.; Julve, M. *Inorg. Chem.* **1990**, *29*, 3967. (g) Zhang, Z. Y.; Liao, D. Z.; Jiang, Z. H.; Hao, S. Q.; Yao, X. K.; Wang, H. G.; Wang, G. L. *Inorg. Chim. Acta* **1990**, *173*, 201. (h) Ribas, J.; Diaz, C.; Costa, R.; Journaux, Y.; Mathonière, C.; Kahn, O.; Gleizes, A. *Inorg. Chem.* **1990**, *29*, 2042. (i) Fabretti, A. C.; Giusti, A.; Albano, V. G.; Castellari, C.; Gatteschi, D.; Sessoli, R. J. *Chem. Soc., Dalton Trans.* **1991**, 2133. (j) Ribas, J.; García, A.; Costa, R.; Monfort, M.; Alvarez, S.; Zanchini, C.; Solans, X.; Domenech, M. V. *Inorg. Chem.* **1991**, *30*, 841. (k) Escuer, A.; Vicente, R.; Ribas, J.; Costa, R.; Solans, X. *Inorg. Chem.* **1992**, *31*, 2627. (l) Benelli, C.; Fabretti, A. C.; Giusti, A. *J. Chem. Soc., Dalton Trans.* **1993**, 409. (m) Costa, R.; Garcia, A.; Ribas, J.; Mallah, T.; Journaux, Y.; Sletten, J.; Solans, X.; Rodríguez, V. *Inorg. Chem.* **1993**, *32*, 3733. (n) Real, J. A.; Mollar, M.; Ruiz, R.; Faus, J.; Lloret, F.; Julve, M.; Philoche-Levisalles, M. *J. Chem. Soc., Dalton Trans.* **1993**, 1483.

(4) (a) Girerd, J. J.; Jeannin, S.; Jeannin, Y.; Kahn, O. *Inorg. Chem.* **1978**, *17*, 3034. (b) Chauvel, C.; Girerd, J. J.; Jeannin, Y.; Kahn, O.; Lavigne, G. *Inorg. Chem.* **1979**, *18*, 3015. (c) Veit, R.; Girerd, J. J.; Kahn, O.; Robert, F.; Jeannin, Y.; El Murr, N. *Inorg. Chem.* **1984**, *23*, 4448. (d) Gleizes, A.; Verdaguer, M. *J. Am. Chem. Soc.* **1984**, *106*, 3727. (e) Veit, R.; Girerd, J. J.; Kahn, O.; Robert, F.; Jeannin, Y. *Inorg. Chem.* **1986**, *25*, 4175. (f) Vicente, R.; Ribas, J.; Alvarez, S.; Seguí, A.; Solans, X.; Verdaguer, M. *Inorg. Chem.* **1987**, *26*, 4004. (g) Okawa, H.; Matsumoto, N.; Koikawa, M.; Takeda, K.; Kida, S. *J. Chem. Soc., Dalton Trans.* **1990**, 1383. (h) Journaux, Y.; lloret, F.; Kahn, O. *Inorg. Chem.* **1990**, *29*, 3048. (i) Mitsumi, M.; Okawa, H.; Sakiyama, H.; Ohba, M.; Matsumoto, N.; Kurisaki, T.; Wakita, H. *J. Chem. Soc., Dalton Trans.* **1993**, 2991.

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Although the Jahn−Teller effect is well documented in the chemistry of copper(II),[9] its influence on the magnitude of the exchange coupling in polynuclear copper(II) complexes remained unexplored most likely because the lack of copper(II) dimers exhibiting a compressed octahedral environment. In the present contribution, we treat this point using as examples the compounds of formula $[Cu_2(bpm)(H_2O)_4(SO_4)_2]\cdot 3H_2O$ (**1**) and $[Cu_2(bpm)(H_2O)_8](SO_4)_2\cdot 2H_2O$ (**2**) (bpm = 2,2′-bipyrimidine). The copper atoms in each dimer exhibit distorted octahedral surroundings, being elongated for both copper atoms in the former and one elongated and the other compressed in the latter. Their preparation, crystal structure, and magnetic characterization are the main subject of the present work.

Experimental Section

Materials. 2,2′-Bipyrimidine and copper(II) sulfate pentahydrate were purchased from commercial sources and used as received. Elemental analysis (C, H, N) were conducted by the Microanalytical Service of the Università degli Studi della Calabria (Italy). Metal analysis was made on a Shimadzu AA-680 atomic absorption/flame emission spectrometer.

Preparation of Complexes $[Cu_2(bpm)(H_2O)_4(SO_4)_2]\cdot 3H_2O$ (1) and $[Cu_2(bpm)(H_2O)_8](SO_4)_2\cdot 2H_2O$ (2). Compound **1** separates as blue plates by slow evaporation at room temperature of aqueous solutions (4 mL) containing stoichiometric amounts of copper(II) sulfate (0.01 mmol) and bpm (0.02 mmol). Crystals of **1** suitable for X-ray analysis were obtained by cutting some of these. Compound **2** was obtained as blue parallelepipeds by recrystallization of **1** in water. Anal. Calcd for $C_8H_{20}Cu_2N_4O_{15}S_2$ (**1**): C, 15.92; H, 3.34; N, 9.28; Cu, 21.06. Found: C, 15.41; H, 3.23; N, 9.13; Cu, 20.71. Anal. Calcd for $C_8H_{26}Cu_2N_4O_{18}S_2$ (**2**): C, 14.61; H, 3.99; N, 8.52; Cu, 19.33. Found: C, 14.30; H, 3.80; N, 8.14; Cu, 18.87.

Magnetic Susceptibility Measurements. These measurements for compounds **1** and **2** were carried out in the temperature range 3−300 K in a field of 1 T by using a Metronique Ingenierie MS03 SQUID magnetometer. Calibration was made with $(NH_4)_2Mn(SO_4)_2\cdot 6H_2O$. The corrections for the diamagnetism using Pascal's constants[10] are $-298 \cdot 10^{-6}$ and $-337 \cdot 10^{-6}$ cm^3 mol^{-1} for complexes **1** and **2**, respectively.

X-ray Data Collection and Structure Refinement. Diffraction data were collected at room temperature on a Siemens R3m/V automatic diffractometer by using graphite monochromatized Mo Kα radiation and a $\omega-2\theta$ scan technique. Unit cell dimensions and crystal orientation matrices were obtained from least-squares refinement of 25 strong reflections in the $15 \le \theta \le 30°$ range. A summary of the crystallographic data and structure refinement is listed in Table 1. A more complete list of crystallographic data is reported in Table S1.[11] A total of 4940 (**1**) and 2876 (**2**) reflections were collected in the range $3 \le \theta \le 54°$ with index ranges $0 \le h \le 9$, $0 \le k \le 32$, $-14 \le l \le 13$ (**1**) and $0 \le h \le 17$, $0 \le k \le 15$, $-18 \le l \le 0$ (**2**); 4422 (**1**) and 2530 (**2**) of them were unique, and from these, 3576 (**1**) and 1766 (**2**) were assumed as observed ($I > 3\sigma(I)$). Examination of two standard reflections, monitored after every 150, showed no sign of crystal deterioration. Lorentz-polarization and ψ-scan absorption corrections[12] were applied to the intensity data. The maximum and minimum transmission factors were 0.485 and 0.353 for **1** and 0.438 and 0.348 for **2**.

Table 1. Crystallographic Data for Complexes $[Cu_2(bpm)(H_2O)_4(SO_4)_2]\cdot 3H_2O$ (**1**) and $[Cu_2(bpm)(H_2O)_8](SO_4)_2\cdot 2H_2O$ (**2**)

	1	**2**
chem formula	$C_8H_{20}N_4Cu_2O_{15}S_2$	$C_8H_{26}N_4Cu_2O_{18}S_2$
a, Å	7.651(1)	13.401(2)
b, Å	25.119(3)	12.116(2)
c, Å	11.050(1)	14.178(2)
β, deg	108.80(1)	90
V, Å^3	2010.4(4)	2302(6)
Z	4	4
fw	603.5	657.5
space group	$P2_1/n$	$Pbcn$
T, K	298	298
λ, Å	0.710 73	0.710 73
ϱ_{calcd}, g cm^{-3}	1.994	1.897
μ, cm^{-1}	24.0	21.1
R^a	0.0358	0.0390
$R_w{}^b$	0.0424	0.0438

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

The structures were solved by standard Patterson methods with the SHELXTL PLUS program[13] and subsequently completed by Fourier recycling. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the water molecules were located on a ΔF map and refined with constraints. The hydrogen atoms from bpm were set in calculated positions and refined as riding atoms. A common thermal parameter was assigned to these atoms. The final full-matrix least-squares refinement, minimizing the function $\sum w(|F_o| - |F_c|)^2$ with $w = 1/[\sigma^2(F_o) + 0.0020F_o{}^2]$ for both compounds **1** and **2**, converged to final residuals R (R_w) of 0.036 (0.042) for **1** and 0.039 (0.044) for **2**. The goodness of fit is 1.19 (**1**) and 1.07 (**2**). The number of reflections/number of variable parameters was 11.1 and 9.5 for **1** and **2**, respectively. All calculations were performed on a Micro-Vax II computer, using the SHELXTL-PLUS system. The final geometrical calculations and graphical manipulations were carried out with the PARST program[14] and the XP utility of the SHELXTL-PLUS system, respectively. Final fractional coordinates are gathered in Tables 2 (**1**) and 3 (**2**) and selected bond distances and angles in Tables 4 (**1**) and 5 (**2**). Anisotropic thermal parameters, hydrogen atom coordinates, remaining bond distances and angles, hydrogen bonds and least-squares planes are listed in Tables S2−S11.

Results and Discussion

Description of the Structures $[Cu_2(bpm)(H_2O)_4(SO_4)_2]\cdot 3H_2O$ (1). The crystal structure of **1** is made up of neutral bpm-bridged copper(II) units of formula $[Cu_2(bpm)(H_2O)_4(SO_4)_2]$ and crystallization water molecules. The molecular geometry and the atom numbering scheme for **1** is shown in Figure 1a. The sulfate group acts as a bis-monodentate ligand in such a way to build a ladder-like polymer in which two sulfato-bridged copper(II) chains are held together by bridging bpm. The hydrogen bonds involving the sulfate groups and coordinated water molecules from adjacents units lead to the 2D-network which is shown in Figure 1b. The propagation of these sheets in the third direction is achieved by hydrogen bonding involving the water molecules of crystallization.

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(5) (a) Brewer, G.; Sinn, E. *Inorg. Chem.* **1985**, *24*, 4580. (b) Julve, M.; De Munno, G.; Bruno, G.; Verdaguer, M. *Inorg. Chem.* **1988**, *27*, 3160. (c) Julve, M.; Verdaguer, M.; De Munno, G.; Real, J. A.; Bruno, G. *Inorg. Chem.* **1993**, *32*, 795. (d) De Munno, G.; Julve, M.; Verdaguer, M.; Bruno, G. *Inorg. Chem.* **1993**, *32*, 2215. (e) De Munno, G.; Julve, M.; Nicoló, F.; Lloret, F.; Faus, J.; Ruiz, R.; Sinn, E. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 613. (f) De Munno, G.; Julve, M.; Lloret, F.; Faus, J.; Caneschi, A. *J. Chem. Soc., Dalton Trans.* **1994**, 1175 and references therein.

(6) Girerd, J. J.; Kahn, O.; Verdaguer, M. *Inorg. Chem.* **1980**, *19*, 274.

(7) Kahn, O., Pei, Y., Journaux, Y. In *Molecular Inorganic Magnetic Materials*; Bruce, D. W., O'Hare, D., Eds.; Wiley: New York, 1992; p 59.

(8) (a) Kahn, O.; Pei, Y.; Verdaguer, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782. (b) Nakatani, K.; Carriat, J. Y.; Journaux, Y.; Kahn. O.; Lloret, F.; Renard, J. P.; Pei, Y.; Sletten, J.; Verdaguer, M. *J. Am. Chem. Soc.* **1989**, *111*, 5739. (c) Lloret, F.; Julve, M.; Ruiz, R.; Journaux, Y.; Nakatani, K.; Kahn, O.; Sletten, J. *Inorg. Chem.* **1993**, *32*, 27.

(9) Hathaway, B. J. *Struct. Bonding (Berlin)* **1984**, *57*, 55.

(10) Bourdreaux, E. A.; Mulay, L. N. *Theory and Applications of Molecular Paramagnetism*; John Wiley & Sons: New York, 1976; p 491.

(11) Supplementary Material.

(12) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

(13) SHELXTL-PLUS, Version 4.11/V Siemens Analytical X-Ray Instruments Inc., Madison, WI, 1990.

(14) M. Nardelli, *Comput. Chem.* **1983**, *7*, 95.

Table 2. Final Atomic Fractional Coordinates and Equivalent Isotropic Displacement Parameters[a,b] for Non-Hydrogen Atoms of Complex **1**

atom	*x*/*a*	*y*/*b*	*z*/*c*	10^3U_{eq}, Å^2
Cu(1)	0.2437(1)	0.1597(1)	0.1002(1)	21(1)
Cu(2)	−0.2435(1)	0.0991(1)	−0.3590(1)	21(1)
O(1)	0.2154(4)	0.1929(1)	0.2546(2)	33(1)
O(2)	0.5083(3)	0.1450(1)	0.1734(2)	27(1)
O(3)	−0.5080(3)	0.1129(1)	−0.4345(2)	27(1)
O(4)	−0.2240(3)	0.0481(1)	−0.4907(2)	27(1)
N(1)	−0.0277(4)	0.1681(1)	−0.0018(3)	22(1)
C(1)	−0.1619(5)	0.1956(1)	0.0250(3)	26(1)
C(2)	−0.3376(5)	0.1983(2)	−0.0633(4)	30(1)
C(3)	−0.3705(5)	0.1734(1)	−0.1784(3)	26(1)
N(2)	−0.2371(4)	0.1455(1)	−0.2063(3)	20(1)
C(4)	−0.0739(4)	0.1449(1)	−0.1153(3)	18(1)
C(5)	0.0742(4)	0.1147(1)	−0.1445(3)	19(1)
N(3)	0.2389(4)	0.1151(1)	−0.0558(3)	21(1)
C(6)	0.3712(5)	0.0864(1)	−0.0803(3)	26(1)
C(7)	0.3343(5)	0.0584(2)	−0.1935(4)	33(1)
C(8)	0.1587(5)	0.0605(2)	−0.2800(3)	30(1)
N(4)	0.0257(4)	0.0890(1)	−0.2555(3)	21(1)
S(1)	−0.3052(1)	−0.0366(1)	−0.2726(1)	21(1)
O(5)	−0.1791(3)	−0.0698(1)	−0.1728(2)	33(1)
O(6)	−0.2807(4)	0.0200(1)	−0.2398(2)	31(1)
O(7)	−0.4986(3)	−0.0526(1)	−0.2905(2)	29(1)
O(8)	−0.2691(3)	−0.0450(1)	−0.3967(2)	30(1)
S(2)	−0.2842(1)	0.2143(1)	−0.5355(1)	23(1)
O(9)	−0.1912(3)	0.2618(1)	−0.4698(3)	34(1)
O(10)	−0.1757(3)	0.1666(1)	−0.4783(3)	31(1)
O(11)	−0.4730(4)	0.2088(1)	−0.5294(3)	37(1)
O(12)	−0.2919(5)	0.2169(1)	−0.6707(3)	45(1)
O(13)	−0.2942(4)	0.3060(1)	−0.8155(3)	54(1)
O(14)	0.2067(5)	−0.0505(2)	−0.0244(4)	65(1)
O(15)	0.0044(6)	0.1334(2)	0.3441(4)	80(2)

[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 3. Final Atomic Fractional Coordinates and Equivalent Isotropic Displacement Parameters[a,b] for Non-Hydrogen Atoms of Complex **2**

atom	*x*/*a*	*y*/*b*	*z*/*c*	10^3U_{eq}, Å^2
Cu(1)	0	0.6151(1)	0.2500	24(1)
Cu(2)	0	0.1480(1)	0.2500	24(1)
O(1)	0.0988(2)	0.7297(2)	0.3150(2)	51(1)
O(2)	0.0862(2)	0.6158(2)	0.1377(2)	33(1)
O(3)	0.0886(2)	0.0391(2)	0.3124(2)	35(1)
O(4)	0.1009(2)	0.1322(2)	0.1144(2)	32(1)
N(1)	0.0729(2)	0.4716(2)	0.3173(2)	30(1)
C(1)	0.1434(3)	0.4681(3)	0.3837(3)	38(1)
C(2)	0.1804(3)	0.3708(3)	0.4168(3)	42(1)
C(3)	0.1428(3)	0.2732(3)	0.3797(2)	34(1)
N(2)	0.0723(2)	0.2757(2)	0.3131(2)	24(1)
C(4)	0.0401(3)	0.3751(2)	0.2862(2)	23(1)
S(1)	0.2569(1)	0.3778(1)	0.1224(1)	24(1)
O(5)	0.1532(2)	0.4098(2)	0.1111(2)	38(1)
O(6)	0.3193(2)	0.4335(2)	0.0518(2)	44(1)
O(7)	0.2935(3)	0.4012(3)	0.2170(2)	60(1)
O(8)	0.2644(2)	0.2578(2)	0.1072(3)	55(1)
O(9)	0.5162(2)	0.3813(2)	0.0656(2)	38(1)

[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 4. Selected Bond Lengths (Å) and Interbond Angles (deg) for Complex **1**[a]

Distances			
Cu(1)−O(1)	1.973(3)	Cu(2)−O(3)	1.955(2)
Cu(1)−O(2)	1.958(2)	Cu(2)−O(4)	1.980(3)
Cu(1)−N(1)	2.029(3)	Cu(2)−N(2)	2.038(3)
Cu(1)−N(3)	2.046(3)	Cu(2)−N(4)	2.024(3)
Cu(1)−O(5a)	2.499(3)	Cu(2)−O(6)	2.452(3)
Cu(1)−O(9b)	2.231(3)	Cu(2)−O(10)	2.306(3)
Angles			
O(1)−Cu(1)−O(2)	96.3(1)	O(3)−Cu(2)−O(4)	96.5(1)
O(1)−Cu(1)−N(3)	169.3(1)	O(3)−Cu(2)−N(4)	171.2(1)
O(1)−Cu(1)−N(1)	93.4(1)	O(3)−Cu(2)−N(2)	89.9(1)
O(1)−Cu(1)−O(5a)	90.9(1)	O(3)−Cu(2)−O(6)	95.1(1)
O(1)−Cu(1)−O(9b)	91.5(1)	O(3)−Cu(2)−O(10)	91.1(1)
O(2)−Cu(1)−N(3)	88.9(1)	O(4)−Cu(2)−N(4)	91.7(1)
O(2)−Cu(1)−N(1)	170.3(1)	O(4)−Cu(2)−N(2)	172.2(1)
O(2)−Cu(1)−O(5a)	88.9(1)	O(4)−Cu(2)−O(6)	85.4(1)
O(2)−Cu(1)−O(9b)	89.6(1)	O(4)−Cu(2)−O(10)	88.4(1)
N(1)−Cu(1)−N(3)	81.5(1)	N(2)−Cu(2)−N(4)	81.7(1)
N(1)−Cu(1)−O(5a)	90.0(1)	N(2)−Cu(2)−O(6)	89.7(1)
N(1)−Cu(1)−O(9b)	91.0(1)	N(2)−Cu(2)−O(10)	96.0(1)
N(3)−Cu(1)−O(5a)	79.8(1)	N(4)−Cu(2)−O(6)	82.4(1)
N(3)−Cu(1)−O(9b)	97.9(1)	N(4)−Cu(2)−O(10)	92.3(1)
O(5a)−Cu(1)−O(9b)	177.4(1)	O(6)−Cu(2)−O(10)	171.7(1)

[a] Symmetry code: (a) −*x*, −*y*, −*z*; (b) 0.5 + *x*, 0.5 − *y*, 0.5 + *z*.

Table 5. Selected Bond Lengths (Å) and Interbond Angles (deg) for Complex **2**[a]

Distances			
Cu(1)−O(1)	2.128(3)	Cu(2)−O(3)	1.983(3)
Cu(1)−O(2)	1.968(3)	Cu(2)−O(4)	2.358(3)
Cu(1)−N(1)	2.211(3)	Cu(2)−N(2)	2.033(3)
Angles			
O(1)−Cu(1)−O(1a)	98.6(2)	O(3)−Cu(2)−O(3a)	96.6(1)
O(1)−Cu(1)−N(1a)	167.1(1)	O(3)−Cu(2)−N(2a)	171.1(1)
O(1)−Cu(1)−N(1)	93.0(1)	O(3)−Cu(2)−N(2)	91.4(1)
O(1)−Cu(1)−O(2)	89.0(1)	O(3)−Cu(2)−O(4)	88.1(1)
O(1)−Cu(1)−O(2a)	90.7(1)	O(3)−Cu(2)−O(4a)	85.7(1)
N(1)−Cu(1)−N(1a)	76.2(1)	N(2)−Cu(2)−N(2a)	80.9(1)
N(1)−Cu(1)−O(2)	95.3(1)	N(2)−Cu(2)−O(4)	98.5(1)
N(1a)−Cu(1)−O(2)	85.0(1)	N(2)−Cu(2)−O(4a)	88.6(1)
O(2)−Cu(1)−O(2a)	179.5(1)	O(4)−Cu(2)−O(4a)	170.7(1)

[a] Symmetry code: (a) −*x*, *y*, 0.5 − *z*.

In spite of the lack of a crystallographic inversion center between the two pyrimidine rings of bpm, the distorted octahedral surrounding around Cu(1) and Cu(2) atoms is rather similar: two nitrogen atoms of bpm and two oxygen atoms of water define the equatorial positions, whereas two oxygen atoms of sulfate groups occupy the axial ones. The average Cu−N distance (2.037(3) Å for Cu(1) and 2.031(3) Å for Cu(2)) is close to that found in other bpm-bridged copper(II) complexes[5bc,15] and somewhat greater than the mean Cu−O(water) distance (1.965(3) Å for Cu(1) and 1.967(3) Å for Cu(2)). In both copper atoms, the axial Cu−O bonds are longer than the equatorial ones and one axial Cu−O distance is shorter than the other one (2.499(1) and 2.231(3) Å for Cu(1)−O(5a) and Cu(1)−O(9b) and 2.452(3) and 2.306(3) Å for Cu(2)−O(6) and Cu(2)−O(10)). The four equatorial atoms around the copper atoms are almost planar with maximum deviations from the mean planes of 0.089(3) Å at N(3) and 0.014(3) Å at N(4). Cu(1) and Cu(2) atoms are displaced 0.080(1) and 0.062(1) Å, respectively, from these planes toward O(9b) and O(10).

The pyrimidyl rings of bpm are planar as expected (the largest deviation from the mean planes is 0.006(4) Å), but they form a dihedral angle of 3.2(1)°. The value of the dihedral angle between the equatorial plane and the mean bpm plane is 5.2(1)° at Cu(1) and 5.1(1)° at Cu(2). The angles subtended by

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(15) (a) De Munno, G.; Bruno, G. *Acta Crystallogr., Sect. C* **1984**, *40*, 2030. (b) De Munno, G.; Julve, M.; Lloret, F.; Faus, J.; Verdaguer, M.; Caneschi, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1046. (c) De Munno, G.; Real, J. A.; Julve, M.; Muñoz, M. C. *Inorg. Chim. Acta* **1993**, *211*, 227. (d) Castro, I.; Sletten, J.; Glærum, L. K.; Lloret, F.; Faus, J.; Julve, M. *J. Chem. Soc., Dalton Trans.* **1994**, 2777.

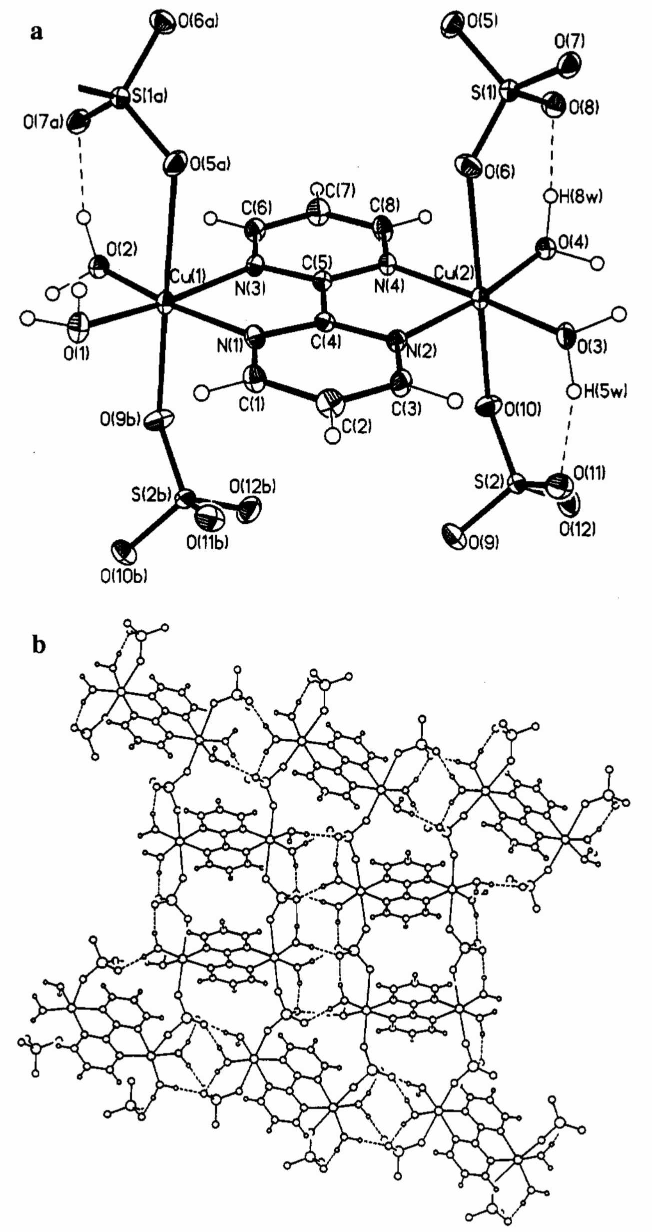

Figure 1. (a) Perspective drawing of **1** with the atom-numbering scheme (thermal ellipsoids are drawn at the 30% probability level). (b) View of a sheet of **1** extending in the *yz* plane (hydrogen bonds are indicated by broken lines). Symmetry code: (a) $-x, -y, -z$; (b) $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$.

bpm at Cu(1) and Cu(2) are 81.5(1) and 81.7(1)°, respectively. The bond distances and angles of the bpm molecule fall within the range of values found in other similar bpm compounds. The metal–metal separation through bridging bpm is 5.456(1) Å, a value which lies within the range observed for bpm-bridged copper(II) complexes.

The sulfate anions have their expected tetrahedral geometry. The average value of the sulfur–oxygen bond distance is 1.479(3) Å at S(1) and 1.472(3) Å at S(2). Among the intraion bond angles, only two of them (O(5)–S(1)–O(6) = 111.4(1)° and O(9)–S(2)–O(11) = 112.5(2)°) deviate significantly from the ideal value. The sulfate groups act not only as bis-monodentate bridging ligands but are also involved in intramolecular hydrogen bonding with the coordinated water molecules as shown in Figure 1a. Additional hydrogen bonds between the sulfato groups and coordinated water molecules of adjacent Cu(bpm)Cu units allow them to spread in a two dimensional arrangement. As shown in Figure 1b, double rows in which the Cu(bpm)Cu units are arranged in such a way to have their mean bpm planes parallel alternate in the two dimensional framework. The mean bpm planes of the alternating double rows are not parallel one to the other, the dihedral angle between them being 70.9(1)°. Within this framework we may find the following: (i) copper atoms of parallel units (Cu(1) and Cu(2a)) which are held together by bridging sulfato groups with a metal–metal separation of 7.104(1) Å; (ii) copper atoms of nonparallel units (Cu(1) and Cu(2b)) which are held together by bridging sulfato groups with a metal–metal separation of 6.072(1) Å; (c) copper atoms of parallel displaced units (Cu(1) and Cu(2c) and Cu(2) and Cu(2d)), which are held together by double hydrogen bridges between sulfato groups and coordinated water molecules, the metal metal distances being 6.189(1) Å for Cu(1)···Cu(2c) [(c) = $1 + x, y, 1 + z$] and 6.484(1) Å for Cu(2)···Cu(2d) [(2d) = $-1 - x, -y, -1, -z$].

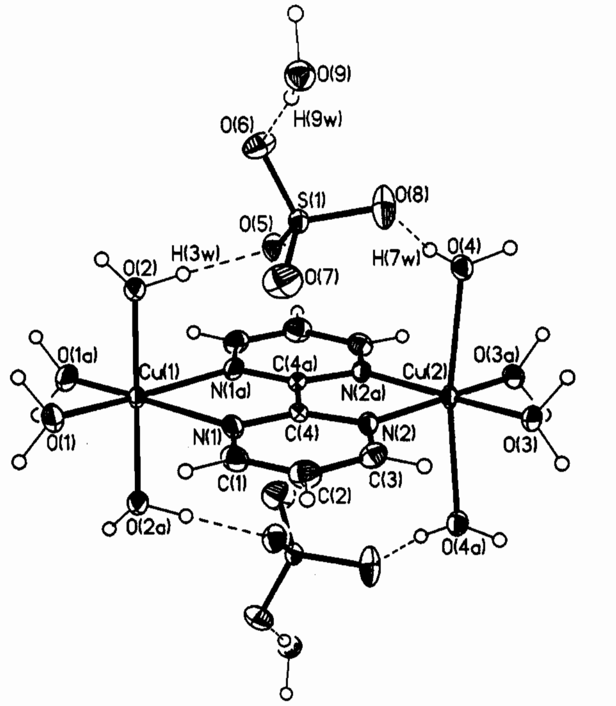

Figure 2. Perspective drawing of **2** with the atom-numbering scheme (thermal ellipsoids are drawn at the 30% probability level). Symmetry code: (a) $-x, y, 0.5 - z$.

[$Cu_2(bpm)(H_2O)_8$](SO_4)$_2$·2H_2O (2). Compound **2** consists of (*μ*-2,2′-bipyrimidine-*N*,*N*′,*N*″,*N*‴)bis([tetraaquacopper(II)] dinuclear cations, uncoordinated sulfate anions, and water molecules of crystallization. The molecular geometry of **2** with the atom numbering scheme is depicted in Figure 2. The sulfate counterions contribute to the packing by forming hydrogen bonds with both coordinated and crystallization water molecules. A 2-fold axis passes through the Cu(1) and Cu(2) atoms.

As in the preceding structure, the copper atoms are hexacoordinated: two nitrogen atoms from bpm and four oxygen atoms from water molecules build the octahedral surrounding. At first sight, the disposition of the $(H_2O)_4$Cu(1)(bpm)Cu(2)$(H_2O)_4$ moiety appears similar to that found in the [M_2(bpm)$(H_2O)_8$]$(SO_4)_2$·2H_2O complexes with M = Ni(II) (**3**),[16] Fe(II),[17] Co(II),[5f] and Zn(II),[18] where the metal centers have a distorted octahedral environment. Nevertheless, a closer examination reveals several significant differences. Indeed, while in the last

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(16) De Munno, G.; Julve, M.; Lloret, F.; Derory, A. *J. Chem. Soc., Dalton Trans.* **1993**, 1179.

(17) Andrés, E.; De Munno, G.; Julve, M.; Real, J. A.; Lloret, F. *J. Chem. Soc., Dalton Trans.* **1993**, 2169.

(18) De Munno, G.; Julve, M. *Acta Crystallogr., Sect. C*, **1994**, *50*, 1034.

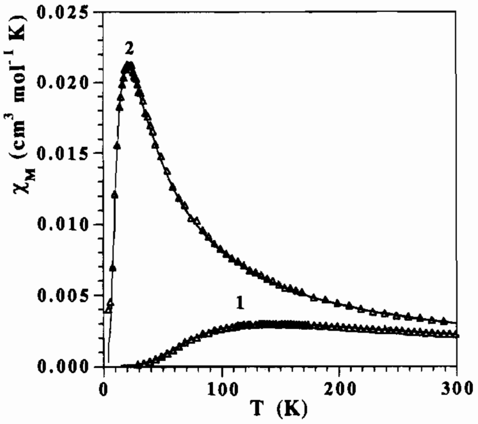


Figure 3. Thermal variation of the molar magnetic susceptibility for complexes **1** and **2**: (△) experimental data; (—) best theoretical fit.

compounds the two metal centers are exactly equivalent by symmetry (a crystallographic inversion center is present at the center of the molecule between the two bpm rings), in **2**, belonging to a different spatial group, this symmetry equivalence is removed and a different distortion of the octahedral geometry around the two metal atoms of the same molecule occurs. Indeed, while Cu(2) shows a normal Jahn–Teller effect with an elongation of the bonds in axial positions [2.358(3) Å for Cu(2)–O(4)] with respect to those in equatorial positions [1.983(3) and 2.033(3) Å for Cu(2)–O(3) and Cu(2)–N(2), respectively], the deformation of the octahedral environment of Cu(1) is through a compression in which the axial positions are shortened [1.968(3) for Cu(1)–O(2)] and the equatorial positions are lengthened [2.128(3) and 2.211(3) Å for Cu(1)–O(1) and Cu(1)–N(1), respectively]. As a consequence, the bite angle of bpm is different in the two sides [76.2(1)° at Cu(1) and 80.9(1)° at Cu(2)], the smaller value being observed for the longer Cu–N bonds. The four equatorial atoms around Cu(2) are practically coplanar with deviations from the least-squares planes lower than 0.080(3) Å. The equatorial plane around Cu(1) [N(1), N(2a), O(1), O(1a)] is much more distorted, the largest deviation from the mean plane being 0.125(3) Å.

The pyrimidyl rings of bpm are planar with deviations from the mean planes not greater than 0.009 Å. They form a dihedral angle of only 1.8°, a value somewhat smaller than that of **1**. The values of the dihedral angles between the bpm plane and the mean equatorial planes of Cu(1) and Cu(2) are practically identical (5.0(1) and 4.8(1)°, respectively). The carbon–carbon inter-ring bond length in **2** [1.487(7) Å for C(4)–C(4a)] is practically identical to that found in **1** [1.484(5) for C(4)–C(5)] and agrees well with that observed in the free bpm in the solid state.[19] The distance between the two metal atoms through the bpm ligands is 5.660(1) Å. This value is larger than that found in **1** [5.456(1) Å] and in other bpm-bridged dinuclear copper(II) complexes, its value being dependent on the particular geometry of **2**. The shortest separation between copper atoms belonging to different Cu–bpm–Cu units is 6.456(1) Å.

Different Cu–bpm–Cu molecules are held together by several hydrogen bonds in which coordinated water molecules, uncoordinated sulfate groups and crystallization water molecules are involved. Although in both complexes **1** and **2** the electroneutrality of the Cu–(bpm)–Cu dinuclear units is achieved by sulfate anions, they play a different structural role in them: bridging bis-monodentate in the former compound and uncoordinated in the latter one. Some of the hydrogen bonds involving the sulfate anion and both coordinated and crystallization water molecules are shown in Figure 2 as broken lines.

Magnetic Properties. The χ_M vs T curves for complexes **1** and **2** (χ_M being the molar magnetic susceptibility per dinuclear unit) are displayed in Figure 3. Both curves exhibit a behavior characteristic of antiferromagnetically coupled copper(II) ions with a maximum in the susceptibility occurring at about 140 K for **1** and 20 K for **2**. The data for both complexes were successfully fitted to a modified Bleaney–Bowers expression

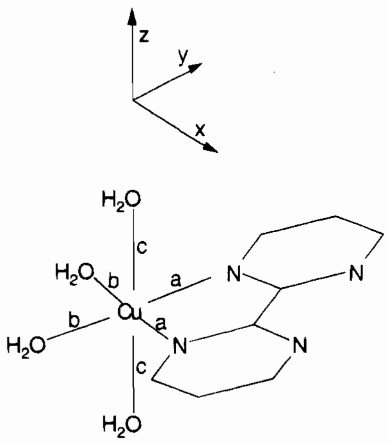
$$\chi_M = 2N\beta^2 g^2/kT(3 + \exp(-J/kT)) \qquad (1)$$

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

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

with $S_1 = S_2 = {}^1/_2$ and N, g, β and T having their usual meaning. The best fit results are $J = -159$ cm^{-1}, $g = 2.07$, and $R = 3.3 \times 10^{-5}$ for **1** and $J = -24$ cm^{-1}, $g = 2.18$ and $R = 9.6 \times 10^{-5}$ for **2**. R is the agreement factor defined as $R = \sum_i(\chi_{\rm exptl}(i) - \chi_{\rm calcd}(i))^2/\sum_i(\chi_{\rm calcd}(i))^2$.

At first sight, the difference magnitude of the coupling between copper(II) ions through bridging bpm in **1** and **2** seems surprising. In previous works with bpm-bridged copper(II) complexes,[5b,c] we have shown that values of antiferromagnetic coupling about -200 cm^{-1} can be attained when the σ in-plane exchange pathway is operative. This situation corresponds to that is observed in **1**. The large coupling in this compound arises from the overlap between the $d_{x^2-y^2}$ magnetic orbitals centered on Cu(1) and Cu(2) [the x and y axes being roughly defined by the Cu(1)–N(3) and Cu(1)–N(1) bonds, respectively] through the N(bpm) atoms. The elongated octahedral environment of Cu(1) and Cu(2) atoms in **1** precludes a significant admixture of the d_{z^2} orbital in the $d_{x^2-y^2}$ ground state. When one looks at the structure of complex **2**, an important change occurs: whereas the octahedral elongation is kept by Cu(2) ($d_{x^2-y^2}$ ground state as in both copper atoms in **1**), Cu(1) exhibits octahedral compression and consequently, its magnetic orbital corresponds to a mixture of d_{z^2} and $d_{x^2-y^2}$ orbitals. In other works, the σ in-plane overlap between the $d_{x^2-y^2}$ orbitals of Cu(1) and Cu(2) through bpm in **2** is significantly reduced, leading to a weaker coupling as observed. In order to evaluate the admixture between the d_{z^2} and $d_{x^2-y^2}$ orbitals in Cu(1) from **2**, we have performed extended Hückel calculations[20,21] on the monomeric $[Cu(bpm)(H_2O)_4]^{2+}$ model system (see structure **I**) with a modified Wolfsberg–Helmholz formula.[22] Atomic parameters used are shown in Table 6.[21,23] The bond distances



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(19) Fernholt, L.; Rømming, D.; Sandal, S. *Acta Chem. Scand., Ser. A*, **1981**, *35*, 707.

Table 6. Orbital Exponents (Contraction Coefficients in Double-ζ Expansion Given in Parentheses) and Energies Used in the Extended Hückel Calculations

atom	orbital	$\zeta_i(c_i)$	H_{ii}, eV
Cu	4s	2.200	−11.40
	4p	2.200	−6.06
	3d	5.950 (0.5933), 2.300 (0.6168)	−14.00
C	2s	1.625	−21.40
	2p	1.625	−11.40
O	2s	2.275	−32.30
	2p	2.275	−14.80
H	1s	1.300	−13.60
N	2s	1.950	−26.00
	2p	1.950	−13.40

Table 7. Values of the Structural Parameters for Selected Steps in the Hypothetical Cu(bpm)$(H_2O)_4{}^{2+}$ Mononuclear Complex[a]

	bond dist, Å		
step	*a*	*b*	*c*
1	2.033	1.983	2.358
7	2.211	2.128	1.968
12	2.358	2.249	1.643

[a] Four oxygen atoms from water molecules and two nitrogens from bpm build the octahedral surrounding around the metal atom. The two bpm nitrogens and the two oxygen atoms in trans positions respect to them are kept coplanar in the calculations.

of the model system, which are denoted as *a*, *b*, and *c* in structure I, are modified stepwise, the starting point (step 1 in Table 7) being very close to the situation of the copper atoms in **1** and to Cu(2) in **2**. The next steps are generated by adding fixed amounts of $\Delta a = 0.030$, $\Delta b = 0.024$, and $\Delta c = -0.065$ to the starting *a*, *b*, and *c* values in such a way that step 7 reflects the real situation of Cu(1) in **2**. The octahedral compression has been pushed until extreme conditions (step 12). The energy values of the $d_{x^2-y^2}$ and d_{z^2} orbitals obtained from these calculations are plotted in Figure 4. It can be seen that the magnetic orbital in step 1 is $d_{x^2-y^2}$, the d_{z^2} orbital being much deeper in energy. The energy gap between both magnetic orbitals decreases as the octahedral compression increases and the d_{z^2} orbital would describe the unpaired electron of the metal atom under a extreme compression (step 12). For such case, the overlap integral would be zero due to the strick orthogonality between the two magnetic orbitals on Cu(1) (d_{z^2}) and Cu(2) ($d_{x^2-y^2}$), and a weak ferromagnetic coupling is predicted.[24] To our knowledge, a copper(II) dimer filling these structural features has not been isolated. The crossing point in Figure 4 (step 7) corresponds to the monomeric fragment of Cu(1) in complex **2**. It is clear that the magnetic orbital is a mixture of ca. 50% of the $d_{x^2-y^2}$ and d_{z^2} orbitals. The decrease of spin density on the former orbital accounts for the weaker antiferromagnetic coupling in **2** respect to **1**.

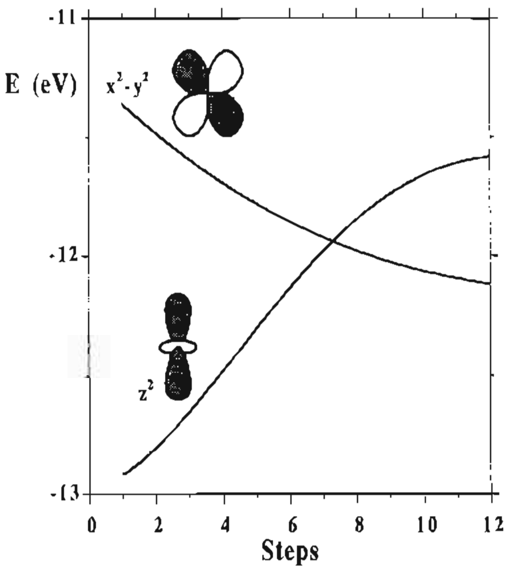

Figure 4. Plot of the energy of the $d_{x^2-y^2}$ and d_{z^2} magnetic orbitals from extended Hückel calculations in the hypothetical [Cu(bpm)$(H_2O)_4]^{2+}$ mononuclear complex as a function of the metal to ligand bond distances (see text).

In the light of these results, two points deserve special comments: (i) first, a control of the Jahn–Teller effect appears as a nice strategy to achieve ferromagnetic coupling between copper(II) ions, but unfortunately, this is not an easy task; (ii) second, the identification of the structural factor which is responsable for the different structure of the related compounds **1** and **2** is of utmost importance. A simple comparison of both structures suggests that the different role of the sulfate group (bis-monodentate bridge in **1** and uncoordinated in **2**) could be at the heart of this phenomenon. Further work remains to be done by using different counterions in other order to check their influence on both structure and magnetic properties of the $Cu_2(bpm)^{4+}$ dinuclear unit and to settle a strategy to synthesize these bond-stretch isomers.[25]

Acknowledgment. This work was supported by the Spanish DGICYT (Project PB91-0807-C02-01), the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica, and the Human Capital and Mobility Program (Network on Magnetic Molecular Materials) through Contract ERBCHRXDCT920080. J.C. also thanks the Spanish DGICYT for a predoctoral fellowship.

Supplementary Material Available: Tables listing crystal data, atomic coordinates and temperature factors for non-hydrogen atoms, hydrogen atom coordinates, intramolecular bond distances and angles, hydrogen bonding, and least-squares planes (Tables S1–S11) (17 pages). Ordering information is given on any current masthead page.

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(20) Mealli, C.; Proserpio, D. M. Computer Aided Composition of Atomic Orbitals (CACAO Program). PC version, July 1992; kindly supplied by C. Mealli. See also: *J. Chem. Educ.* **1990**, *67*, 3399.

(21) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397.

(22) Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

(23) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

(24) Julve, M.; Verdaguer, M.; Charlot, M. F.; Kahn, O.; Claude, R. *Inorg. Chim. Acta* **1984**, *82*, 5.

(25) Gütlich, P.; Goodwin, H. A.; Hendrickson, D. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 425 and references therein.