

# Synthesis, Crystal Structure, Magnetic Properties, and Theoretical Studies of $[\{\text{Cu}(\text{mepirizole})\text{Br}\}_2(\mu\text{-OH})(\mu\text{-pz})]$ (Mepirizole = 4-Methoxy-2-(5-methoxy-3-methyl-1H-pyrazol-1-yl)-6-methylpyrimidine; pz = Pyrazolate), a Novel $\mu$ -Pyrazolato– $\mu$ -Hydroxo-Dibridged Copper(II) Complex

Emilio Escrivà,<sup>\*,†</sup> Julia García-Lozano,<sup>†</sup> José Martínez-Lillo,<sup>†</sup> Hugo Nuñez,<sup>†</sup> Juan Server-Carrió,<sup>†</sup> Lucía Soto,<sup>†</sup> Rosa Carrasco,<sup>†</sup> and Joan Cano<sup>§</sup>

Departament de Química Inorgànica, Universitat de València, c/Vicent Andrés Estellés, s/n, 46100 Burjassot (València), Spain, Laboratoire de Chimie Bioorganique et Bioinorganique, UMR 8124, Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud F-91405, Orsay, France, and Laboratoire de Chimie Inorganique, UMR 8613, Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud F-91405, Orsay, France

Received February 5, 2003

A novel  $\mu$ -pyrazolato– $\mu$ -hydroxo-dibridged copper(II) complex has been synthesized and structurally characterized:  $[\{\text{Cu}(\text{mepirizole})\text{Br}\}_2(\mu\text{-OH})(\mu\text{-pz})]$  (mepirizole = 4-methoxy-2-(5-methoxy-3-methyl-1H-pyrazol-1-yl)-6-methylpyrimidine; pz = pyrazolate). The title compound crystallizes in the monoclinic system, space group  $P2_1/c$ , with  $a = 15.618(2)$  Å,  $b = 15.369(3)$  Å,  $c = 16.071(3)$  Å, and  $\beta = 112.250(1)^\circ$ . The structure is built up of dinuclear  $[\{\text{Cu}(\text{mepirizole})\text{Br}\}_2(\mu\text{-OH})(\mu\text{-pz})]$  units with five-coordinated copper(II) ions ( $\text{CuBrN}_3\text{O}$  chromophores) linked by  $\mu_2\text{-OH}$  and  $\mu_2\text{-pyrazolato}$  bridges that are well separated from each others. The intramolecular copper–copper distance is  $3.378(3)$  Å. Magnetic susceptibility data show that the copper atoms are strongly antiferromagnetically coupled with  $J = -770$  cm<sup>-1</sup>. The obtained triplet–singlet energy gap is compared with those reported for a series of related dimers. The strong antiferromagnetic coupling arising from the complementarity of the hydroxo and pyrazolato bridges has been discussed on the basis of DFT calculations.

## Introduction

Dinuclear copper(II) complexes have attracted considerable attention in the two past decades. In particular, considerable knowledge has been gained in understanding the magneto–structural correlations in several families of symmetrical dibridged dicopper complexes, either including single atoms as bridges or extended-bridging ligands. Among other reasons, the use of these kinds of systems as models for the active sites of several multicopper-containing proteins has encouraged this interest. Since the coordination environment of the copper in the active site is not always well understood, these model studies will shed light on this important question.<sup>1–8</sup>

In general, the nature (antiferromagnetic or ferromagnetic) and magnitude of magnetic exchange interactions depend on several factors, such as the bridge identity, the metal–metal distance, the topology of the bridging framework, the dihedral angle between the planes of the magnetic orbitals, the metal stereochemistry, etc.<sup>9–18</sup> It is well-known that many bridging ligands lead to antiferromagnetic interactions. But, in some

- (1) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding* **1983**, 53, 1.
- (2) Wilcox, D. E.; Long, J. R.; Solomon, E. I. *J. Am. Chem. Soc.* **1984**, 10, 2186.
- (3) Ling, J.; Farooq, A.; Karlin, K. D.; Loehr, T. M.; Sanders-Loehr, J. *Inorg. Chem.* **1992**, 31, 2552.
- (4) Karlin, K. D. *Science* **1993**, 261, 701.
- (5) Karlin, K. D.; Tyeklár, Z. *Adv. Inorg. Biochem.* **1994**, 9, 123.
- (6) Kitajima, N.; Moro-Oka, Y. *Chem. Rev.* **1994**, 94, 737.
- (7) Solomon, E. I.; Sundaramand, U. M.; Machonkin, T. E. *Chem. Rev.* **1996**, 96, 2563.
- (8) Asokan, A.; Manoharan, P. T. *Inorg. Chem.* **1999**, 38, 5642 and references therein.
- (9) Hay, P. J.; Thibault, J. C.; Hoffman, R. *J. Am. Chem. Soc.* **1975**, 97, 4884.

\* To whom correspondence should be addressed. E-mail: escrivà@uv.es.

<sup>†</sup> Universitat de València.

<sup>‡</sup> Laboratoire de Chimie Bioorganique et Bioinorganique, Institut de Chimie Moléculaire d'Orsay.

<sup>§</sup> Laboratoire de Chimie Inorganique, Institut de Chimie Moléculaire d'Orsay.

systems with two different bridging ligands, the two bridges may either add or counterbalance their effects. These phenomena, which are known as orbital complementarity or countercomplementarity, were treated by Nishida et al.,<sup>19,20</sup> Mckee et al.,<sup>21,22</sup> and one of us.<sup>23–26</sup>

Ferromagnetic interactions are important to design new magnets. However, this kind of interaction is often weak and, in consequence, the critical temperatures are too low<sup>12,27–30</sup> to find an application. In the late 1980s, antiferromagnetic interactions, very much stronger than the ferromagnetic ones, present in some heteropolynuclear systems were employed to obtain properties similar to the ones of ferromagnetic systems from noncompensating spins moments.<sup>31,32</sup> These cases are known as ferrimagnetic systems. In the 1990s, the first well-characterized ferrimagnet at room temperature was synthesized in molecular magnetism.<sup>33–35</sup> In this way, it is very interesting to find bridging ligands capable of providing a very strong antiferromagnetic interaction between metal ions. In this sense, a very strong antiferromagnetic interaction has been found in the compound presented in this paper, which makes of it a good model for designing ferrimagnetic magnets.

Mepirizole is a biologically active pyrimidine–pyrazole derivative that behaves as a bidentate ligand through two

nitrogen atoms, one from each ring, with significant steric hindrance in the formation of metal complexes.<sup>36–40</sup> It is well-known the increasing interest focused in recent years on the coordinating behavior of pyrazole and related pyrazole-including polyfunctional ligands.<sup>41–44</sup> Most of the reported dinuclear copper(II) complexes including pyrazolato bridges are asymmetrical (or nonsymmetrical) presenting a second bridging group such as alkoxo, azido, carboxylato, etc. A few examples of related dinuclear complexes with a [(μ-OH)(μ-pz)] central core have been reported for some divalent 3d metals.<sup>44–46</sup> However, there are reported several μ-pyrazolato–μ-alkoxo-dibridged copper(II) complexes<sup>47–53</sup> where the bridging oxygen atom belongs to an alkoxo group—which usually functionalizes a binucleating ligand—but it is not a *purely isolated* hydroxo.

We report here the synthesis, crystal structure, magnetic properties, and theoretical studies of [{Cu(mepirizole)Br}<sub>2</sub>(μ-OH)(μ-pz)] (compound **1**; mepirizole = 4-methoxy-2-(5-methoxy-3-methyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine; pz = pyrazolato), a novel μ-pyrazolato–μ-hydroxo-dibridged copper(II) complex, which is the first structurally characterized copper(II) dinuclear complex where the copper atoms are linked by pyrazolato nitrogen atoms and a hydroxo oxygen atom. We have previously described the synthesis of a bis(μ-hydroxo)copper(II) compound including mepirizole as a peripheral ligand, formulated as [{Cu(mepirizole)}<sub>2</sub>(μ-OH)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (compound **2**).<sup>54</sup> Attempts to obtain suitable crystals for an X-ray study were unsuccessful, and consequently, compound **2** was not structurally characterized.

(10) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834 and references therein.  
 (11) Alvarez, S.; Julve, M.; Verdager, M. *Inorg. Chem.* **1990**, *29*, 4507.  
 (12) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.  
 (13) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *Inorg. Chem.* **1997**, *36*, 3683.  
 (14) Thompson, L. K.; Xu, Z. Q.; Goeta, A. E.; Howard, J. A. K.; Clase, H. J.; Miller, D. O. *Inorg. Chem.* **1998**, *37*, 3217.  
 (15) Xu, Z. Q.; Thompson, L. K.; Miller, D. O. *Inorg. Chem.* **1997**, *36*, 3985.  
 (16) Fabrizi de Biani, F.; Ruiz, E.; Cano, J.; Novoa, J. J.; Alvarez, S. *Inorg. Chem.* **2000**, *39*, 3221.  
 (17) Graham, B.; Hearn, M. T. W.; Junk, P. C.; Kepert, C. M.; Mabbs, F. E.; Moubaraki, B.; Murray, K. S.; Spiccia, L. *Inorg. Chem.* **2001**, *40*, 1536 and references therein.  
 (18) Manikandan, P.; Muthukumar, R.; Thomas, K. R. J.; Varghese, B.; Chandramonli, G. V. R.; Manoharan, P. T. *Inorg. Chem.* **2001**, *40*, 2378.  
 (19) Nishida, Y.; Takeuchi, M.; Takahashi, K.; Kida, S. *Chem. Lett.* **1985**, 631.  
 (20) Nishida, Y.; Takeuchi, M.; Takahashi, K.; Kida, S. *Chem. Lett.* **1983**, 1815.  
 (21) McKee, V.; Zvagulis, M.; Reed, C. A. *Inorg. Chem.* **1985**, *24*, 2914.  
 (22) McKee, V.; Zvagulis, M.; Dagdian, J. V.; Patch, M. G.; Reed, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 4765.  
 (23) Cano, J. *Molecular Magnetism: Mechanism of Interactions and Structural Magnetic Correlations*. Doctoral Thesis, 1997.  
 (24) Thompson, L. K.; Tandon, S. S.; Lloret, F.; Cano, J.; Julve, M. *Inorg. Chem.* **1997**, *36*, 3301.  
 (25) Gutierrez, L.; Alzuet, G.; Real, J. A.; Cano, J.; Borrás, J.; Castiñeiras, A. *Inorg. Chem.* **2000**, *39*, 3608.  
 (26) Gutierrez, L.; Alzuet, G.; Real, J. A.; Cano, J.; Borrás, J.; Castiñeiras, A. *Eur. J. Inorg. Chem.* **2002**, *8*, 2094.  
 (27) Hay, P. J.; Thiebault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.  
 (28) Anderson, P. W. *Phys. Rev.* **1959**, *115*, 2.  
 (29) Awaga, K.; Maruyama, Y. *Phys. Rev. B* **1991**, *44*, 2589.  
 (30) Gadet, V.; Mallah, T.; Castro, I.; Verdager, M. *J. Am. Chem. Soc.* **1992**, *114*, 9213.  
 (31) Kahn, O.; Pei, Y.; Verdager, M.; Renard, J. P.; Sletten, J. *J. Am. Chem. Soc.* **1988**, *110*, 782.  
 (32) Caneschi, A.; Gatteschi, D.; Renard, J. P.; Rey, P.; Sessoli, R. *Inorg. Chem.* **1989**, *28*, 1976.  
 (33) Mallah, T.; Thiébaud, S.; Verdager, M.; Veillet, P. *Science*, **1993**, *262*, 1554.  
 (34) Entley, W. R.; Girolami, G. S. *Science* **1995**, *268*, 397.

(35) Ferlay, S.; Mallah, T.; Ouahès, R.; Veillet, P.; Verdager, M. *Nature* **1995**, *378*, 701.  
 (36) Soto, L.; García-Lozano, J.; Escrivà, E.; Legros, J.-P.; Tuchagues, J.-P.; Dahan F.; Fuertes, A. *Inorg. Chem.* **1989**, *28*, 3378 and references therein.  
 (37) Benetó, M.; Soto, L.; García-Lozano, J.; Escrivà, E.; Legros, J.-P.; Dahan, F. *J. Chem. Soc., Dalton Trans.* **1991**, 1057.  
 (38) Soto, L.; García-Lozano, J.; Escrivà, E.; Benetó, M.; Dahan, F.; Tuchagues, J.-P.; Legros, J.-P. *J. Chem. Soc., Dalton Trans.* **1991**, 2619.  
 (39) García-Lozano, J.; Server-Carrió, J.; Escrivà, E.; Folgado, J. V.; Molla, M. C. *Polyhedron* **1997**, *16*, 939.  
 (40) Trofimenko, S. *Prog. Inorg. Chem.* **1986**, *34*, 115.  
 (41) Steel, J. P. *Coord. Chem. Rev.* **1990**, *106*, 227.  
 (42) Bode, R. H.; Bol, J. E.; Driessen, W. L.; Hulsbergen, F. B.; Reedijk, J.; Spek, A. L. *Inorg. Chem.* **1999**, *38*, 1239 and references therein.  
 (43) Martens, C. F.; Schenning, A. P. H. J.; Feiters, M. C.; Berens, H. W.; van der Linden, J. G. M.; Admiraal, G.; Beurskens, P. T.; Kooijman, H.; Spek, A. L.; Nolte, R. J. M. *Inorg. Chem.* **1995**, *34*, 4735 and references therein.  
 (44) Komatsuzaki, H.; Ichikawa, S.; Hikichi, S.; Akita, M.; Moro-oka, Y. *Inorg. Chem.* **1998**, *37*, 3652.  
 (45) López, G.; García, G.; Sánchez, G.; García, J.; Ruiz, J.; Hermoso, J. A.; Vegas, A.; Martínez-Ripoll, M. *Inorg. Chem.* **1992**, *31*, 1518.  
 (46) Ackermann, J.; Meyer, F.; Kaifer, E.; Pritzkow, H. *Chem.—Eur. J.* **2002**, *8*, 247.  
 (47) Mazurek, W.; Kennedy, B. J.; Murray, K. S.; O'Connor, M. J.; Rodgers, J. R.; Snow, M. R.; Wed, A.; Zwack, G. P. R. *Inorg. Chem.* **1985**, *24*, 3258.  
 (48) Doman, T. N.; Williams, D. E.; Banks, J. F.; Buchanan, R. M.; Chang, H.-R.; Webb, R. J.; Hendrickson, D. N. *Inorg. Chem.* **1990**, *29*, 1058.  
 (49) Nishida Y.; Kida, S. *Inorg. Chem.* **1988**, *27*, 447.  
 (50) Nonoyama, K.; Mori, W.; Nakajima, K.; Nonoyama, M. *Polyhedron* **1997**, *16*, 3815.  
 (51) Nie, H.; Aubin, S. M. J.; Mashuta, M. S.; Porter, R. A.; Richardson, J. F.; Hendrickson, D. N.; Buchanan, R. M. *Inorg. Chem.* **1996**, *35*, 3325.  
 (52) Kara, H.; Elerman, Y.; Prout, K. Z. *Naturforsch* **2000**, *55b*, 796.  
 (53) Kara, H.; Elerman, Y.; Prout, K. Z. *Naturforsch* **2001**, *56b*, 56, 719.  
 (54) García, J.; Molla, M.; Borrás, J. *Polyhedron* **1985**, *4*, 757.

Notwithstanding, both chemical and spectroscopic characterizations of **2** (see below) support that it is a  $\mu_2$ -hydroxo-bridged dicopper compound. We have approached the magnetic characterization of compound **2** to compare both related mepirizole-containing copper(II) dinuclear complexes with symmetric and dissymmetric bridges. Finally, to explain the strong antiferromagnetic interaction observed in **1**, DFT calculations are reported.

## Experimental Section

**Preparation of [Cu(mepirizole)Br]<sub>2</sub>( $\mu$ -OH)( $\mu$ -pz)].** An ethanolic solution (0.2 mmol in 2 mL) of sodium pyrazolate (from pyrazole and sodium ethoxide) was mixed with an equimolar solution of copper(II) bromide in the same solvent. The chelating ligand mepirizole (10 mL of a  $2 \times 10^{-2}$  M ethanolic solution) was added with stirring, and the product precipitated. Suitable green crystals for X-ray analysis were obtained upon slow evaporation of the mother liquor at room temperature. Anal. Found: C, 35.6; H, 3.9; Cu, 15.0; N, 16.7. Calcd for C<sub>25</sub>H<sub>32</sub>Br<sub>2</sub>Cu<sub>2</sub>N<sub>10</sub>O<sub>5</sub>: C, 35.8; H, 3.8; Cu, 15.1; N, 16.7.

**Preparation of Compound 2.** Compound **2** was prepared as previously described.<sup>54</sup> Anal. Found: C, 32.0; H, 3.9; Cu, 15.2; N, 13.7. Calcd for C<sub>11</sub>H<sub>15</sub>ClCuN<sub>4</sub>O<sub>7</sub>: C, 31.9; H, 3.7; Cu, 15.3; N, 13.5.

**Physical Measurements.** Polycrystalline powder EPR spectra were recorded at room temperature on a Bruker ESP-300 equipped with a variable-temperature device. Magnetic susceptibility was measured by means of a commercial SQUID magnetometer, Quantum Design model MPMS7, down to 80 K. Experimental susceptibilities were corrected for both the diamagnetic contribution, estimated from the Pascal's constants,<sup>55</sup> and the TIP (taken as  $60 \times 10^{-6}$  cm<sup>3</sup> mol<sup>-1</sup> per Cu(II)).

**X-ray Crystallographic Study of [Cu(mepirizole)Br]<sub>2</sub>( $\mu$ -OH)( $\mu$ -pz)].** The selected prismatic crystal of the complex (approximate dimensions 0.15 × 0.20 × 0.30 mm<sup>3</sup>) was mounted on an Enraf-Nonius CAD4 single-crystal diffractometer, and intensity measurements were carried out at 295 K using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71070$  Å). The unit cell dimensions were determined from the angular settings of 25 reflections in the angle range  $8 < \theta < 15^\circ$ . The intensity data of 7952 reflections were measured between the limits  $1 < \theta < 27^\circ$ , in the  $hkl$  ranges 0 to 19, 0 to 18, and  $-20$  to 20, using the  $\omega/2\theta$  scan technique. Data reduction was performed with the X-RAY76 system.<sup>56</sup> Empirical absorption correction was applied by following the procedure DIFABS.<sup>57</sup> From the 7692 independent reflections 4633 were considered observed with  $I > 2\sigma(I)$ . Minimum and maximum absorption correction coefficients were 0.474 and 0.593, respectively. The structure was solved by direct methods using the program SIR92.<sup>58</sup> Non-hydrogen atoms were anisotropically refined by least squares on  $F^2$  with SHELXL97.<sup>59</sup> Atomic scattering factors and anomalous dispersion corrections were taken from ref 60. Hydrogens bonded to C atoms were placed at calculated positions,

(55) Reference 12, p 3.

(56) Stewart, J. M.; Machin, P. A.; Dickinson, C. W.; Ammon, H. L.; Heck, H.; Flack, H. *The X-RAY76 System*; Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976.

(57) Walker, N.; Stuart, D. *Acta Crystallogr., Sect. A* **1983**, *39*, 158.

(58) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, G.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

(59) Sheldrick, G. M. *SHELXL97*; University of Göttingen: Göttingen, Germany, 1997.

(60) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 71 and 149.

**Table 1.** Crystallographic Data for [Cu(mepirizole)Br]<sub>2</sub>( $\mu$ -OH)( $\mu$ -pz)]

formula	C <sub>25</sub> H <sub>32</sub> N <sub>10</sub> O <sub>5</sub> Br <sub>2</sub> Cu <sub>2</sub>
fw	839.5
space group (No.)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (14)
<i>a</i> , Å	15.618(2)
<i>b</i> , Å	15.369(3)
<i>c</i> , Å	16.071(3)
$\alpha$ , deg	90.0
$\beta$ , deg	112.250(1)
$\gamma$ , deg	90.0
<i>V</i> , Å <sup>3</sup>	3570.3(9)
<i>Z</i>	4
$\lambda$ (Mo K $\alpha$ ), Å	0.71070
$\mu$ (Mo K $\alpha$ ), mm <sup>-1</sup>	3.476
$\rho$ (calcd), g cm <sup>-3</sup>	1.56
<i>T</i> , °C	22
R1 <sup>a</sup>	0.074
wR2 <sup>b</sup>	0.182

<sup>a</sup> R1 =  $\sum ||F_o| - |F_c|| / \sum |F_o|$  for reflections with  $I > 2\sigma(I)$ . <sup>b</sup> wR2 =  $\{\sum [w(F_o^2 - F_c^2)]^2 / \sum [w(F_c^2)]\}^{1/2}$  for all reflections;  $w = 1/[\sigma^2(F_o^2) + (aP)^2]$ , where  $P = [2F_c^2 + F_o^2]/3$  and *a* is a constant set by the program.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for the Title Complex

Cu(1)–O(1)	1.900(5)	Cu(2)–O(1)	1.927(5)
Cu(1)–Br(1)	2.465(1)	Cu(2)–Br(2)	2.497(1)
Cu(1)–N(1)	1.996(5)	Cu(2)–N(2)	1.945(5)
Cu(1)–N(3)	2.057(6)	Cu(2)–N(10)	2.000(6)
Cu(1)–N(6)	2.246(5)	Cu(2)–N(7)	2.294(5)
O(1)–Cu(1)–Br(1)	90.4(2)	O(1)–Cu(2)–Br(2)	159.1(2)
O(1)–Cu(1)–N(1)	85.9(2)	O(1)–Cu(2)–N(2)	86.9(2)
O(1)–Cu(1)–N(3)	175.3(2)	O(1)–Cu(2)–N(10)	91.9(2)
O(1)–Cu(1)–N(6)	103.1(2)	O(1)–Cu(2)–N(7)	104.6(2)
Br(1)–Cu(1)–N(1)	148.5(2)	Br(2)–Cu(2)–N(2)	94.2(2)
Br(1)–Cu(1)–N(3)	94.3(2)	Br(2)–Cu(2)–N(10)	85.2(2)
Br(1)–Cu(1)–N(6)	102.8(1)	Br(2)–Cu(2)–N(7)	94.6(2)
N(1)–Cu(1)–N(3)	90.3(2)	N(2)–Cu(2)–N(10)	174.7(2)
N(1)–Cu(1)–N(6)	108.4(2)	N(2)–Cu(2)–N(7)	110.9(2)
N(3)–Cu(1)–N(6)	75.5(2)	N(10)–Cu(2)–N(7)	74.4(2)
Cu(1)–N(1)–N(2)	120.6(4)	Cu(2)–N(2)–N(1)	120.8(4)
Cu(1)–O(1)–Cu(2)	123.9(2)		

and the hydrogen bonded to O1 was located by difference synthesis. All of them were kept fixed in the refinement with isotropic temperature factors related to their bonded atom. There were a total of 397 refined parameters. After the final refinement, the goodness of fit on  $F^2 = 1.015$  and the largest difference peak and hole = 0.65 and  $-0.67$  e Å<sup>-3</sup>, respectively. Graphical representation was produced with ORTEP3 for Windows.<sup>61</sup> Other relevant data for the crystal structure study are listed in Table 1. Selected bond distances and angles are listed in Table 2.

**Computational Details.** A detailed description of the computational strategy adopted in this work has been described elsewhere<sup>62</sup> and is only briefly reviewed here. For the evaluation of the coupling constant of dinuclear models, two separate calculations were carried out by means of density functional theory,<sup>63</sup> one for the triplet and another for the singlet state. The hybrid B3LYP method,<sup>64</sup> as implemented in Gaussian98,<sup>65</sup> has been used in all calculations, mixing the exact Hartree–Fock exchange<sup>66</sup> with Becke's expression for the exchange and with the Lee–Yang–Parr correlation functional.<sup>67</sup> Double- $\zeta$  quality and triple- $\zeta$  quality basis sets proposed by Ahlrichs<sup>68</sup> have been employed for nonmetallic and metallic atoms, respectively. Also, for the metallic atoms, we added two

(61) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565

(62) Ruiz, E.; Alemany, P.; Alvarez, S.; Cano, J. *J. Am. Chem. Soc.* **1997**, *119*, 1927.

(63) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: New York, 1989.

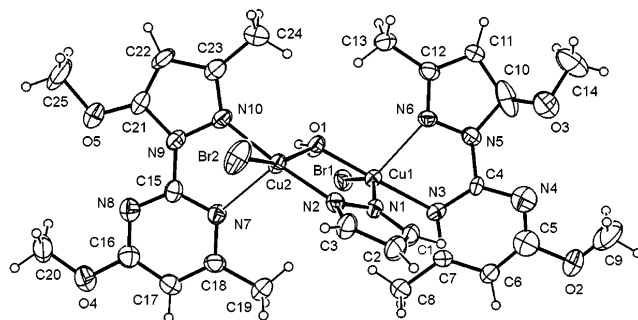
(64) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

extra polarization p functions. The presence of a low-energy excited singlet makes it difficult to evaluate accurately the energy of the lowest singlet by a single-determinant method. To solve this problem, broken-symmetry wave functions, as proposed by Noodleman et al., have been used.<sup>69–72</sup> Previously, it has been found that, among the most common functionals, the B3LYP method combined with the broken-symmetry treatment is the strategy which provides the best results for calculating coupling constants.<sup>62,73–77</sup> It is clear that for broken-symmetry Hartree–Fock calculations it is necessary to make a correction due to the multideterminant character of the wave function of the low-multiplicity state.<sup>76</sup> On the other hand, for DFT calculations we adopt single-determinant wave functions for which DFT is well defined.<sup>78–80</sup> Then, we use the broken-symmetry energy calculated by DFT methods as the real energy of the state.

## Results and Discussion

**Crystal Structure of 1.** The structure of the title compound is built up of dinuclear [{Cu(mepirizole)Br<sub>2</sub>(μ-OH)(μ-pz)}] units with five-coordinated copper(II) ions (CuBrN<sub>3</sub>O chromophores) linked by μ<sub>2</sub>-OH and μ<sub>2</sub>-pyrazolato bridges that are well separated from each other. The intramolecular copper–copper distance is 3.378(3) Å, and the shortest intermolecular copper–copper distance is 8.036(3) Å. Figure 1 shows a perspective view of the dinuclear unit with the atomic numbering scheme.

The coordination geometry of both metal atoms in the molecule is intermediate between a square pyramid (SP) and trigonal bipyramid (TBP). Considering the chromophores as SP, then one mepirizole nitrogen (N6 in the Cu1 coordination polyhedron and N7 in the Cu2 one) occupies the axial position. Basal coordination positions are occupied by the



**Figure 1.** Perspective view and atomic numbering of the [{Cu(mepirizole)Br<sub>2</sub>(μ-OH)(μ-pz)}] dinuclear units.

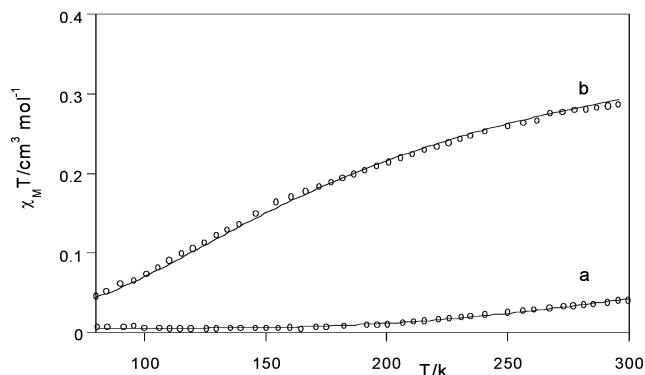
other coordinated mepirizole nitrogen atoms (N3 or N10 for Cu1 and Cu2, respectively), an oxygen (O1) from the μ-hydroxo bridge, a nitrogen atom from the bridging pyrazolato anion, and a bromine atom. Notwithstanding, there is a remarkable difference in both metal atom environments: the axial nitrogen atom belongs to the pyrazolic ring of mepirizole in Cu1 but to the pyrimidinic one in Cu2. For Cu1 environment, deviations from a best least-squares plane through N1–N3–Br1–O1 are 0.356(5), 0.504(6), 0.010(1), and 0.344(5) Å, respectively. In the Cu2 coordination polyhedron, deviations from a best least-squares plane through N10–N2–Br2–O1 are 0.252(6), 0.152(5), 0.010(1), and 0.168(5) Å, respectively. As usual, the copper atom deviates toward the axial ligand by 0.391(1) Å in Cu1 and 0.293(1) Å in Cu2 (4 + 1 coordination mode). The angles around the copper atom in the basal plane vary from 85.9(2) to 94.3(2)° in the Cu1 coordination polyhedron and 85.2(2) to 94.2(2)° in the Cu2 one, indicating an appreciable distortion from an idealized SP geometry. Such a distortion can be quantitatively characterized using the parameter  $\tau$  as defined by Addison et al.<sup>81</sup> The calculated values  $\tau = 0.42$  for Cu1 and  $\tau = 0.26$  for Cu2 (relative to 1 for a regular TBP and 0 for a regular SP) indicate a significant degree of distortion of the coordination polyhedron, particularly for the Cu1 atom.

The axial Cu–N distances fall within the normal range and are in agreement with those found in other mepirizole-containing copper(II) complexes.<sup>36–40</sup> The Cu–O(hydroxo) are close to those reported for related μ-OH-bridged copper(II) dinuclear complexes.<sup>14,48</sup> Finally, the Cu–Br distance of 2.497(1) Å agrees with those reported for five-coordinated copper(II) complexes with bromine atoms occupying equatorial positions in SP geometries.<sup>82–84</sup> On the other hand, the longer Cu–N(mepirizole) distances (Cu1–N6 = 2.246(5) Å and Cu2–N7 = 2.294(6) Å) are very close to those reported for other mepirizole-containing copper(II) complexes involving N(mepirizole) atoms in apical positions.<sup>36</sup>

The dihedral angle between the two basal coordination planes is 161.1(1)°. Furthermore, the angle between the pyrazolato bridge and the basal coordination planes is 21.9-

- (65) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.
- (66) Becke, A. D. *J. Phys. Rev.* **1988**, *A38*, 3098.
- (67) Lee, C.; Yang, W.; Parr, R. G. *J. Phys. Rev.* **1988**, *B37*, 785.
- (68) Schaefer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
- (69) Noodleman, L.; Peng, C. Y.; Case, D. A.; Mouesca, J. M. *Coord. Chem. Rev.* **1995**, *144*, 199.
- (70) Noodleman, L.; Case, D. A. *Adv. Inorg. Chem.* **1992**, *38*, 423.
- (71) Noodleman, L.; Davidson, E. R. *Chem. Phys.* **1986**, *109*, 1.
- (72) Noodleman, L. *J. Chem. Phys.* **1981**, *74*, 5737.
- (73) Cano, J.; Alemany, P.; Alvarez, S.; Verdager, M.; Ruiz, E. *Chem.—Eur. J.* **1998**, *4*, 476.
- (74) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Am. Chem. Soc.* **1998**, *120*, 11122.
- (75) Cano, J.; Ruiz, E.; Alemany, P.; Lloret, F.; Alvarez, S. *J. Chem. Soc., Dalton Trans.* **1999**, 1669.
- (76) Ruiz, E.; Cano, J.; Alvarez, S.; Alemany, P. *J. Comput. Chem.* **1999**, *20*, 1391.
- (77) Castro, I.; Calatayud, M. L.; Sletten, J.; Lloret, F.; Cano, J.; Julve, M.; Seitz, G.; Mann, K. *Inorg. Chem.* **1999**, *38*, 4680.
- (78) Perdew, J. P.; Savin, A.; Burke, K. *J. Phys. Rev. A* **1995**, *51*, 4531.
- (79) Miehlisch, B.; Stoll, H.; Savin, A. *Mol. Phys.* **1997**, *91*, 527.
- (80) Giorso, A.; Malrieu, J. P.; Salahub, D. R. *Theor. Chim. Acta* **1995**, *91*, 225.

- (81) Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
- (82) Landee, C. P.; Greeney, R. E. *Inorg. Chem.* **1986**, *25*, 3771.
- (83) Murphy, G.; Osullivan, C.; Murphy, B.; Hathaway, B. *Inorg. Chem.* **1998**, *37*, 240.
- (84) Ferraro, J. R.; Walker, W. R. *Inorg. Chem.* **1965**, *4*, 1382.



**Figure 2.** Magnetic behavior of  $[\{\text{Cu}(\text{mepirizole})\text{Br}_2(\mu\text{-OH})(\mu\text{-pz})\}]$  (a) and  $[\{\text{Cu}(\text{mepirizole})\}_2(\mu\text{-OH})_2](\text{ClO}_4)_2$  (b).

(2)° for Cu1 and 7.8(2)° for Cu2. The five-membered metallocyclic structure Cu1–Cu2–N1–N2–O1 shows an approximate envelope conformation with the oxygen atom at the flap (0.263(5) Å out of the plane defined by the copper and nitrogen atoms).

Interatomic distances and bond angles in the mepirizole molecules are in good agreement with those previously reported.<sup>36–40</sup> The individual pyrimidine and pyrazole rings are planar (deviation from planarity ranging from 0.01 to 0.03 Å). A significant difference in the conformations of both mepirizole molecules must be stressed. So, whereas the molecule linked to Cu2 atom is almost planar (torsion angle N10–N9–C15–N7 of 1.2(1)°, with a dihedral angle between the pyrazolic and pyrimidinic rings of 4.0(0.3)°), the molecule coordinated to Cu1 atom deviates significantly from planarity (torsion angle N6–N5–C4–N3 of 11.8(1) Å and dihedral angle of 14.6(0.4)°). As a whole, the mepirizole molecules are roughly oriented perpendicularly to the respective copper(II) basal coordination planes (dihedral angles of 98.8(1) Å in Cu1 atom and 75.0(1) Å in Cu2 one). The normalized bite defined by  $b = 2d_0/(d_1 + d_2)$  (where  $d_0$  is the nonbonding distance between the two donor atoms and  $d_1$  and  $d_2$  are the distances of these atoms to the metal center) is  $b = 1.23$  for the mepirizole molecule coordinated to Cu1 atom and  $b = 1.21$  for the molecule linked to Cu2. In previously characterized mepirizole-containing copper(II) complexes the normalized bite fluctuates between 1.20 and 1.30.<sup>36–40</sup>

**Magnetic Properties.** Both compounds are EPR silent and show no triplet spectrum, displaying at room temperature a weak signal of a monomeric impurity (at  $g = 2.14$  for compound **1** and  $g = 2.12$  for compound **2**).

The room-temperature magnetic moments of compounds **1** and **2** are 0.57 and 1.51  $\mu_B$ , respectively, indicating strong antiferromagnetic interactions between the metal centers. The variable-temperature magnetic studies were carried out in the temperature range 80–300 K (see Figure 2). The experimental data were fitted to the Bleaney–Bowers<sup>85</sup> eq 1 for a dinuclear copper(II) complex where  $J$  is the singlet–triplet energy gap (defined by the Hamiltonian  $H = -J S_1 S_2$ ) with  $S_1 = S_2 = 1/2$  and  $N$ ,  $g$ ,  $\beta$ , and  $T$  having the

usual meanings. The least-squares fitting procedure led to  $J = -770 \text{ cm}^{-1}$  and  $g = 2.12$  with an agreement factor of  $R = 5.2 \times 10^{-4}$  ( $R$  is defined as  $\sum[(\chi_M)_{\text{obsd}} - (\chi_M)_{\text{calcd}}]^2 / \sum[(\chi_M)_{\text{obsd}}]^2$ ) for compound **1** and  $J = -240 \text{ cm}^{-1}$  and  $g = 2.14$  with an agreement factor of  $R = 5.7 \times 10^{-4}$  for compound **2**. Since the diamagnetic correction is of the same order as the uncorrected molar susceptibility, the uncertainty in the corrected values of  $\chi_M$  is large, affording estimated  $J$  values reliable only within 5–10%.<sup>85</sup>

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

If the obtained  $J$  value for compound **1** is compared with those reported for related systems, some considerations may be stated. In Table 3 are gathered the most relevant data for the structural and magnetically characterized  $\mu$ -pyrazolato- $\mu$ -(alkoxo/hydroxo)-dibridged copper(II) dinuclear complexes. The singlet–triplet gap estimated for compound **1** is by far the highest among those reported for related systems. From structural and magnetic data collected in Table 3, any straightforward correlation between the  $J$  coupling constant and several structural parameters cannot be outlined. Perhaps, a rough correlation could be considered between the  $J$  values and the dihedral angle between basal equatorial coordination planes (see Figure 3). Notwithstanding, it must be stressed that significant deviations of the tentatively outlined correlation are observed for some compounds. New Cu(II) compounds with the same bridging ligands are being synthesized to have a representative number of data that allow us to establish a magneto–structural correlation and perform a proper analysis.

**Theoretical Study.** DFT calculations have been performed to understand the magnitude of this interaction. So, the symmetry-adapted HOMO's (highest occupied molecular orbitals) of the bridging ligands mix with the in-phase and out-of-phase combinations of the metal orbitals ( $d_{x^2-y^2} \pm d_{z^2-y^2}$ , in the dinuclear Cu(II) complexes case) to give the corresponding SOMO's (single occupied molecular orbitals)  $\phi^S$  and  $\phi^{AS}$ , where the superscripts AS and S refer to the antisymmetric and symmetric character with respect to the mirror plane perpendicular to the molecular plane.

Each one of the two bridging ligands, in their corresponding dinuclear compounds (IBLS, individual bridging ligand system), can present the same more stable combination in the SOMO's ( $\phi^i$ ), the energy gaps ( $\Delta = E_{AS} - E_S$ ) between the SOMO's taking the same sign. In this case, when both bridging ligands are present in a system, the individual contributions are added and a bigger value for  $\Delta$  is expected. So we say that we are in an orbital complementarity situation (CS). According to Hoffman's approach,<sup>27</sup> the magnetic coupling constant is built by a ferro- and an antiferromagnetic contribution. The last one is considered to be proportional to the square of the energy gap ( $\Delta$ ) between the SOMO's. In this way, a bigger antiferromagnetic interaction will be expected in a CS than in the IBLS's (see Figure 4).

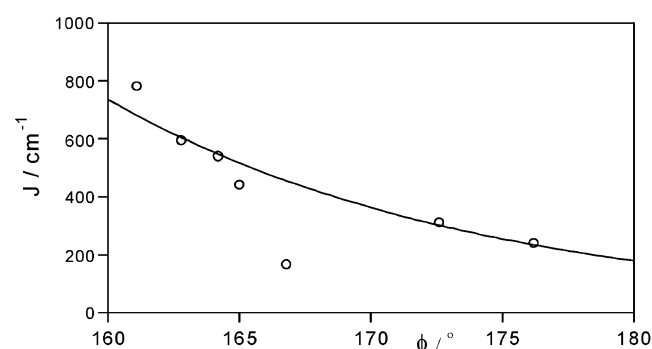
When, in their corresponding IBLS's, two bridging ligands exhibit a  $\Delta$  value of different energetic order and different

(85) O'Connor, C. *Prog. Inorg. Chem.* **1982**, 20, 203.

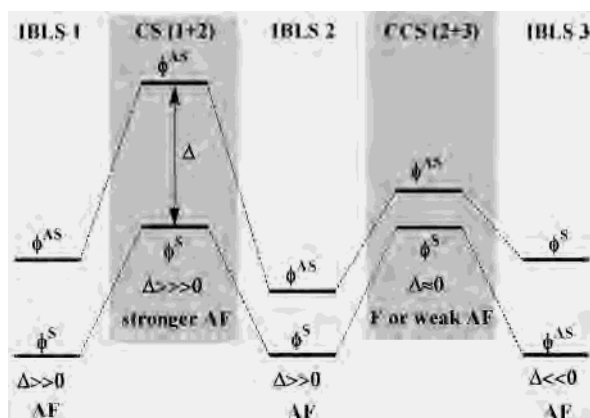
**Table 3.** Relevant Structural and Magnetic Data for μ-Pyrazolato–μ-(Alkoxo/Hydroxo)-Dibridged Copper(II) Complexes

compd <sup>a</sup>	chromophore	Cu–Cu, Å	Cu–O–Cu, deg	Cu–O, <sup>b</sup> Å	φ, <sup>c</sup> deg	–J, cm <sup>–1</sup>	ref
[{Cu(L <sup>1</sup> )Cu}(μ-pz)]·H <sub>2</sub> O	CuN <sub>2</sub> O <sub>2</sub>	3.359	125.1	1.897	176.2	240	47
[{Cu(L)Cu}(μ-pz)]	CuN <sub>2</sub> O <sub>2</sub>	3.360	121.8	1.916	164.2	540	48
[{Cu(L <sup>1</sup> )Cu}(μ-pz)]	CuN <sub>2</sub> O <sub>2</sub>	3.349	121.7	1.894	172.6	310	49
[{Cu(L <sup>2</sup> )Cu}(μ-pz)]	CuN <sub>2</sub> O <sub>2</sub>	3.401	121.3	1.929	162.8	595	49
[{Cu(pmm)Cu}(μ-pz)]	CuN <sub>3</sub> O	3.373	125.1	1.901	165.4	(e)	50
[{Cu(tmihpn)Cu}{μ-(3,5-pz)}](ClO <sub>4</sub> ) <sub>2</sub> ·2CH <sub>3</sub> CN <sup>f</sup>	Cu <sub>4</sub> O	3.320/3.346	116.3/118.9	1.955/1.936	–	260	51
[{Cu(L <sup>3</sup> )Cu}{μ-(3,5-pz)}]	CuN <sub>2</sub> O <sub>2</sub>	3.355	124.7	1.898	166.8	164	52
[{Cu(L <sup>4</sup> )Cu}{μ-(3,5-pz)}]	CuN <sub>2</sub> O <sub>2</sub>	3.365	125.6	1.901	165.0	440	53
[{Cu(L <sup>5</sup> )Cu}{μ-OH}](ClO <sub>4</sub> ) <sub>2</sub> ·2CH <sub>3</sub> CH <sub>2</sub> OH	CuN <sub>2</sub> O <sub>2</sub> O	3.540	d	2.025	d	d	46
[{Cu(L <sup>6</sup> )Cu}{μ-OH}](BF <sub>4</sub> ) <sub>2</sub>	CuN <sub>2</sub> O <sub>2</sub>	3.447	d	1.995	d	d	46
[{Cu(mepirizole)Br} <sub>2</sub> (μ-OH)(μ-pz)]	CuBrN <sub>3</sub> O	3.378	123.9	1.914	161.1	770	this work

<sup>a</sup> pz = pyrazolate; 3,5-pz = 3,5-dimethylpyrazolate; L = 1,3-bis(salicylideneamino)butan-2-ol; L<sup>1</sup> = 1,3-bis(salicylideneamino)propan-2-ol; L<sup>2</sup> = 1,3-bis(salicylideneamino)pentan-2-ol; pmm = *N,N'*-bis{2-pyridylmethyl}malamide; L<sup>3</sup> = 1,3-bis(2-hydroxy-5-chlorosalicylideneamino)propan-2-ol; L<sup>4</sup> = 1,3-bis(2-hydroxy-1-naphthylideneamino)propan-2-ol; L<sup>5</sup> = *N*1-[3-[3-dimethylaminopropyl(methyl)aminomethyl]-1*H*-5-pyrazolylmethyl]-*N*1,*N*3,*N*3-trimethyl-1,3-propanediamine; L<sup>6</sup> = *N*1-[1,3-bis(((3-(dimethylamino)propyl)amino)methyl)-1*H*-pyrazolylmethyl]-*N*1-(3-(dimethylamino)propyl)-*N*3,*N*3-dimethyl-1,3-propanediamine; tmihpn = *N,N,N',N'*-tetrakis(1-methylimidazol-2-yl)-methyl-1,3-diaminopropano-2-ol; mepirizole = 4-methoxy-2-(5-methoxy-3-methyl-1*H*-pyrazol-1-yl)-6-methylpyrimidine. <sup>b</sup> Average Cu–O(bridge) distance. <sup>c</sup> Dihedral angle between basal coordination planes. <sup>d</sup> Unavailable value. <sup>e</sup> μ<sub>eff</sub> (room temperature) = 0.54 μ<sub>B</sub>. <sup>f</sup> The complex crystallizes with two independent dinuclear cations per asymmetric unit.

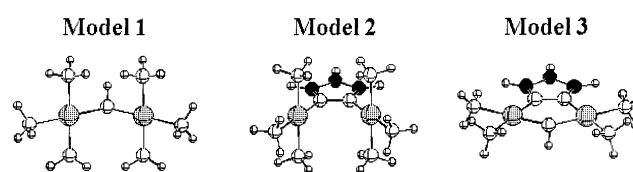


**Figure 3.** Variation of the 2J parameter vs φ parameter (see text) in μ-pyrazolato–μ-(alkoxo/hydroxo)-dibridged copper(II) dimers.



**Figure 4.** Examples of the orbital countercomplementarity (CCS) and complementarity (CS) from the individual bridging ligand system (IBLS). The numbers in parentheses indicate the IBLSs which are involved in the more complex model. Δ is the energy gap between the SOMO's, φ<sup>AS</sup> and φ<sup>S</sup> are the symmetric (in phase) and antisymmetric (out-of-phase) combinations of the metal orbitals in the SOMO's, and F and AF indicate ferro- and antiferromagnetic interactions.

sign, the individual contributions are then opposed and a smaller Δ value is expected in a system where both bridging ligands act in unison. So we say that we are in an orbital countercomplementarity situation (CCS). In accordance with Hoffman's approach,<sup>27</sup> a weak antiferromagnetic contribution can be found, and a global ferromagnetic interaction can be obtained if the energetic full compensation between the IBLS's occurs (see Figure 4).



**Figure 5.** Dinuclear Cu(II) models for DFT calculations.

To understand the strong magnetic interaction found in compound **1**, theoretical calculations based on the density functional theory have been performed to obtain the Δ value from the energy of the SOMO's in the triplet state. At the same time, we have calculated the exchange coupling constant applying the broken-symmetry approach as reported in previous papers<sup>62,73–77</sup> (see Computational Details). The more optimal arrangement of the copper(II) ion equatorial plane is taken to minimize the undesirable interactions in the IBLS's (see Figure 5). The hydroxo and pyrazolate are the only bridging ligand in models 1 and 2, respectively. In model 3 the hydroxo and pyrazolate ligands are both present. The structural parameters in those models have been taken as an average of the experimental structural data.

The Δ value obtained for model 1 is 4282 cm<sup>–1</sup>. The positive sign points out that the symmetric combination of the SOMO's (φ) is more stable in this model. The Δ absolute value is big enough to provide a global interaction of antiferromagnetic nature. So the calculated J value is –215 cm<sup>–1</sup>. A magnetic interaction so strong as this one is due to the large value of the CuOCu angle (α, 123.9°). It is well-known that the magnitude and nature of the interaction in bis(hydroxo) dinuclear copper(II) complexes depends on the α angle.<sup>9,13,62,86</sup> So the ferromagnetic and antiferromagnetic interactions are found for α values lower and greater than 97.5°, respectively.<sup>86</sup> Furthermore, the antiferromagnetic interaction is greater as the α value increases. Such a high α value as the one shown in compound **1** is only present in some systems where one of the two bridging ligands is a hydroxo and the other a different bridging ligand.<sup>87–89</sup>

(86) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.

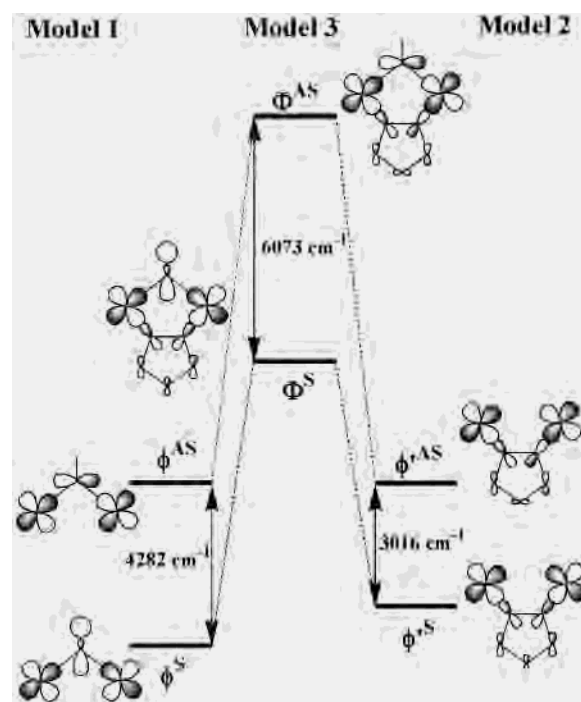
(87) Meenakumari, S.; Tiwari, S. K.; Chakravarty, A. R. *J. Chem. Soc., Dalton Trans.* **1993**, 2175.

An antiferromagnetic interaction is found for model 2 ( $J = -71 \text{ cm}^{-1}$ ) because of an important energy gap between the SOMO's ( $\Delta = 3016 \text{ cm}^{-1}$ ). The calculated exchange constant takes a value close to the ones found in systems with similar bridging ligands, such as the pyridazine ligand.<sup>23</sup> The magnitude of the interaction is reasonable for a short exchange pathway that involves only four atoms (NCCN). Differences in the  $J$  constant values between systems with a pyrazolate or a pyridazine bridging ligand are due to the symmetry and energy of the HOMO's of these ligands.

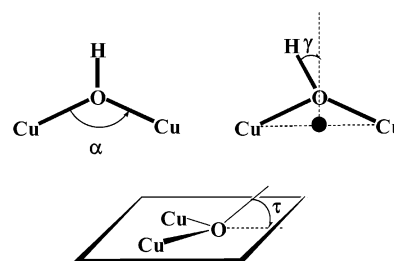
The  $\Delta$  values for models 1 and 2 take the same sign. Therefore, the compound **1** is an orbital complementary case. This is shown in the bigger  $\Delta$  value ( $6073 \text{ cm}^{-1}$ ) obtained for model 3 (see Figure 6). In consequence, two strong magnetic interactions are added to provide a stronger one. So the calculated  $J$  value is  $-440 \text{ cm}^{-1}$ . Thus, we can conclude the following: Strong antiferromagnetic interactions are carried out by the pyrazolate and hydroxo ligands. The strong interaction through the hydroxo ligand is due to an huge  $\alpha$  angle value tuned by the other bridging ligand and the peripheral ligands. Finally, the additive character of the interaction is due to the orbital complementarity phenomena.

The value of the  $J$  coupling constant has been calculated in the full homodinuclear molecule corresponding to the compound **1**. This value ( $J = -344 \text{ cm}^{-1}$ ) is in agreement with the previous ones obtained for the simple models. It is well-known that the  $J$  constant value depends on the relative position of the hydrogen atom of the hydroxo group.<sup>13,62</sup> Also, this relative position, defined by the  $\tau$  torsion angle, which describes the direction of the OH bond out of the molecular CuOCu plane, depends on the  $\alpha$  angle. This dependence has

- (88) Burger, K. S.; Chaudhuri, P.; Weighardt, K. *J. Chem. Soc., Dalton Trans.* **1996**, 247.
- (89) Boxwell, C. J.; Bhalla, R.; Cronin, L.; Turner, S. S.; Walton, P. H. *J. Chem. Soc., Dalton Trans.* **1998**, 2449.
- (90) Thompson, L. K.; Hartstock, F. W.; Robichaud, P.; Hanson, A. W. *Can. J. Chem.* **1984**, 62, 2754 and references therein.
- (91) Chen, L.; Thompson, L. K.; Bridson, J. N. *Inorg. Chim. Acta* **1993**, 214, 67.
- (92) Thompson, L. K.; Mandal, S. K.; Rosenberg, L.; Lee, F. L.; Gabe, E. *J. Inorg. Chim. Acta* **1987**, 133, 81.
- (93) Chen, L.; Thompson, L. K.; Bridson, J. N. *Inorg. Chim. Acta* **1996**, 244, 87.
- (94) Chen, L.; Thompson, L. K.; Bridson, J. N. *Inorg. Chem.* **1993**, 32, 2938.
- (95) Zhang, Y.; Thompson, L. K.; Bubenik, M.; Bridson, J. N. *J. Chem. Soc., Chem. Commun.* **1993**, 1375.
- (96) Hulsbergen, F. B.; ten Hoedt, R. W. M.; Verschoor, G. C.; Reedijk, J.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1983**, 539.
- (97) Ardizzoia, G. A.; Angaroni, M. A.; La Monica, G.; Cariati, F.; Moret, M.; Masciocchi, N. *J. Chem. Soc., Chem Commun.* **1990**, 1021.
- (98) Tandon, S. S.; Mandal, S. K.; Thompson, L. K.; Hynes, R. C. *Inorg. Chem.* **1992**, 31, 2215.
- (99) Thompson, L. K.; Mandal, S. K.; Gabe, E. J.; Lee, F. L.; Addison, A. W. *Inorg. Chem.* **1987**, 26, 657.
- (100) Thompson, L. K.; Woon, T. C.; Murphy, D. B.; Gabe, E. J.; Lee, F.; Le Page, Y. *Inorg. Chem.* **1985**, 24, 4719.
- (101) Thompson, L. K.; Tandon, S. S.; Manuel, M. E. *Inorg. Chem.* **1995**, 34, 2356.
- (102) Lee, G. H.; Tsai, H. L. *Inorg. Chem. Commun.* **1999**, 2, 392.
- (103) Chow, M. Y.; Zhou, Z. Y.; Mak, T. C. W. *Inorg. Chem.* **1992**, 31, 4900.
- (104) Tamura, H.; Ogawa, K.; Mori, W.; Kishita, M. *Inorg. Chim. Acta* **1981**, 54, L87.
- (105) Christou, G.; Perlepes, S. P.; Folting, K.; Huffman, J.; Webb R. J.; Hendrickson, D. N. *J. Chem. Soc., Chem Commun.* **1990**, 746.
- (106) Tokii, T.; Nagamatsu, M.; Hamada, H.; Nakashima, M. *Chem. Lett.* **1992**, 1091.



**Figure 6.** MO diagrams for a model dinuclear copper(II) unit with a  $\mu$ -hydroxo (model 1), a  $\mu$ -pyrazolate (model 2), and both bridging ligands (model 3).



**Figure 7.** Structural parameters in the  $\mu$ -hydroxo dinuclear copper(II) complexes.

been well studied by one of us in the bis(hydroxo) dinuclear copper(II) complexes.<sup>13,62</sup> Although this dependence exists, in some cases, the formation of inter- or intramolecular hydrogen bonds can control the position of this hydrogen atom.<sup>26</sup> In compound **1**, because of the asymmetry in the CuOCu unity, there is a deviation of the hydrogen atom (OH) (angle  $\gamma$ ; see Figure 7) out of the plane perpendicular to the CuOCu plane that contains the O atom (OH) and the intermediate point between the two copper(II) ions. To estimate the influence of the hydrogen position on the magnetic coupling constant, we have calculated the exchange coupling constant of the full molecule (compound **1**) for the experimental  $\tau$  angle and  $\gamma = 0^\circ$  ( $J = -488 \text{ cm}^{-1}$ ),  $\tau = 0^\circ$ , and  $\gamma = 0^\circ$  ( $J = -559 \text{ cm}^{-1}$ ) and  $\tau = 90^\circ$  and  $\gamma = 0^\circ$  ( $J = -431 \text{ cm}^{-1}$ ). These results are in good agreement with the ones obtained by Ruiz et al.<sup>13,62</sup> for the bis(hydroxo) dinuclear copper(II) complexes. The control of the hydrogen atom position by hydrogen bonds is very difficult but can help us to increase meaningfully the magnetic interaction.

In Table 4 we show a quite representative number of examples of polynuclear copper(II) complexes with two different bridging ligands, whose crystal structures are

**Table 4.** Cases of Compounds Presenting Two Different Bridging Ligands: Analysis of the Complementarity and Countercomplementarity Phenomena

compd <sup>a</sup>	CuXCu, <sup>b</sup> deg	J, cm <sup>-1</sup>	ref
Complementarity Case			
μ-Pyridazine + μ-Hydroxo			
[Cu <sub>2</sub> (PAP)(μ <sub>2</sub> -OH)Cl <sub>3</sub> ]·1.5H <sub>2</sub> O	101.0	-201	90
[Cu <sub>2</sub> (PAP)(μ <sub>2</sub> -OH)Br <sub>3</sub> ]·1.5H <sub>2</sub> O	102.1	-191	90
[Cu <sub>2</sub> (PTP)(μ <sub>2</sub> -OH)Cl <sub>3</sub> ]·1.2CHCl <sub>3</sub>	104.0	-390	91
[Cu <sub>2</sub> (EtBITP)(μ <sub>2</sub> -OH)(μ <sub>2</sub> -Cl)Cl <sub>2</sub> ]·dmf	104.7	-260	92
[Cu <sub>2</sub> (PTP)(μ <sub>2</sub> -OH)(μ <sub>2</sub> -Cl)Cl <sub>2</sub> ]·2CH <sub>3</sub> CN	106.2	-296	93
[Cu <sub>2</sub> (PTPH)(μ <sub>2</sub> -OH)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]NO <sub>3</sub>	109.0	-308	94
[Cu <sub>2</sub> (PTPH)(μ <sub>2</sub> -OH)(NO <sub>3</sub> ) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ]	112.0	-313	94
[Cu <sub>4</sub> (OPAP)(μ <sub>2</sub> -OH) <sub>2</sub> (μ <sub>2</sub> -NO <sub>3</sub> ) <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	112.8	-535	95
[Cu <sub>2</sub> (PAP)(μ <sub>2</sub> -OH)(IO <sub>3</sub> ) <sub>3</sub> ]·4H <sub>2</sub> O	113.8	-290	90
<i>catena</i> -{[Cu <sub>3</sub> (μ <sub>2</sub> -NO <sub>3</sub> )(μ <sub>2</sub> -OH)(μ <sub>2</sub> -pyzt) <sub>3</sub> (pyz) <sub>2</sub> ]·1H <sub>2</sub> O}	114.0	-600	96
<i>cyclo</i> -[Cu(μ <sub>2</sub> -OH)(μ-Me <sub>2</sub> pyzt)(dnbz)] <sub>8</sub>	114.7	strong AF	97
[Cu <sub>2</sub> (PAP4Me)(μ <sub>2</sub> -OH)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ]NO <sub>3</sub>	115.3	-497	90
[Cu <sub>2</sub> (PAP)(μ <sub>2</sub> -OH)Cl(SO <sub>4</sub> ) <sub>2</sub> ]·2H <sub>2</sub> O	115.5	-532	90
[Cu <sub>2</sub> (TNL)(μ <sub>2</sub> -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>6</sub> (EtOH) <sub>2</sub> ](CF <sub>3</sub> SO <sub>3</sub> ) <sub>6</sub>	116.0	-436	98
[Cu <sub>2</sub> (TNL4)(μ <sub>2</sub> -OH) <sub>2</sub> (H <sub>2</sub> O) <sub>8</sub> ](CF <sub>3</sub> SO <sub>3</sub> ) <sub>6</sub>	116.3	-336	98
[Cu <sub>2</sub> (PPD)(μ <sub>2</sub> -OH)Cl <sub>3</sub> (H <sub>2</sub> O)]·0.8H <sub>2</sub> O	117.8	-898	99
[Cu <sub>2</sub> (PPDMe <sub>2</sub> )(μ <sub>2</sub> -OH)(NO <sub>3</sub> ) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub> ](NO <sub>3</sub> )·H <sub>2</sub> O	119.3	-750	100
[Cu <sub>2</sub> (PPDMe <sub>2</sub> )(μ <sub>2</sub> -OH)Cl <sub>2</sub> ][CuCl <sub>3</sub> <sup>-</sup> (H <sub>2</sub> O)]·H <sub>2</sub> O	126.0	strong AF	100
[Cu <sub>2</sub> (MIP)(μ <sub>2</sub> -OH)Cl <sub>3</sub> (H <sub>2</sub> O)]·H <sub>2</sub> O	126.2	-800	90
μ-Pyridazine + μ-Azido			
[Cu <sub>2</sub> (PAP)(μ <sub>2</sub> -N <sub>3</sub> )Br <sub>3</sub> ]·CH <sub>2</sub> Cl <sub>2</sub>	108.7	-241	101
[Cu <sub>2</sub> (PAP6Me)(μ <sub>2</sub> -N <sub>3</sub> )(μ <sub>2</sub> -Br)Br <sub>2</sub> ]·1.68H <sub>2</sub> O	110.9	-234	101
[Cu <sub>2</sub> (PAN)(μ <sub>2</sub> -N <sub>3</sub> )(μ <sub>2</sub> -NO <sub>3</sub> )NO <sub>3</sub> ]·CH <sub>3</sub> OH·CH <sub>3</sub> CN·4.5H <sub>2</sub> O	111.1	-220	101
[Cu <sub>2</sub> (PAP6Me)(μ <sub>2</sub> -N <sub>3</sub> )(μ <sub>2</sub> -H <sub>2</sub> O)(NO <sub>3</sub> ) <sub>2</sub> ](NO <sub>3</sub> )	111.7	-187	101
[Cu <sub>2</sub> (PPDMe <sub>2</sub> )(μ <sub>2</sub> -N <sub>3</sub> )Br <sub>3</sub> (CH <sub>3</sub> OH)]	122.5	-921	101
μ-1,2-Imidazole + μ-Azido			
[Cu <sub>2</sub> (BLEP)(μ <sub>2</sub> -N <sub>3</sub> )(N <sub>3</sub> ) <sub>2</sub> ]·C <sub>3</sub> H <sub>7</sub> OH	116.8	strong AF	102
Countercomplementarity Case			
μ-Carboxylate + μ-Azido			
<i>catena</i> -[Cu <sub>2</sub> (μ-Me <sub>3</sub> NCO <sub>2</sub> ) <sub>2</sub> (μ <sub>2</sub> -N <sub>3</sub> ) <sub>2</sub> (μ-NO <sub>3</sub> ) <sub>2</sub> ] <sub>n</sub>	119.2	no report	103
μ-Carbonate + μ-1,2-Imidazole			
[Cu <sub>2</sub> (DMAP)(μ-CO <sub>3</sub> Me)(MeOH) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>		no report	46
μ-Carboxylate + μ-Hydroxo			
[Cu(μ <sub>2</sub> -HCO <sub>2</sub> )(μ <sub>2</sub> -OH)]	100.0	ferro	104
[Cu <sub>2</sub> (μ <sub>2</sub> -OH)(μ <sub>2</sub> -MeCO <sub>2</sub> )(H <sub>2</sub> O)(phen) <sub>2</sub> ](NO <sub>3</sub> ) <sub>2</sub>	103.4	+111.0	87
[Cu <sub>2</sub> (μ <sub>2</sub> -OH)(μ <sub>2</sub> -MeCO <sub>2</sub> )(H <sub>2</sub> O)(bipy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	103.8	+38.6	87
[Cu <sub>2</sub> (μ <sub>2</sub> -OH)(μ <sub>2</sub> -MeCO <sub>2</sub> )(MeOH)L <sup>6</sup> ](ClO <sub>4</sub> ) <sub>2</sub> ·1.5thf	109.3	+2.6	87
[Cu <sub>2</sub> (μ <sub>2</sub> -OH)(μ <sub>2</sub> -MeCO <sub>2</sub> )(H <sub>2</sub> O)(bipy) <sub>2</sub> ](ClO <sub>4</sub> ) <sub>2</sub>	109.8	+3.6	105
[Cu <sub>2</sub> (μ <sub>2</sub> -OH)(μ <sub>2</sub> -MeCO <sub>2</sub> ) <sub>2</sub> (bipy) <sub>2</sub> ](BF <sub>4</sub> ) <sub>2</sub>	110.7	+99	106
[Cu <sub>3</sub> (MPTS) <sub>2</sub> (μ <sub>2</sub> -OH) <sub>2</sub> (μ <sub>2</sub> -MeCO <sub>2</sub> ) <sub>2</sub> (dmf) <sub>2</sub> ]	115.0	+93	25
[Cu <sub>3</sub> (PNS) <sub>2</sub> (μ <sub>2</sub> -OH) <sub>2</sub> (μ <sub>2</sub> -MeCO <sub>2</sub> ) <sub>2</sub> ] <sub>n</sub>	112.3	+56	26
[Cu <sub>3</sub> (PBS) <sub>2</sub> (μ <sub>2</sub> -OH) <sub>2</sub> (μ <sub>2</sub> -MeCO <sub>2</sub> ) <sub>2</sub> (dmf) <sub>2</sub> ]	113.3	+94	26
[Cu <sub>2</sub> (μ <sub>2</sub> -OH)(μ <sub>2</sub> -MeCO <sub>2</sub> )(H <sub>2</sub> O)(dmen) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub> <sup>-</sup>	120.0	-20.2	87
[Cu <sub>2</sub> (μ <sub>2</sub> -OH)(μ <sub>2</sub> -MeCO <sub>2</sub> )(H <sub>2</sub> O)(dmen) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub> ·2NaClO <sub>4</sub>			
[Cu <sub>2</sub> (μ <sub>2</sub> -OH)(μ <sub>2</sub> -MeCO <sub>2</sub> )(H <sub>2</sub> O)(tmen) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub>	120.1	-55.6	87
[Cu <sub>2</sub> (μ <sub>2</sub> -OH)(μ <sub>2</sub> -C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> )L <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub>	124	-132	88

<sup>a</sup> AF and F = antiferromagnetic and ferromagnetic exchange coupling. Ligand abbreviations: PAP = 1,4-bis(2'-pyridyl)aminophthalazine; PTP = 1,4-bis(2'-pyridylthio)phthalazine; EtBITP = 3,6-bis(2-benzeimidazolthio)pyridazine; dmf = dimethylformamide; OPAP = (6,6'-1,2-phenylenedioxy)bis(2'-pyridylamino)phthalazine; pyzt = 1,2-pyrazolate; pyz = 1,2-pyrazole; Me<sub>2</sub>pyzt = 3,5-dimethylpyrazolate; dnbs = dinitrobenzene; PAP4Me = 1,4-bis(4'-methyl-2'-pyridyl)aminophthalazine; TNL = 1,4,6,9-tetrakis((2-pyridyl)amino)benzopyridazine; TNL4 = 1,4,6,9-tetrakis((4-methyl-2-pyridyl)amino)benzopyridazine; PPD = 3,6-bis(1-pyrazolyl)pyridazine; PPDMe<sub>2</sub> = 3,6-bis(3,5-dimethyl-1-pyrazolyl)pyridazine; MIP = 1,4-bis(1'-methyl-2'-imidazolyl)phthalazine; PAP6Me = 1,4-bis(6'-methyl-2'-pyridyl)aminophthalazine; PAN = 1,4-bis(2'-pyridylamino)naphthalazine; BLEP = 3,5-bis(1'-(4'-(2''-pyridyl)-2'-thiabutyl)pyrazolyl); DMAP = 3,5-bis((dimethylamino)ethyl(methyl)aminomethyl)pyrazolyl; thf = tetrahydrofuran; PNS = (pyrid-2-ylmethyl)naphthalenesulfonylamide; PBS = (pyrid-2-ylmethyl)benzenesulfonylamide; MPTS = (2-methylpyridyl)toluenesulfonylamide; phen = 1,10-phenanthroline; bipy = 2,2'-bipyridine; L<sup>6</sup> = a hexaimidazole dinucleating ligand; dmen = dimethylethylenediamine; tmen = tetramethylethylenediamine; L<sub>2</sub> = 1,4,7-trimethyl-1,4,7-triazacyclononane.

<sup>b</sup> X = O or N.

reported, that support our conclusions in the text and illustrate the complementarity and countercomplementarity phenomena. No compound with solved crystal structure has been found for the rest of the proposed couples of bridges, such as the case of the μ-carboxylate + μ-pyridazine bridging ligands. In some cases, as the only μ-carboxylate + μ-azido compound found, the magnetic behavior is not reported. Strong antiferromagnetic interactions are found in the complementarity case, higher generally for higher CuXCu

angles. On the contrary, in the countercomplementarity case, ferro- or weak antiferromagnetic interactions are found. In any case, these antiferromagnetic interactions are weaker than those present for similar CuXCu angles in the complementarity case. From the results in this work and other works from one of us,<sup>23-26</sup> we can conclude that, in a system with two metallic ions bridged by two different bridging ligands, we can expect the orbital complementarity phenomena (strong antiferromagnetic interactions) when there is a couple



between two of the following bridging ligands: azide; hydroxo; pyrazolate; pyridazine. On the other hand, we can expect the orbital countercomplementarity phenomena (possible ferromagnetic interaction) when one of the bridging ligands is a carboxylate and the other is an azide, a hydroxo, a pyrazolate, or a pyridazine ligand. Thus, for instance,  $[\text{Cu}_2(\mu_2\text{-OH})(\mu_2\text{-C}_6\text{H}_5\text{CO}_2)\text{L}_2][\text{ClO}_4]_2$ , with a CuXCu angle of  $124^\circ$ , presents a much weaker interaction ( $J = -132 \text{ cm}^{-1}$ ) than  $[\text{Cu}_2(\text{MIP})(\mu_2\text{-OH})\text{Cl}_3(\text{H}_2\text{O})]\cdot\text{H}_2\text{O}$  ( $J = -800 \text{ cm}^{-1}$ ),  $[\text{Cu}_2(\text{PPDMe}_2)(\mu_2\text{-OH})(\text{NO}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)\cdot\text{H}_2\text{O}$  ( $J =$

$-750 \text{ cm}^{-1}$ ), or other  $\mu$ -pyridazine +  $\mu$ -hydroxo compounds with similar angles.

**Acknowledgment.** We are grateful to the DGICYT (Grant PB98-1453) for financial support. We thank Dr. C. Gómez for his assistance with susceptibility measurements.

**Supporting Information Available:** Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

IC034126J