

Contribution from the Istituto di Chimica e Tecnologia dei Radioelementi, CNR, Padova, Italy, Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, Firenze, Italy, and Dipartimento di Chimica, Università di Firenze, Firenze, Italy

## Anisotropic Exchange in Dinuclear Complexes with Polyatomic Bridges. 2.<sup>1</sup> Crystal and Molecular Structure and EPR Spectra of Tetraphenylphosphonium Bis( $\mu$ -pyrazolato)bis[dihydrobis(1-pyrazolyl)borato]( $\mu$ -chloro)dicuprate(II). Magneto-Structural Correlations in Bis( $\mu$ -pyrazolato)-Bridged Copper(II) Complexes

David Ajò, Alessandro Bencini,\* and Fabrizio Mani

Received November 4, 1987

The X-ray crystal structure of  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4)\cdot 0.5(\text{CH}_3)_2\text{CO}$  ( $\text{H}_2\text{B}(\text{pz})_2$  = dihydrobis(1-pyrazolyl)borate; pz = pyrazolate) was determined at room temperature. The crystals are monoclinic, space group  $C2/c$ , with  $a = 17.598$  (7) Å,  $b = 19.681$  (9) Å,  $c = 15.324$  (6) Å,  $\beta = 117.1$  (2)°, and  $Z = 4$ . The least-squares refinement of the structure leads to a conventional  $R$  factor of 0.078. The temperature dependence of the magnetic susceptibility showed that the copper atoms of the dinuclear complex are antiferromagnetically coupled with a singlet-triplet separation of  $\approx 240$  cm<sup>-1</sup>. Single-crystal EPR spectra were recorded at X-band (9 GHz) frequency at room temperature. The measured zero-field splitting tensor was found to be misaligned from the  $g$  tensor, showing that exchange contributions to the anisotropic spin-spin interaction are operative. The singlet-triplet energy gap in bis( $\mu$ -pyrazolato)-bridged copper(II) dimers has been correlated to geometrical distortions by using the orbital model of the isotropic exchange interaction.

### Introduction

Copper(II) is one of the most commonly investigated transition-metal ions. This is due not only to the fact that copper(II) binds a large variety of ligands and gives rise to a large numbers of geometries and stoichiometries but also to the fact that copper coordination compounds are known to act as catalysts in the oxidation of organic molecules.<sup>2-5</sup> In particular, dinuclear copper(II) species are present in a number of naturally occurring enzymes<sup>6-8</sup> and have been also found to be the catalytic active species in a number of reactions.<sup>4-6,9</sup>

Polynuclear copper(II) complexes are still the best systems one has to establish magneto-structural correlations and to test the existing models for describing the nature and intensity of the exchange interactions between paramagnetic centers.<sup>10</sup> The understanding of these interactions in dinuclear and/or oligonuclear species forms the necessary background to design the synthesis of more complex systems with unusual magnetic properties. In particular, anisotropic exchange has been widely studied in the last few years since it allows one to estimate exchange interactions between ground states and excited states.<sup>11</sup> These interactions in copper(II) couples determine, together with direct magnetic interactions, the zero-field splitting of the triplet state arising from the isotropic exchange interaction and can in principle give measurable effects on the EPR spectra.<sup>12</sup>

Among dinuclear copper(II) complexes those containing pyrazolate ions as bridging ligands are still rare, and no crystal structure of a discrete dinuclear compound is available up to now. A few dinuclear complexes have been structurally characterized having triazolate ions as bridging ligands.<sup>13,14</sup> The direct synthesis of copper(II) complexes with pyrazolate anion most often leads to finely divided powders. Crystalline materials have been sometimes obtained by oxidation of parent copper(I) complexes to give tri and tetranuclear complexes.<sup>15,16</sup>

We have recently been able to prepare crystalline materials of composition  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{X})](\text{YPh}_4)\cdot n(\text{CH}_3)_2\text{CO}$  ( $\text{H}_2\text{B}(\text{pz})_2$  = dihydrobis(1-pyrazolyl)borate; pz = pyrazolate; X = Cl, Y = P,  $n = 0.5$ ; X = Br, Y = As,  $n = 1$ ). Since these compounds showed rather strong antiferromagnetic interactions ( $J \approx 240$  cm<sup>-1</sup>) and triplet EPR spectra indicative of sizable exchange contributions to the zero-field splitting, we decided to fully investigate the structure and magnetic properties of these complexes.

We wish to report here the crystal and molecular structure and the single-crystal EPR spectra of  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})]$ -

$(\text{PPh}_4)\cdot 0.5(\text{CH}_3)_2\text{CO}$  with the aim of investigating the nature of the exchange interactions involving ground and excited orbitals in bis(pyrazolato)-bridged copper(II) complexes. We wish to report also the temperature dependence of the magnetic susceptibilities of the complexes in order to establish a correlation between the singlet-triplet splitting ( $J$ ) and the bonding geometry of the bridging pyrazolate ions.

### Experimental Section

**Materials.** All solvents and reagents were reagent grade. The ligand  $\text{KH}_2\text{B}(\text{pz})_2$  was prepared by the literature method.<sup>17</sup> Ethanolic solutions of  $\text{Et}_4\text{N}(\text{H}_2\text{B}(\text{pz})_2)$  were prepared immediately before their use by metathetical reaction of  $\text{Et}_4\text{NCl}$  and  $\text{KH}_2\text{B}(\text{pz})_2$ .

**Synthesis of the Complexes.** The complex  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4)\cdot 0.5(\text{CH}_3)_2\text{CO}$  was prepared at room temperature by mixing solutions of hydrated  $\text{CuCl}_2$  ( $10^{-3}$  mol in 20 cm<sup>3</sup> ethanol),  $\text{Et}_4\text{N}(\text{H}_2\text{B}(\text{pz})_2)$  ( $2 \times 10^{-3}$  mol in 20 cm<sup>3</sup> of a mixture of 1:1 ethanol-acetone) and  $\text{Ph}_4\text{PCl}$  ( $10^{-3}$  mol in a mixture of 1:1 ethanol-acetone). A crystalline product separated after the resulting solution was allowed to stand ov-

- (1) Part I: Bencini, A.; Fabretti, C. A.; Zanchini, C.; Zannini, P. *Inorg. Chem.* **1987**, *26*, 1445.
- (2) Taki Kahn, M. M.; Martell, A. E. *J. Am. Chem. Soc.* **1967**, *89*, 4176.
- (3) Ochiai, E. *Bioinorganic Chemistry*; Allyn and Bacon: Boston, MA, 1977.
- (4) Schouten, J.; Challa, G.; Reedijk, J. *J. Mol. Catal.* **1980**, *9*, 41.
- (5) Rogic, M. M.; Demmin, T. R. *J. Am. Chem. Soc.* **1978**, *100*, 5472.
- (6) Peisach, J.; Aisen, P.; Blumberg, W. E. *The Biochemistry of Copper*; Academic: New York, 1966.
- (7) Solomon, E. I. In *Copper Proteins*; Spiro, T. G., Ed.; Wiley-Interscience: New York, 1981; p 2.
- (8) Solomon, E. I.; Wilcox, D. E. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands; 1985, 463.
- (9) Endres, G. F.; Hay, A. S.; Eustace, J. W. *J. Org. Chem.* **1963**, *28*, 1300.
- (10) *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands, 1985.
- (11) Gatteschi, D.; Bencini, A. In *Magneto-Structural Correlations in Exchange Coupled Systems*; Willett, R. D., Gatteschi, D., Kahn, O., Eds.; Reidel: Dordrecht, The Netherlands; 1985, p 241.
- (12) Owen, J.; Harris, E. A. In *Electron Paramagnetic Resonance*; Geschwind, S., Ed.; Plenum: New York, 1972; p 427.
- (13) Prins, R.; Birker, P. J. M. W. L.; Haasnoot, J. G.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.*, **1985**, *24*, 4128.
- (14) Hendriks, H. M. J.; Birker, P. J. M. W. L.; Verschoor, G. C.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1982**, 623.
- (15) ten Hoedt, R. W. M.; Hulsbergen, F. B.; Verschoor, G. C.; Reedijk, J. *Inorg. Chem.* **1982**, *21*, 2369.
- (16) Hulsbergen, F. B.; ten Hoedt, R. W. M.; Verschoor, G. C.; Reedijk, J.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1983**, 539.
- (17) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.

\* To whom correspondence should be addressed at the Università di Firenze.

**Table I.** Summary of Crystal Data, Intensity Collection, and Structure Refinement

formula	C <sub>42</sub> H <sub>42</sub> N <sub>12</sub> B <sub>2</sub> ClPCu <sub>2</sub> C <sub>1.5</sub> H <sub>3</sub> O <sub>5</sub>
fw	959.08
space group	C2/c
a, Å	17.598 (7)
b, Å	19.681 (9)
c, Å	15.324 (6)
β, deg	117.1 (2)
V, Å <sup>3</sup>	4723.5
Z	4
D <sub>calcd</sub> , g cm <sup>-3</sup>	1.35
cryst size, mm	0.95 × 0.1 × 1.30
μ(Mo Kα), cm <sup>-1</sup>	9.84
transmission factors	0.94–0.88
scan type	ω-2θ
scan width (Δ(2θ)), deg	0.9 + 0.3 tan θ
scan speed, deg min <sup>-1</sup>	5.4
2θ limits, deg	5–50
data collcn range	±h,k,l (h + k = 2n)
no. of data	3296
no. of data with F <sub>o</sub> <sup>2</sup> > 3σ(F <sub>o</sub> <sup>2</sup> )	1852
no. of variables	147
R	0.078
R <sub>w</sub>	0.075

ernight at room temperature. The compound was filtered off and washed twice with CH<sub>2</sub>Cl<sub>2</sub> in order to remove traces of the monomeric neutral bis chelate [Cu(H<sub>2</sub>B(pz)<sub>2</sub>)<sub>2</sub>] complex, which may contaminate the dinuclear compound. Crystals of adequate purity suitable for X-ray analysis and EPR spectroscopy were thus obtained.

The analogous complex [Cu<sub>2</sub>(H<sub>2</sub>B(pz)<sub>2</sub>)<sub>2</sub>(pz)<sub>2</sub>(Br)](AsPh<sub>4</sub>)(CH<sub>3</sub>)<sub>2</sub>CO was obtained with a procedure similar to that above, with hydrated copper bromide and tetraphenyl arsonium bromide used as starting reagents.

Anal. Calcd for C<sub>43.5</sub>H<sub>45</sub>N<sub>12</sub>B<sub>2</sub>ClPO<sub>0.5</sub>Cu<sub>2</sub>: C, 54.5; H, 4.93; N, 17.5; P, 3.23; Cu, 13.3. Found: C, 54.9; H, 5.03; N, 17.4; P, 3.15; Cu, 13.0. Calcd for C<sub>44</sub>H<sub>46</sub>N<sub>12</sub>AsB<sub>2</sub>BrOCu<sub>2</sub>: C, 50.2; H, 4.49; N, 15.6; Cu, 11.8. Found: C, 50.2; H, 4.45; N, 15.9; Cu, 11.9.

ν<sub>max</sub>(BH<sub>2</sub>) (2410 s, 2390 s, 2340 sh, 2280 s, cm<sup>-1</sup>) and ν(CO) values (1730) s cm<sup>-1</sup>) are identical in the two complexes.

The complexes are insoluble in the common organic solvents and in water. They are decomposed by prolonged boiling in DMF or CH<sub>3</sub>CN.

**X-ray Structural Determination.** Single-crystal diffraction data for [Cu<sub>2</sub>(H<sub>2</sub>B(pz)<sub>2</sub>)<sub>2</sub>(pz)<sub>2</sub>(Cl)](PPh<sub>4</sub>)·0.5(CH<sub>3</sub>)<sub>2</sub>CO were collected at room temperature on a Philips PW1100 automated diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.701 70 Å). Details on crystal data, intensity collection, and refinement are reported in Table I. Lattice constants were obtained by a least-squares fit of 21 reflections in the range 10° ≤ 2θ ≤ 20°. Stationary-background counts were taken at each end of the scan for a time equal to half the scan time. The intensities of three standard reflections measured every 90 min did not show any systematic variation. All the crystals examined showed, however, a net decrease of the intensities of the reflections measured at 2θ ≥ ≈40° independently of the crystal dimensions. The R factor for merging equivalent measurements was R = 0.03. Data were processed with use of a σ value of 0.03 in the calculation of σ(I)'s.<sup>18</sup> Corrections for the Lorentz and polarization effects<sup>19a</sup> as well as for absorption<sup>19b</sup> were applied. Direct methods and Fourier techniques were used to solve the structure in the centrosymmetric C2/c space group. The computed programs used in the crystallographic calculations are listed in ref 19.

A total of 1852 reflections having F<sub>o</sub> > 6σ(F<sub>o</sub>) were retained during the refinement. The function minimized was Σw[|F<sub>o</sub>| - |F<sub>c</sub>|]<sup>2</sup> with weights w = 1/(σ<sup>2</sup>(F<sub>o</sub>)). The scattering factors for the neutral atoms were taken from ref 20, and anomalous dispersion terms for the metal atoms were included in F<sub>c</sub>.<sup>21</sup> Cu, P, and Cl atoms were assigned anisotropic temperature factors, whereas all the other atoms were refined isotropically. Hydrogen atoms were introduced in calculated positions

**Table II.** Positional Parameters for Non-Hydrogen Atoms of [Cu<sub>2</sub>(H<sub>2</sub>B(pz)<sub>2</sub>)<sub>2</sub>(pz)<sub>2</sub>Cl]PPh<sub>4</sub>·0.5(CH<sub>3</sub>)<sub>2</sub>CO<sup>a</sup>

atom	x	y	z
Cu	905 (1)	1499 (1)	2369 (1)
P	5000	2755 (2)	2500
Cl	0	519 (2)	2500
N(1)	1093 (5)	1141 (4)	1244 (6)
N(2)	1861 (6)	1030 (5)	1289 (7)
N(3)	2036 (6)	1134 (4)	3334 (7)
N(4)	2707 (6)	993 (5)	3129 (7)
N(5)	-117 (6)	2016 (5)	1441 (7)
N(6)	-846 (5)	2016 (4)	1542 (6)
C(1)	502 (7)	854 (6)	439 (8)
C(2)	937 (8)	540 (6)	-34 (9)
C(3)	1741 (8)	655 (6)	490 (9)
C(4)	3291 (8)	615 (6)	3834 (9)
C(5)	3013 (8)	502 (6)	4530 (10)
C(6)	2236 (7)	821 (6)	4200 (9)
C(7)	-224 (7)	2466 (6)	733 (8)
C(8)	-1015 (8)	2756 (7)	388 (9)
C(9)	-1394 (7)	2455 (6)	928 (8)
B	2678 (10)	1297 (8)	2144 (11)
C(11)	4461 (7)	2232 (6)	1418 (8)
C(12)	4775 (7)	1602 (6)	1351 (9)
C(13)	4352 (8)	1213 (7)	507 (10)
C(14)	3636 (7)	1487 (7)	-265 (9)
C(15)	3347 (8)	2119 (7)	-238 (10)
C(16)	3768 (7)	2501 (6)	635 (9)
C(21)	4256 (7)	3272 (5)	2664 (8)
C(22)	3877 (7)	3010 (6)	3252 (9)
C(23)	3300 (8)	3426 (7)	3406 (10)
C(24)	3096 (8)	4062 (7)	3019 (9)
C(25)	3452 (8)	4311 (7)	2445 (9)
C(26)	4023 (8)	3915 (6)	2283 (9)
C(1*)	6 (15)	4332 (12)	2267 (18)
C(2*)	773 (15)	3928 (12)	2518 (18)
C(3*)	-464 (15)	4285 (12)	2844 (18)
O(1*)	111 (15)	5020 (12)	2094 (18)

<sup>a</sup>Note: Coordinates multiplied by 10<sup>4</sup>.

(C-H = 1.08 pm), and their contributions were included in F<sub>c</sub>. During the last cycles of refinement four peaks as high as 0.9–1.1 e Å<sup>-3</sup> were found separated from any other part of the molecule. They were assigned to a solvate acetone molecule. The site occupation factor of the acetone molecule was refined to 0.25 (4). Residual peaks as high as 0.5–0.9 e Å<sup>-3</sup> were still found around the solvent molecule, indicative of some disorder that we could not solve. The final values of the discrepancy indices, defined by R = Σ[|F<sub>o</sub>| - |F<sub>c</sub>|]/Σ|F<sub>o</sub>| and R<sub>w</sub> = [Σw(|F<sub>o</sub>| - |F<sub>c</sub>|)<sup>2</sup>]/Σw(F<sub>o</sub>)<sup>2</sup>]<sup>1/2</sup>, where R = 0.078 and R<sub>w</sub> = 0.075. In the final least-squares cycle no shift/error ratio was higher than 0.30.

The final atomic positional parameters for the non-hydrogen atoms are listed in Table II. Thermal parameters and positional parameters of the hydrogen atoms are listed in Tables SI and SII,<sup>22</sup> respectively. A listing of the observed and calculated structure factor amplitudes is available as supplementary material.<sup>22</sup>

Single crystals of the complex [Cu<sub>2</sub>(H<sub>2</sub>B(pz)<sub>2</sub>)<sub>2</sub>(pz)<sub>2</sub>(Br)](AsPh<sub>4</sub>)(CH<sub>3</sub>)<sub>2</sub>CO have been found to be isomorphous to the title complex (a = 17.620 (8) Å, b = 19.933 (8) Å, c = 15.325 (5) Å, β = 117.1 (2)°).

**EPR Spectra.** Single crystals suitable for EPR spectroscopy were oriented with a Philips PW1100 automated diffractometer. The crystals used in the experiment were elongated prisms with (-1, -1, 0) and (110) most developed faces. Polycrystalline and single-crystal spectra were recorded at room temperature at X-band (9.35 GHz) on a Varian E-9 spectrometer. The polycrystalline powder spectrum recorded at 77 K showed no significant variation in resolution with respect to the room temperature one.

**Magnetic Susceptibility Measurements.** Temperature dependence of the magnetic susceptibilities was measured by the Faraday method in the temperature range 80–300 K using an Oxford Instrument apparatus equipped with a CF2000 cryostat and a Cahn 2000 microbalance. The instrument was calibrated by using HgCo(NCS)<sub>4</sub>.<sup>23</sup> Diamagnetic corrections were carried out according to ref 24.

**Electronic and IR Spectra.** Diffuse reflectance spectra were recorded in the range 450–2000 nm with a Beckman DK-2A spectrophotometer.

- (18) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg. Chem.* **1967**, *6*, 197.  
 (19) (a) Stewart, J. M.; Kundall, F. A.; Baldwin, J. C. *X-Ray 72 System of Programs*; Technical Report TR 192; University of Maryland: College Park, MD, 1972. (b) Sheldrick, G. "SHELX 76 System of Computing Programs"; University of Cambridge: Cambridge, England, 1976. (c) Johnson, C. K.; *Oak Ridge Natl. Lab. [Rep.]*, ORNL (U.S.) **1965**, ORNL-3794.  
 (20) *International Tables for X-Ray Crystallography*; Knoch: Birmingham, England, 1974; Vol. 4, p 71.  
 (21) Reference 20; p 148.

- (22) See paragraph at end of paper regarding supplementary material.  
 (23) Rade, H. S. *J. Chem. Phys.* **1973**, *77*, 424.  
 (24) O'Connor, C. J. *Prog. Inorg. Chem.* **1982**, *29*, 208.

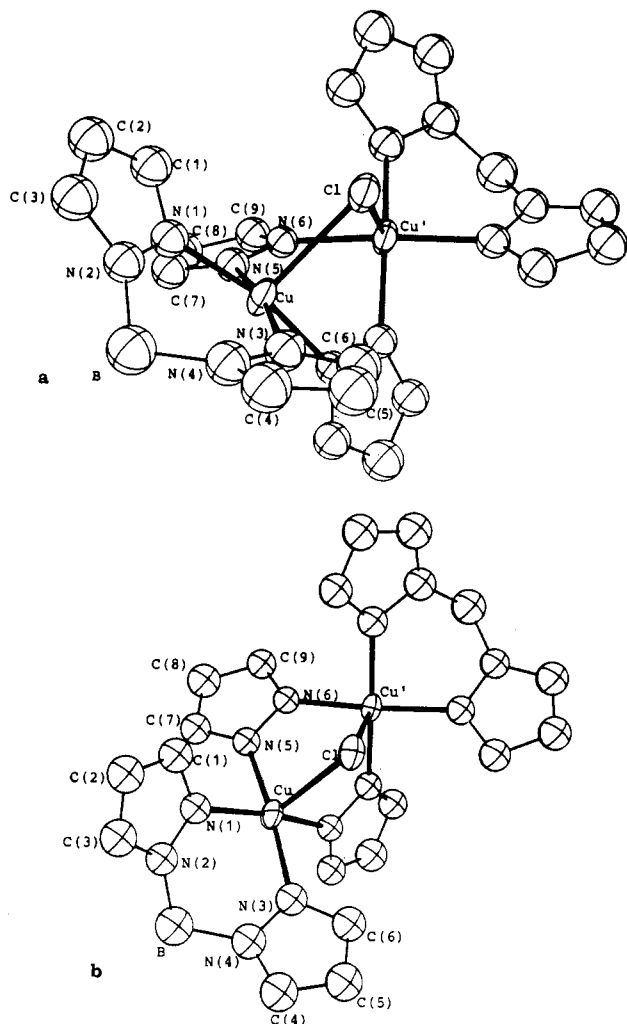


Figure 1. Two ORTEP views of the  $[(\text{H}_2\text{B}(\text{pz})_2)\text{Cu}(\text{pz})_2(\text{Cl})\text{Cu}(\text{H}_2\text{B}(\text{pz})_2)]^-$  anion.

Infrared spectra were recorded with a Perkin-Elmer 283 infrared spectrometer.

### Results and Discussion

**Synthesis of the Complexes.** The reaction of  $\text{KH}_2\text{B}(\text{pz})_2$  with copper(II) halides in polar solvents always leads to the isolation of the neutral bis chelate  $[\text{Cu}(\text{H}_2\text{B}(\text{pz})_2)_2]$  complex.<sup>17</sup> On the other hand it has been recently found by one of us that ethanolic solutions of  $\text{Et}_4\text{NH}_2\text{B}(\text{pz})_2$  and some metal(II) salts in 3:1 molar ratio give the anionic tris chelate  $(\text{Et}_4\text{N})[\text{M}(\text{H}_2\text{B}(\text{pz})_2)_3]$  ( $\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ ) salts.<sup>25</sup> The same reaction carried out with copper(II) halides and a small amount of acetone in the reaction medium affords the dinuclear anionic complex  $[(\text{H}_2\text{B}(\text{pz})_2)\text{Cu}(\text{X})(\text{pz})_2\text{Cu}(\text{H}_2\text{B}(\text{pz})_2)]^-$  ( $\text{X} = \text{Cl}, \text{Br}$ ), which can be isolated in the solid state as the tetraphenylphosphonium or tetraphenylarsonium salt. Likewise the  $\text{H}_2\text{B}(\text{pz})_2^-$  ligand decomposes in the presence of acetone molecule thereby forming pyrazolate anions that coordinate to copper(II). As a matter of fact we found that an acetone solution of either nickel(II) or cobalt(II) halides and  $(\text{Et}_4\text{N})(\text{H}_2\text{B}(\text{pz})_2)$  affords the polynuclear pyrazolate complexes  $[\text{M}(\text{pz})_2]_n$  ( $\text{M} = \text{Co}, \text{Ni}$ ).<sup>26</sup>

**Description of the Structure.** Two perspective views of the dimer structure are shown in Figure 1. In the Figure 1 the labeling scheme of the asymmetric unit is shown. Selected bond distances and angles are reported in Table III.

The structure consists of dimeric  $[(\text{H}_2\text{B}(\text{pz})_2)\text{Cu}(\text{pz})_2(\text{Cl})\text{Cu}(\text{H}_2\text{B}(\text{pz})_2)]^-$  anions and  $[\text{Ph}_4\text{P}]^+$  cations. The chlorine atom of the anion lies on a crystallographic  $C_2$  axis and bridges the two

Table III. Selected Interatomic Distances (Å) and Angles (deg) for the Anion  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})]^-$

Cu-N(1)	2.02 (1)	Cu-N(6)'	2.00 (1)
Cu-N(3)	1.995 (8)	Cu-Cl	2.566 (4)
Cu-N(5)	1.990 (8)	Cu...Cu'	3.387 (6)
Cl-Cu-N(1)	98.8 (3)	N(1)-Cu-N(6)'	168.4 (4)
Cl-Cu-N(3)	96.7 (3)	N(3)-Cu-N(5)	170.0 (4)
Cl-Cu-N(5)	92.9 (3)	N(3)-Cu-N(6)'	88.8 (4)
Cl-Cu-N(6)'	92.7 (3)	N(5)-Cu-N(6)'	87.8 (4)
N(1)-Cu-N(3)	90.6 (4)	Cu-Cl-Cu'	82.6 (2)
N(1)-Cu-N(5)	90.8 (4)		

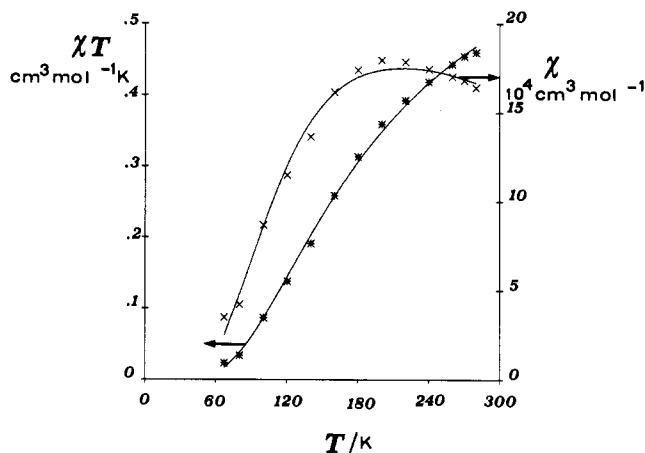


Figure 2. Temperature dependence of the magnetic susceptibility for  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4) \cdot 0.5(\text{CH}_3)_2\text{CO}$ .

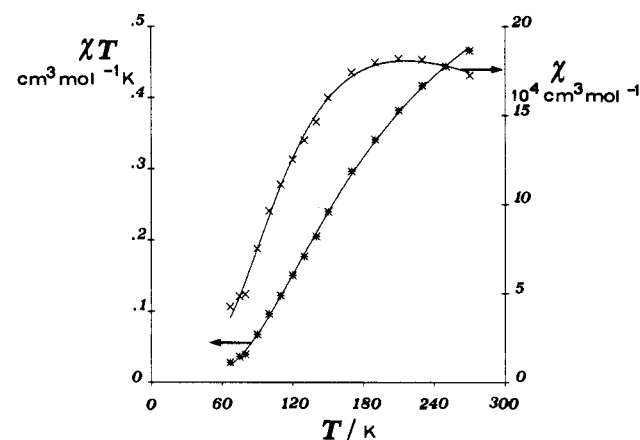


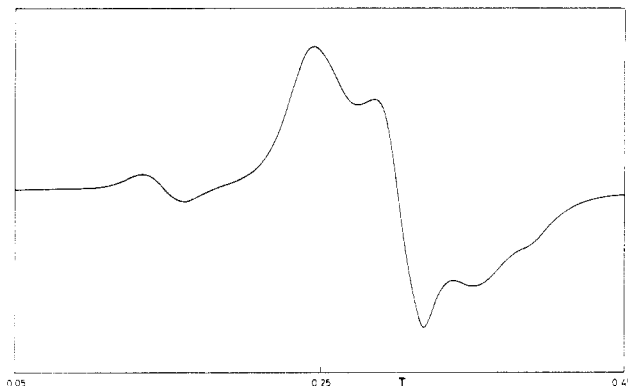
Figure 3. Temperature dependence of the magnetic susceptibility for  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Br})](\text{AsPh}_4) \cdot (\text{CH}_3)_2\text{CO}$ .

copper atoms in a symmetrical fashion ( $\text{Cu}-\text{Cl} = 2.57 \text{ \AA}$ ). The two copper atoms are further bridged by two symmetry-related pyrazolate anions ( $\text{Cu}-\text{N}(5) = 1.99 \text{ \AA}$ ;  $\text{Cu}-\text{N}(6) = 2.00 \text{ \AA}$ ). The coordination environment of copper can be described as a slightly distorted square pyramid having four nitrogens in the basal plane and one chlorine in the axial position. Two of the basal nitrogens, N(1) and N(3), at 2.02 and 2.00 Å, respectively, come from the pyrazolyborate ligands; the other two come from the bridging pyrazolate ions. The copper atoms are displaced 0.15 Å out of the basal plane toward the axial chlorine. The in-plane bond angles are very near to  $90^\circ$  as in the idealized square-pyramidal structure (sum =  $358^\circ$ ) and the largest deviation from the idealized geometry is due to the chlorine atom which makes  $99$  and  $97^\circ$  angles with  $\text{Cu}-\text{N}(1)$  and  $\text{Cu}-\text{N}(3)$ , respectively. The two copper atoms forming the dinuclear unit are symmetry related through the operation  $(-x, y, 1/2 - z)$  and the angle  $\text{Cu}-\text{Cl}-\text{Cu}$  is  $82.6^\circ$ . This implies that the two  $\text{CuN}_4$  coordination planes are not coplanar and make an angle of  $104^\circ$ . The planes of the bridging pyrazolate anions make an angle of  $92^\circ$ .

Bond distances and angles within the pyrazolate anions and the pyrazole molecules of the pyrazolyborate ligand are in the

(25) Mani, F. *Inorg. Chim. Acta* 1986, 117, L1.

(26) Unpublished results from this laboratory.



**Figure 4.** Polycrystalline EPR spectra of  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4)\cdot 0.5(\text{CH}_3)_2\text{CO}$  recorded at X-band at room temperature.

usual range,<sup>15</sup> as are the bond distances and angles in the  $[\text{PPh}_4]^+$  cation.<sup>27</sup>

**Magnetic Measurements.** The temperature dependence of the magnetic susceptibility measured in the range 77–300 K is shown in Figures 2 and 3 for  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4)\cdot 0.5(\text{CH}_3)_2\text{CO}$  and  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Br})](\text{AsPh}_4)\cdot (\text{CH}_3)_2\text{CO}$ , respectively. The solid lines have been computed by using the Bleaney–Bowers equation:<sup>28</sup>

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

where  $\rho$  represents the proportion of uncoupled Cu(II) as an impurity. The best fit parameters obtained through a least-squares procedure are  $g = 2.01$  (2),  $J = 241$  (3)  $\text{cm}^{-1}$ , and  $\rho = 0\%$  and  $g = 2.04$  (1),  $J = 244$  (3)  $\text{cm}^{-1}$ , and  $\rho = 1.1$  (1)% for the chloride and the bromide derivatives, respectively. The spin Hamiltonian we used to describe the exchange interaction has the form  $J\mathbf{S}_1 \cdot \mathbf{S}_2$ .

These data show that copper(II) ions in both complexes are antiferromagnetically coupled, giving rise to a ground singlet state with a thermally populated triplet  $\approx 240$   $\text{cm}^{-1}$  above. The magnitude of the exchange interaction is the same in both complexes, showing that the axially coordinated atoms, Cl and Br respectively, do not appreciably influence the magnetic coupling. A strong antiferromagnetic interaction of the same order of magnitude ( $J = 236$   $\text{cm}^{-1}$ ) was observed in bis(triazolate)-bridged copper(II) dimers<sup>13</sup> in which the triazole molecules bridge the copper atoms in a planar way.

**EPR Spectra.** The polycrystalline powder spectra of  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4)\cdot 0.5(\text{CH}_3)_2\text{CO}$  recorded at room temperature at X-band frequency are shown in Figure 4. On going to 77 K only a small sharpening of the resonances, together with a decrease in intensity, was observed and no hyperfine splitting was resolved probably due to the broadening effect of the  $^{57}\text{Cl}$  ( $I = 7/2$ ) and  $^{14}\text{N}$  ( $I = 1$ ) nuclei. The spectra are characteristic of a triplet spin state with an anisotropic zero-field splitting tensor. No reasonable fit of the spectra was obtained by using the reported formulas for the transition fields along the principal axes, suggesting the existence of noncollinear  $\mathbf{g}$  and  $\mathbf{D}$  tensors.<sup>29,30</sup> This hypothesis was confirmed by the single-crystal analysis.

Single-crystal spectra were recorded at X-band by rotating the crystal with respect to the static magnetic field around three orthogonal axes (laboratory frame)  $X$ ,  $Y$ , and  $Z$ . The  $Z$  axis is along  $-c^*$ ,  $X$  is perpendicular to the  $(-1, -1, 0)$  crystal face, and  $Y$  is orthogonal to  $X$  and  $Z$ . The angular dependence of the  $\Delta M_s = \pm 1$  transition fields in the  $YZ$ ,  $XZ$ , and  $XY$  planes is shown in Figure 5. The best-fit curves, calculated through the nonlinear least squares fitting procedure previously described,<sup>31</sup> are also

**Table IV.** Best-Fit Spin-Hamiltonian Parameters for  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4)\cdot 0.5(\text{CH}_3)_2\text{CO}^a$

$g_x = 2.115$ (4)	$g_y = 2.063$ (4)	$g_z = 2.163$ (4)
-0.82 (5)	0.11 (1)	-0.56 (7)
-0.56 (7)	0.08 (1)	0.83 (5)
0.13 (2)	0.99 (1)	-0.009 (5)
$D_x = \pm 0.0297$ (5)	$D_y = \mp 0.0463$ (4)	$D_z = \pm 0.0166$ (4)
-0.72 (1)	0.459 (4)	-0.52 (4)
-0.42 (2)	0.295 (5)	0.86 (1)
0.546 (3)	0.838 (2)	0.18 (1)

<sup>a</sup> Estimated standard deviations in the last significant digit are given in parentheses. The  $x$ ,  $y$ ,  $z$  and  $x'$ ,  $y'$ ,  $z'$  axes are defined in the text. The  $D_i$  values are in  $\text{cm}^{-1}$ .

shown in Figure 5. The data have been fitted to the spin Hamiltonian  $\mathcal{H} = \mu_B \mathbf{B} \cdot \mathbf{g} \cdot \mathbf{S} + \mathbf{S} \cdot \mathbf{D} \cdot \mathbf{S}$ .

Since the dinuclear molecule possesses an overall  $C_2$  symmetry, only two signals, plus a weak half-field signal, were observed at each orientation; they have been assigned to transitions between the triplet levels of the single magnetically nonequivalent dinuclear moiety present in the crystallographic unit cell. The observed line widths range from 0.02 to 0.04 T and this makes it impossible to safely follow the individual transitions near the crossing points, as is apparent from Figure 5 where no experimental point is shown near the crossing points of the transition fields. In particular, in the  $XY$  plane only the low-field transition was followed with a certain accuracy while the high-field one is affected by a larger error. These facts cause a rather large error in the determination of the  $\mathbf{g}$  tensor to which the fitting procedure is less sensitive, as already observed.<sup>30–32</sup>

The best fit spin-Hamiltonian parameters and the computed standard deviations are reported in Table IV. The symmetry of the molecule requires<sup>33</sup> that the  $g_x$  and  $D_x$  axes are parallel to the  $C_2$  ( $b$ ) crystallographic axis but they are actually making angles of 8 and 11°, respectively, as a consequence of the uncertainty of the measurements in the  $XY$  plane (this is the only plane in which we can perform measurements along the  $Z$  crystallographic axis). This allows us to estimate an overall error in the measured principal directions not less than 10°. The relative orientation of the  $\mathbf{g}$  and  $\mathbf{D}$  principal axes and their orientation relative to the dinuclear molecule are shown in Figure 6. The  $x$  and  $x'$  axes make an angle of 25°, this is significantly larger than the experimental error and indicates that the  $\mathbf{g}$  and  $\mathbf{D}$  tensors are misaligned in the  $xy$  plane. The  $x$  axis is found 8° away from the Cu–Cu direction, i.e. parallel within experimental error to the Cu–Cu direction.

In a copper(II) dimer the experimental  $\mathbf{g}$  tensor is given as the average of the single ion  $\mathbf{g}_i$  tensors:<sup>11</sup>

$$\mathbf{g} = \frac{1}{2}(\mathbf{g}_1 + \mathbf{g}_2) \quad (2)$$

This equation has been successfully applied to interpret the EPR spectra of a number of dinuclear copper(II) complexes.<sup>1,11</sup> All of the tensors in (2) must be of course referred to the same reference axes. In the present case the two  $\mathbf{g}_i$  tensors are expected to be largely misaligned since the local  $z_i$  axes are anticipated to be parallel to the  $\text{Cu}_i\text{–Cl}$  bond and the  $x_i$  and  $y_i$  directions to lie in the  $\text{CuN}_4$  plane. In order to estimate the  $\mathbf{g}_i$  tensors, we performed AOM calculations using the model previously described<sup>34</sup> and the atomic coordinates seen in the crystal structure. In the calculations we fixed the  $e_\pi^{\text{N}}/e_\sigma^{\text{N}}$  and  $e_\pi^{\text{Cl}}/e_\sigma^{\text{Cl}}$  ratios at 0.15 and 0.05, respectively, and let the  $e_\sigma$  parameters vary to reproduce the observed electronic d–d transitions. A reasonable fit of the transitions (calcd  $12.02 \times 10^3$ ,  $17.6 \times 10^3$ ,  $19.3 \times 10^3$ , and  $19.8 \times 10^3$   $\text{cm}^{-1}$ ; obsd  $17.9 \times 10^3$   $\text{cm}^{-1}$ ) was obtained for  $e_\sigma^{\text{N}} = 7500$

- (27) Bogard, M. P.; Rae, A. D. *Cryst. Struct. Commun.* **1982**, *11*, 175.  
 (28) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London, A* **1952**, *266*, 95.  
 (29) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.  
 (30) Bencini, A.; Gatteschi, D.; Zanchini, C.; Haasnoot, J. G.; Prins, R.; Reedijk, J. *Inorg. Chem.* **1985**, *24*, 2812.

- (31) Banci, L.; Bencini, A.; Gatteschi, D.; Zanchini, C. *J. Magn. Reson.* **1982**, *48*, 9.  
 (32) Banci, L.; Bencini, A.; Gatteschi, D. *J. Am. Chem. Soc.* **1983**, *105*, 761.  
 (33) Bencini, A.; Gatteschi, D. In *Transition Metal Chemistry*; Melson, G. A., Figgis, B. N., Eds.; Dekker: New York, 1982; Vol. 8, p 1.  
 (34) Bencini, A.; Benelli, C.; Gatteschi, D. *Coord. Chem. Rev.* **1984**, *60*, 131.

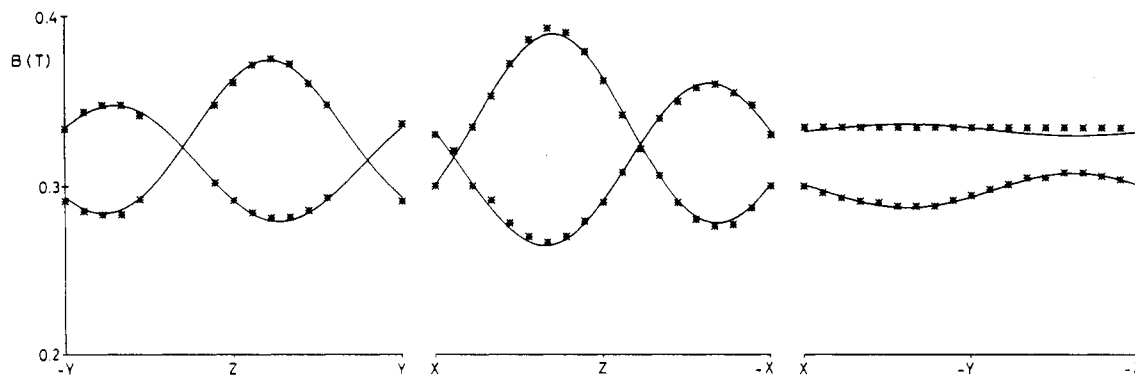


Figure 5. Angular dependence of the transition fields for  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4) \cdot 0.5(\text{CH}_3)_2\text{CO}$  recorded at X-band at room temperature.

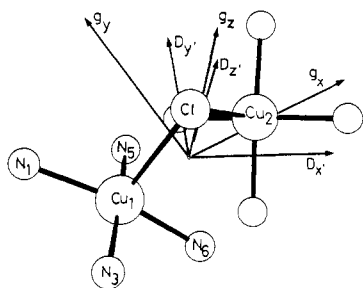


Figure 6. Orientation of the  $\mathbf{g}$  and  $\mathbf{D}$  tensors with regard to the dinuclear unit.

$\text{cm}^{-1}$  and  $e_g^{\text{Cl}} = 2850 \text{ cm}^{-1}$  corresponding to  $Dq$  values of 1800 and  $800 \text{ cm}^{-1}$ , respectively. These parameter values are in nice agreement with those previously reported;<sup>35</sup> in particular, they reflect the already observed strong bonding capability of the pyrazole ligands. With these parameters we computed  $\mathbf{g}_i$  tensors with principal values  $g_x = 2.050$ ,  $g_y = 2.051$ , and  $g_z = 2.232$ . The  $x_1$  axis was computed at  $6^\circ$  from the  $\text{Cu}(1)\text{--N}(6)$  bond,  $z_1$  was at  $4^\circ$  from  $\text{Cu}(1)\text{--Cl}$ . The molecular axes of  $\text{Cu}(2)$  were of course reported by the molecular symmetry elements. These values and directions compare well with the values measured<sup>30</sup> in the bis- $[\mu\text{-}3,5\text{-bis}(\text{pyridin-}2\text{-yl})\text{-}1,2,4\text{-triazolato-}N',N^1,N^2,N'^2]$ bis[aqua-(trifluoromethanesulfonato- $O$ )copper(II)],  $[\text{Cu}(\text{bpt})\text{-(CF}_3\text{SO}_3)_2\text{H}_2\text{O}]_2$ , complex, in which the copper centers are bridged by two triazolates,<sup>13</sup> as well as with those previously observed in other copper(II) square-pyramidal complexes<sup>30-32</sup> in which the unpaired electron is in a  $d_{xy}$  orbital, and we used these  $\mathbf{g}_i$  tensors in (2). This procedure yields a resultant  $\mathbf{g}$  tensor, to be compared with the experimental one, whose principal values are  $g_x = 2.119$ ,  $g_y = 2.051$ ,  $g_z = 2.164$ . The computed  $z$  axis is parallel to the crystallographic  $b$  axis, as required by symmetry, and the  $x$  axis is computed  $8^\circ$  away from the experimental  $x$  axis. The good agreement between the experimental and the computed tensor allows us to conclude that the unpaired electrons are in magnetic orbitals that are essentially  $d_{xy}$  in nature.

The zero-field-splitting tensor in copper(II) dimers is generally written as a sum of two contributions:<sup>12</sup>

$$\mathbf{D} = \mathbf{D}^d + \mathbf{D}^{\text{ex}} \quad (3)$$

The first one represents a direct magnetic interaction between the paramagnetic centers; the second one represents the anisotropic exchange contribution. Usually  $\mathbf{D}^d$  is considered to arise from a dipolar interaction.<sup>30,32</sup> With this assumption  $\mathbf{D}^d$  is easily computed in the  $\mathbf{g}$  reference frame.<sup>36</sup> In the present case, since the two interacting copper centers are largely misaligned, the computed dipolar tensor,  $\mathbf{D}^{\text{dp}}$ , is neither traceless nor symmetric and can be decomposed as a sum of a symmetric traceless and a skew symmetric tensor.<sup>11</sup> This procedure yields  $\mathbf{J}^d = (\text{Tr}(\mathbf{D}^{\text{dp}})/3)$

$= 0.0001 \text{ cm}^{-1}$ ,  $d_X^d = -0.0003 \text{ cm}^{-1}$ ,  $d_Y^d = -0.0002 \text{ cm}^{-1}$ , and  $d_Z^d = -0.0027 \text{ cm}^{-1}$  and a symmetric traceless tensor  $\mathbf{D}^d$  whose principal values are  $D_X^d = 0.0205 \text{ cm}^{-1}$ ,  $D_Y^d = -0.0433 \text{ cm}^{-1}$ , and  $D_Z^d = 0.0229 \text{ cm}^{-1}$ , with the  $Z$  axis parallel to the  $b$  crystallographic axis and  $Y$  parallel to the copper-copper direction. The dipolar contribution to  $\mathbf{J}$  is clearly negligible. The effect of the antisymmetric contribution on the EPR spectra of couples<sup>37</sup> is dependent upon the  $|d_i|/J$  ratio ( $i = X, Y, Z$ ), and it appears to be negligible too, while the anisotropic  $\mathbf{D}^d$  contribution is of the same order of magnitude as the experimental  $\mathbf{D}$  tensor. Using (3), we compute the exchange contribution to  $\mathbf{D}$  as  $\mathbf{D}^{\text{ex}} = \mathbf{D} - \mathbf{D}^d$ . According to the two possible choices of sign for  $\mathbf{D}$ , we obtain two tensors referred to the principal  $\mathbf{g}$  axes system:

$$\mathbf{D}^{\text{ex}}_1 = \begin{pmatrix} -0.0130 & -0.0326 & 0.0048 \\ -0.0326 & -0.0067 & 0.0043 \\ 0.0048 & 0.0043 & 0.0199 \end{pmatrix} \quad \mathbf{D}^{\text{ex}}_2 = \begin{pmatrix} -0.0334 & -0.0236 & 0.0636 \\ -0.0236 & -0.0337 & 0.0415 \\ 0.0636 & 0.0415 & 0.0673 \end{pmatrix}$$

Both  $\mathbf{D}^{\text{ex}}_1$  and  $\mathbf{D}^{\text{ex}}_2$  are not diagonal and have large out of diagonal elements. Since we cannot experimentally determine the absolute sign of the  $\mathbf{D}$  tensor, we cannot decide which of the above two tensors describe the anisotropic exchange interactions in the present case. It is immediately apparent that the above tensors differ from the tensor describing the anisotropic exchange interactions observed in other dinuclear copper(II) systems with  $d_{xy}$  magnetic orbitals in the sign of the greatest diagonal element. In the previously reported cases,<sup>1,30-32</sup> in fact, the sign of  $D^{\text{ex}}_{zz}$  was found to be negative. This fact was ascribed to a ferromagnetic interaction between the ground  $d_{xy}$  orbital on one ion and the excited  $d_{x^2-y^2}$  orbital on the other. This interaction was also found to be dominant over the other interactions involving the  $d_{xz}$  and  $d_{yz}$  orbitals and the  $d_{xy}$  one. It must be emphasized at this point that in the present complex antisymmetric exchange<sup>37-39</sup> can give a contribution to  $\mathbf{D}$  also. Since the symmetry of the complex is  $C_2$ , only the  $d^z$  component of the skew symmetric exchange tensor can be different from zero.<sup>37</sup> This yields an axial contribution to  $\mathbf{D}^{\text{ex}}$  of the type  $D^{\text{ex}}_{zz} = |d^z|^2/4J = 0.0011 |d^z|^2$ ,  $D^{\text{ex}}_{xx} = D^{\text{ex}}_{yy} = -0.00055 |d^z|^2$ . Values of  $d^z$  larger than  $4.2 \text{ cm}^{-1}$  and  $8 \text{ cm}^{-1}$  can alter the sign of  $D^{\text{ex}}_{zz}$  in tensors  $\mathbf{D}^{\text{ex}}_1$  and  $\mathbf{D}^{\text{ex}}_2$ , respectively. If, however, for the sake of simplicity, the effect of antisymmetric exchange contributions is neglected, the components of the anisotropic exchange tensor are given by<sup>1,37-39</sup>

$$\begin{pmatrix} (\Delta g_{xx}^2 \times J_{xz,xz,xy})/8 & (\Delta g_{xx}\Delta g_{yy} \times J_{xz,yz,xy})/2 & (\Delta g_{xx}\Delta g_{zz} \times J_{xz,x^2-y^2,xy})/4 \\ (\Delta g_{xx}\Delta g_{yy} \times J_{yz,yz,xy})/2 & (\Delta g_{yy}^2 \times J_{yz,yz,xy})/8 & -(\Delta g_{yy}\Delta g_{zz} \times J_{yz,x^2-y^2,xy})/4 \\ (\Delta g_{xx}\Delta g_{zz} \times J_{xz,x^2-y^2,xy})/4 & -(\Delta g_{yy}\Delta g_{zz} \times J_{yz,x^2-y^2,xy})/4 & (\Delta g_{zz}^2 \times J_{x^2-y^2,x^2-y^2,xy})/32 \end{pmatrix} \quad (4)$$

where  $J_{e,e',g} = \langle e_1g_2|H_{\text{ex}}|e'_1g_2\rangle = \langle e_2g_1|H_{\text{ex}}|e'_2g_1\rangle$  are exchange integrals involving the ground state of one ion,  $|g_i\rangle$ , and the excited states,  $|e_j\rangle$ ,  $|e'_j\rangle$ , on the other and  $\Delta g_{ii} = 2.0023 - g_{ii}$ . When (4)

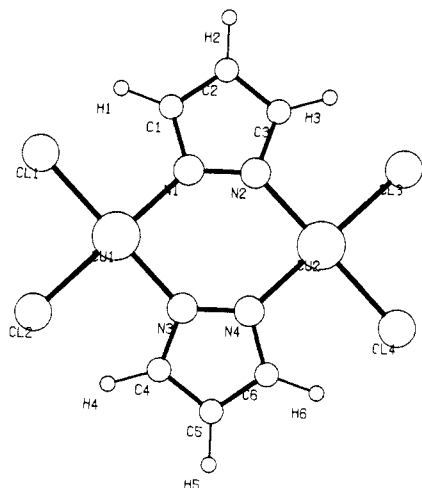
(35) Banci, L.; Benelli, C.; Gatteschi, D.; Mani, F. *Inorg. Chem.* **1982**, *21*, 1133.

(36) Abragam, A.; Bleaney, B. *Electron Paramagnetic Resonance of Transition Metal Ions*; Clarendon: Oxford, England, 1970.

(37) Bencini, A.; Gatteschi, D. *Mol. Phys.* **1982**, *47*, 161.

(38) Moriya, T. In *Magnetism*; Rado, G. T., Suhl, H., Eds.; Academic: New York, 1963; Vol. 1, p 85.

(39) Moriya, T. *Phys. Rev.* **1960**, *120*, 91.



**Figure 7.** Model complex used in the EH calculation in the planar geometry.

is made traceless, we get the appropriate tensor to be compared with  $D^{ex}_1$  and  $D^{ex}_2$  (see eq 4–6 of ref 1). In any case since both  $D^{ex}_{1,zz}$  and  $D^{ex}_{2,zz}$  are positive the following inequality must be verified:

$$0 > \frac{1}{3}|(D^{ex}_{xx} + D^{ex}_{yy})| > \frac{2}{3}|D^{ex}_{zz}| \quad D^{ex}_{xx}, D^{ex}_{yy} < 0 \quad (5)$$

if we assume for  $D^{ex}_{zz}$  the negative sign as observed in other copper(II) dimers.<sup>1,30–32</sup> From (5) it follows that in the present complex sizable ferromagnetic interactions  $J_{xz,xz,xy}$  and  $J_{yz,yz,xy}$  are operative, while, on the contrary, these interactions were found to be negligible in all the other cases. The out of diagonal elements allow the direct evaluation of the anisotropic exchange integrals as

$$\begin{aligned} J_{xz,yz,xy} &= -10.7 \quad (-7.8) & J_{xz,x^2-y^2,xy} &= 2.3 \quad (30) \\ J_{yz,x^2-y^2,xy} &= -2.1 \quad (-19.9) \end{aligned} \quad (6)$$

expressed in  $\text{cm}^{-1}$ . The values in parentheses in (6) refer to  $D^{ex}_2$ .

At the present status of the theory no quantum-mechanical calculation can give a good estimate of the exchange integrals responsible for the anisotropic interactions, and therefore we cannot prove the validity of our analysis. Some qualitative considerations can however be drawn.<sup>40</sup> The value of the exchange integrals like, for example,  $J_{xz,xz,xy}$ , depend on the extrema of the overlap density  $\rho_{xz,xy} = \langle xz|xy \rangle$ . Passing from a planar conformation to a more distorted one causes an increase of  $\rho_{xz,xy}$ ; furthermore, the presence of the bridging chlorine leads one to anticipate a delocalization of the electronic density on the bridging chlorine atom, which is expected to increase the overlap density too.

**Magneto-Structural Correlations in Bis( $\mu$ -pyrazolato)-Bridged Copper(II) Complexes.** Although the complexes  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{X})](\text{YPh}_4) \cdot n(\text{CH}_3)_2\text{CO}$  constitute the first genuine examples of discrete bis(pyrazolato)-bridged copper(II) complexes, we can compare their magnetic properties with those of bis[ $\mu$ -3,5-bis(pyridin-2-yl)-1,2,4-triazolato- $N',N^1,N^2,N^1$ ]bis[aqua(trifluoromethanesulfonato-*O*)copper(II)],  $[\text{Cu}(\text{bpt})(\text{CF}_3\text{SO}_3)_2\text{H}_2\text{O}]_2$ , in which the copper centers are bridged by two triazolates.<sup>13</sup> In all of the complexes the exchange interaction is antiferromagnetic. The  $J$  values are 241, 244, and  $236 \text{ cm}^{-1}$  for  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4) \cdot 0.5(\text{CH}_3)_2\text{CO}$ ,  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Br})](\text{AsPh}_4) \cdot (\text{CH}_3)_2\text{CO}$  and  $[\text{Cu}(\text{bpt})(\text{CF}_3\text{SO}_3)_2\text{H}_2\text{O}]_2$ , respectively.

In the bpt complex, the copper ions are in a square-pyramidal coordination environment and the two basal planes are coplanar. Also the two triazolato bridging molecules are coplanar. This arrangement is rather different from that observed in the present complexes where both the two  $\text{CuN}_4$  coordination planes and the planes of the pyrazolates are not parallel. In order to estimate how deviations from the coplanar situation can influence the

**Table V.** Valence Ionization Potentials and Coefficients and Exponents of the Slater Atomic Functions<sup>a</sup> Used in the Extended Hückel Calculations

atom type	orbital	VSIP, eV	$c_1$	$\zeta_1$	$c_2$	$\zeta_2$
Cu	3d	-14.0	0.5933	5.95	0.5744	2.3
	4s	-11.4	1.0000	2.22		
	4p	-6.06	1.0000	2.22		
N	2s	-26.0	1.0000	1.95		
	2p	-13.4	1.0000	1.95		
Cl	3s	-27.1	1.0000	2.03		
	3p	-15.6	1.0000	2.03		
C	2s	-22.5	1.0000	1.62		
	2p	-13.7	1.0000	1.62		
H	1s	-13.6	1.0000	1.30		

<sup>a</sup>Double-zeta functions were used for the d copper orbitals.

strength of the exchange interaction in bis(pyrazolato)-bridged copper(II) dimers, we have performed extended Hückel (EH) calculations<sup>41</sup> on the model complex  $[\text{Cl}_2\text{Cu}(\text{pz})_2]^{2-}$  shown in Figure 7 in a number of geometrical conformations. In all of the calculations we kept the Cu–Cl and Cu–N bond lengths at 2.28 and 1.98 Å, respectively, and the bond lengths and angles in the pyrazole molecules at the average of the values observed in the crystal structure of  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4) \cdot 0.5(\text{CH}_3)_2\text{CO}$ . The parameters used in the calculations are reported in Table V. The overall symmetry of the molecule was  $C_s(yz)$  in all the calculations. The nondiagonal elements  $H_{ij}$  of the Hückel matrix have been computed through the relation  $H_{ij} = 1.75S_{ij}(H_{ii} + H_{jj})/2$ , where  $S_{ij}$  is the overlap integral between the  $\varphi_i$  and  $\varphi_j$  atomic orbitals. Atomic orbitals of Slater type were used, taking single- $\zeta$  radial functions for all of the atomic orbitals except 3d copper functions for which a double- $\zeta$  basis was used.

In Figure 8 the energies of the highest occupied molecular orbitals (HOMO's) computed for  $[\text{Cl}_2\text{Cu}(\text{pz})_2]^{2-}$  in the planar geometry of Figure 7 are shown. The composition of the orbitals is analyzed by using a fragment basis,  $[\text{Cl}_2\text{Cu}]_2$  and  $[\text{pz}]_2^{2-}$  being the two interacting fragments. On the left-hand side of Figure 8 the energies of the 10 HOMO's of the  $[\text{Cl}_2\text{Cu}]_2$  fragment, which are mainly copper d orbitals in character, are shown. Contour maps of the two HOMO's are also reported for the two in-plane orbitals. The orbitals are labeled according to their main metal d component and their symmetry with respect to the mirror plane of the molecule (s = symmetric, a = antisymmetric). On the right-hand side of Figure 8 the energies and contour maps of the HOMO's of the  $[\text{pz}]_2^{2-}$  fragment are shown. All of the orbitals have a large component of nitrogen p atomic orbitals. The highest four orbitals lie on the  $z = 0$  Å plane and are formed by the  $p_x$  and  $p_y$  atomic orbitals on the N and C atoms. The other orbitals are linear combinations of mainly  $p_z$  atomic orbitals; their contour maps refer to a plane with  $z = 0.2$  Å. The highest two antibonding molecular orbitals of the dimer,  $xy_a$  and  $xy_s$ , which are responsible for the magnetic properties of the dimer, result from the interaction between the highest occupied in-plane molecular orbitals of the  $[\text{Cl}_2\text{Cu}]_2$  fragment, which are mainly  $d_{xy}$  copper orbitals, and the two HOMO's of the  $[\text{pz}]_2^{2-}$  fragment. The computed energy separation between  $xy_a$  and  $xy_s$  is 0.177 eV.

Starting from this basic configuration, which corresponds to the structure observed in the  $[\text{Cu}(\text{bpt})(\text{CF}_3\text{SO}_3)_2\text{H}_2\text{O}]_2$  complex,<sup>13</sup> we performed two geometrical distortions to mimic the actual structure of the  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4) \cdot 0.5(\text{CH}_3)_2\text{CO}$  complex. In the first distortion we moved the  $\text{CuCl}_2$  planes away from the  $xy$  plane while keeping fixed the pyrazole molecules. In the second distortion we moved the pyrazole molecules away from the  $xy$  plane keeping fixed the two  $\text{CuCl}_2$  moieties. These two distortions have been in fact observed in  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4) \cdot 0.5(\text{CH}_3)_2\text{CO}$ . The variation of the energy of the two HOMO's and of their difference as a function of the above distortions are shown in Figure 9. In Figure 9a,b the energy levels

(40) Charlot, M. F.; Journaux, Y.; Kahn, O.; Bencini, A.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1986**, *25*, 1060.

(41) Hoffman, R.; Fujimoto, J. R.; Swenson, C.; Wan, C. C. *J. Am. Chem. Soc.* **1973**, *95*, 7644.

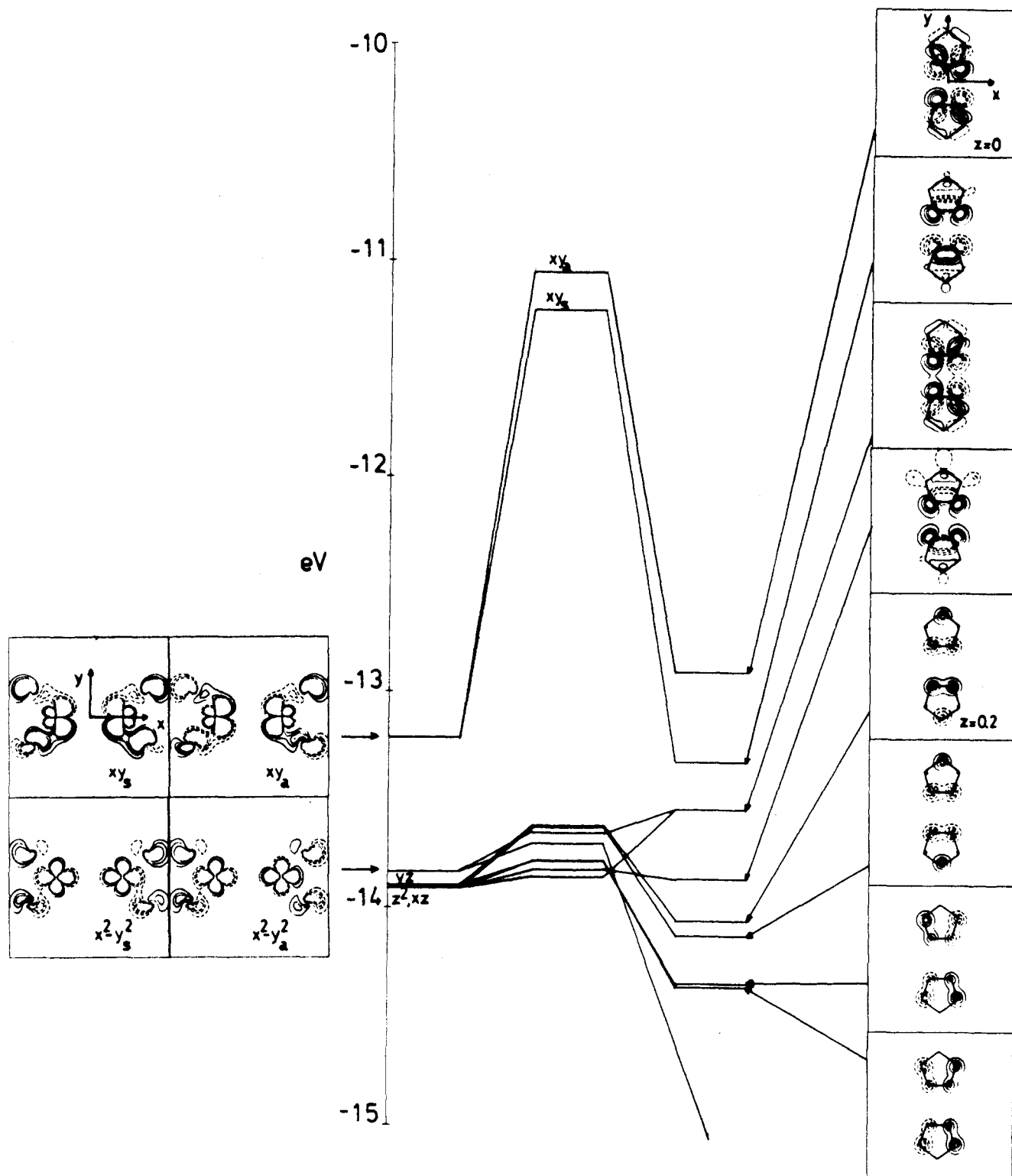


Figure 8. Energies and composition of the highest occupied molecular orbitals for  $[\text{Cl}_2\text{Cu}(\text{pz})]_2^{2-}$  (see text).

and their difference are plotted against the dihedral angle  $\delta$  between the two  $\text{CuCl}_2$  planes; in Figure 9c,d they are reported as a function of the dihedral angle  $\delta'$  between the planes of the pyrazole molecules.

In Figure 10 the variation of the energy of the HOMO's and their energy difference as a function of  $\delta$  for  $\delta' = 90^\circ$  is shown.

The above calculations can be used within the orbital model<sup>42-44</sup> of the exchange interaction to correlate the  $J$  value to the geo-

metrical distortions. In this framework, in fact,  $J$  can be written as

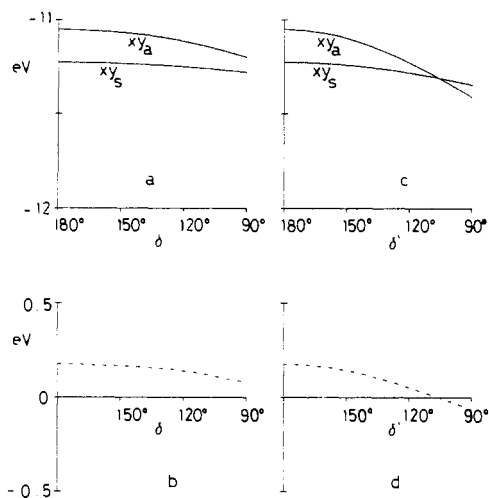
$$J = J_F + J_{AF} = -K_{12} + (\epsilon_s - \epsilon_a)^2 / (J_{11} - J_{12}) \quad (7)$$

where  $\epsilon_i$  is the energy of the  $\varphi_i$  orbital and  $K_{12}$ ,  $J_{11}$ , and  $J_{12}$  are exchange and Coulomb integrals between the two localized molecular orbitals  $\varphi_1$  and  $\varphi_2$  obtained from the two molecular orbitals  $\varphi_a$  and  $\varphi_s$ . The first term in (7) is always ferromagnetic. The second term represents the antiferromagnetic contribution to  $J$ . Equation 7 has been successfully applied to correlate observed trends in  $J$  values to geometrical distortions in series of similar complexes.<sup>10,42,45</sup> These magneto-structural correlations rest on

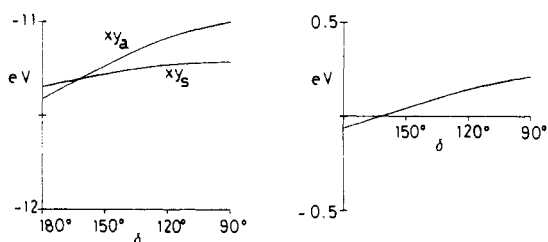
(42) Hay, P. J.; Thibeault, J. C.; Hoffman, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

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

(44) Kahn, O.; Briat, B. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1441.



**Figure 9.** Dependence of the energy of the two highest occupied molecular orbitals of  $[\text{Cl}_2\text{Cu}(\text{pz})_2]^{2-}$  (a and c) and of their difference (b and d) on the  $\delta$  and  $\delta'$  angles (see text). When  $\delta$  is varying, the  $\delta'$  angle is fixed at  $180^\circ$ ; when  $\delta'$  is varying, the  $\delta$  angle is fixed at  $180^\circ$ .



**Figure 10.** Effect of varying the  $\delta$  angle with  $\delta' = 90^\circ$  (see text) on the energy of the highest occupied molecular orbitals of  $[\text{Cl}_2\text{Cu}(\text{pz})_2]^{2-}$  (left) and on their difference (right).

the hypothesis that in a series of similar complexes the largest variation in (7) is given by  $(\epsilon_s - \epsilon_a)^2$ , the other terms remaining *quasi*-constant.

From Figure 9 we learn that the energy difference  $(\epsilon_a - \epsilon_s)$  shows a little variation on the  $\delta$  angle. A larger variation is observed on the  $\delta'$  angle; in particular, for  $\delta' \simeq 100^\circ$  the  $xy_a$  and  $xy_s$  orbitals are degenerate ( $\epsilon_a - \epsilon_s \simeq 0$  eV) and  $J_{\text{AF}}$  is expected to be zero. In this situation, if  $J_{\text{F}}$  has a sizable value, an overall ferromagnetic interaction can be expected. However for  $180^\circ \leq \delta' \leq 110^\circ$  a small variation of  $(\epsilon_a - \epsilon_s)$  is computed, comparable to that computed as a function of  $\delta$ .

In Figure 10 we see that, for  $\delta' = 90^\circ$ , the energy difference  $(\epsilon_a - \epsilon_s)$  still increases on moving the two  $\text{CuCl}_2$  planes from coplanarity. In particular the largest splitting is computed for  $\delta = 90^\circ$  ( $\epsilon_a - \epsilon_s = 0.231$  eV).

These calculations show that the exchange interaction propagated through double pyrazole bridges is rather insensitive to geometrical distortions. The deviation from coplanarity of the pyrazole molecules has the largest effect on the exchange inter-

action and can in principle also change the sign of the interaction. This effect is compensated by the noncoplanarity of the copper coordination planes. From Figure 10, where both these effects are considered together, we learn that for  $\delta \simeq 90^\circ$  and  $\delta' \simeq 90^\circ$  a splitting is computed even larger than that calculated in the planar situation. These findings can explain why the singlet-triplet separation does not vary on passing from the planar  $[\text{Cu}(\text{bpt})(\text{CF}_3\text{SO}_3)\text{H}_2\text{O}]_2$  complex to the more distorted  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4) \cdot 0.5(\text{CH}_3)_2\text{CO}$  one. The distortion seen in the latter complex corresponds to  $\delta = 104^\circ$  and  $\delta' = 93^\circ$ .

## Conclusions

The complex  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4) \cdot 0.5(\text{CH}_3)_2\text{CO}$  is an uncommon example of discrete complexes with two bridging pyrazolato ions. The comparative study of its magnetic properties allows us to conclude that the pyrazole molecule can be very effective in transmitting exchange interactions. The isotropic exchange interaction, which involves the ground magnetic orbitals on the two ions,<sup>42-44</sup> is rather insensitive to geometrical distortions such as deviations from the coplanarity of the metals and/or of the pyrazoles. On the basis of EH calculations, we are led to expect a net ferromagnetic interaction when the two pyrazole planes form an angle  $\simeq 90^\circ$  while the copper coordination planes are coplanar, a situation never met experimentally up to now. In all of the other cases a net antiferromagnetic interaction is expected.

Anisotropic exchange interactions, which involve the ground and excited states<sup>11</sup>, have been also measured in the present complex by EPR spectroscopy. Assuming that no antisymmetric exchange<sup>38,39</sup> contributions are operative, these have been shown to be mainly determined by the interaction between the ground  $xy$  state on one ion with excited  $xz$  and/or  $yz$  states on the other. This is rather unusual since in a number of copper(II) dimers,<sup>11,30-32</sup> including the  $[\text{Cu}(\text{bpt})(\text{CF}_3\text{SO}_3)\text{H}_2\text{O}]_2$  complex,<sup>30</sup> the main anisotropic interaction was found to involve the  $xy$  and  $x^2 - y^2$  orbitals. These findings can be a direct consequence of the presence of a bridging chloride ion in axial position. This bridging ion does not appreciably influence the isotropic exchange, while it probably plays the major role in determining the anisotropic exchange. Its presence in fact removes the orthogonality between the  $xy$  and  $xz$  or  $yz$  orbitals on two different ions allowing for an overlap density different from zero which makes the exchange integrals<sup>40</sup> in  $J_{xz,xz,xy}$  and  $J_{yz,yz,xy}$  sizably different from zero and larger than the  $xy - x^2 - y^2$  interaction. Unfortunately there is no quantum-mechanical model that safely allows one to compute the value of the anisotropic and antisymmetric exchange interactions, and we cannot go beyond this semiquantitative interpretation of the experimental EPR data.

**Acknowledgment.** Thanks are expressed to F. De Zuane, ICTR-CNR, Padova, Italy, and A. Traversi, ISSECC-CNR, Firenze, Italy, for technical assistance.

**Registry No.**  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2(\text{Cl})](\text{PPh}_4) \cdot 0.5(\text{CH}_3)_2\text{CO}$ , 114719-54-9;  $[\text{Cu}_2(\text{H}_2\text{B}(\text{pz})_2)_2(\text{pz})_2\text{Br}](\text{AsPh}_4) \cdot (\text{CH}_3)_2\text{CO}$ , 114737-73-4;  $[\text{Cl}_2\text{Cu}(\text{pz})_2]^{2-}$ , 114719-55-0.

**Supplementary Material Available:** Table S1 (thermal parameters for non-hydrogen atoms) and Table S2 (positional parameters for hydrogen atoms) (2 pages); Table S3 (observed and calculated structure factors) (11 pages). Ordering information is given on any current masthead page.

(45) Bencini, A.; Benelli, C.; Gatteschi, D.; Zanchini, C. *Inorg. Chem.* **1986**, *25*, 398.