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Ligand Conformation Enforces Trigonal Bipyramidal Coordination Geometry in a New Dinuclear Bis(pyrazolato)-Bridged Copper(II) Complex: Synthesis, Crystal Structure, and Properties of $[Cu(Npy_2pz)]_2(ClO_4)_2 \cdot 2CH_3CN$

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The reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with the new tripodal ligand $HNpy_2pz$ (*N*-bis[(pyridin-2-yl)methyl][1*H*-pyrazol-3-yl)methyl]amine) in the presence of 1 equiv of triethylamine results in the formation of a doubly pyrazolato-bridged dicopper(II) complex, $[Cu(Npy_2pz)]_2(ClO_4)_2 \cdot 2CH_3CN$ (**1**). The crystal structure of **1** was determined by X-ray crystallography and was found to consist of two nearly identical discrete dinuclear molecules with bis(pyrazolato) bridges. The copper(II) ion has a trigonal bipyramid geometry achieved by the coordination of an aliphatic nitrogen, two pyridine moieties, and two pyrazolato nitrogens. Variable temperature-dependent magnetic data show that antiferromagnetic interactions operate in **1** as a result of the binding angle of the pyrazolato bridge. In solution, the stability of the dinuclear cation, $[Cu(py_2pz)]_2^{2+}$, is highly dependent on the concentration, as indicated by ESI-MS, ligand field, cyclic voltammetry, EPR, and ^1H NMR studies.

Introduction

Dinuclear copper complexes have been intensively studied as a result of the efforts to understand the factors that are responsible for the magnetic-exchange interactions between coupled metal centers.[1-4] In addition, the importance of exchange coupling in the dinuclear copper proteins has stimulated much interest in the design of polydentate ligands and their copper complexes as small-molecule analogues of metalloproteins that mediate dioxygen activation, electron transfer, and transport processes.[5-9]

In general, an unsaturated coordination environment for the single-coordinate metal and the presence of a bridging atom or ligand are essential requirements for the design of dinuclear metal complexes. Particularly, the self-assembly of tripodal N4 ligands with copper salts results in the formation of five-coordinated complexes, with the ligand protecting one side of the copper ion and leaving one coordination site free and thus being sterically accessible for dioxygen activation or binding of small bridging ligands.[7,8,10-15] Tripodal tetradentate amine ligands have shown a great deal of versatility by coordination to the copper ions.[10,16-24] Also,

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it has been reported that the nature of the donor groups of the tripodal tetradentate amines have dramatic effects upon the structure, redox potential, and spectroscopic features of the corresponding complexes.[25−27]

Although important differences in the reactivity and properties of copper(II) complexes with tripodal N4 ligands can result from small changes in the binding arms, the effects of a bridging-binding arm have not been as extensively investigated. This has led us to undertake the task of designing tripodal ligands with a pyrazole arm. In addition to its remarkable capacity to coordinate to metal ions, the pyrazole entity has also the ability to bring two metal centers into close proximity and provide an intramolecular pathway for spin-exchange interactions. Further changes in the substituents on the pyrazole ring can induce favored configurations with the control of the coordination metal polyhedron, thus allowing changes in the intermetallic distances and control of the spin-exchange interactions. In this report, we describe the synthesis, crystal structure, and spectroscopic and magnetic properties of a new discrete bis(μ-pyrazolato)dicopper(II) complex, $[Cu(Npy_2pz)]_2(ClO_4)_2 \cdot 2CH_3CN$ (**1**), having the copper(II) ion in a trigonal bipyramidal (TBP) geometry, with all coordination sites being occupied by ligand donor atoms only and containing just pyrazolato bridges. The variable-temperature magnetic measurements revealed unusually strong antiferromagnetic coupling between the two copper(II) ions, compared with that of similar doubly bridged copper(II) dinuclear complexes. The magnetic properties of compound **1** will be discussed in the light of the binding angle of the pyrazolato bridge. Also, the solution stability of the dinuclear cation, $[Cu(py_2pz)]_2^{2+}$, is presented.

Experimental Section

Materials and Methods. Starting materials were purchased from commercial sources (Merck or Aldrich), and all manipulations were performed using the materials as received. Spectroscopic-grade solvents were used in syntheses and characterizations. C, H, and N analyses were performed with a Perkin-Elmer 2400 series II analyzer. Infrared spectra (4000−300 cm^{-1}, resolution 4 cm^{-1}) were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer equipped with a Golden Gate ATR device, using the reflectance technique. Diffuse reflectance spectra were obtained on a Perkin-Elmer Lambda 900 spectrophotometer with MgO as a reference. The solution UV/vis spectra of the compounds were recorded in the range of 200−1000 nm with a Cary 50 Varian UV/Vis/NIR spectrometer. Electrospray mass spectra (ESI-MS) in CH_3CN were recorded on a Thermo Finnigan AQA apparatus. X-band powder EPR spectra were obtained on a JEOL RE2x electron-spin resonance spectrometer using DPPH ($g = 2.0036$) as a standard. Magnetic-susceptibility measurements (2−300 K) were carried out at 0.1 T using a Quantum Design MPMS-5 5T SQUID magnetometer. Data were corrected for the magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants. The electrochemical measurements were performed with an Autolab PGstat10 potentiostat controlled by GPES4 software. A three-electrode system was used, consisting of a platinum working electrode, a platinum auxiliary electrode, and an Ag/AgCl reference electrode. The experiments were carried at room temperature under argon with tetrabutylammonium hexafluorophosphate as the electrolyte. All potentials are reported relative to Ag/AgCl. The ^1H 1D- and 2D-COSY NMR spectra were recorded on a DPX300 Bruker spectrometer. All chemical shifts were reported with respect to the residual solvent peak. The longitudinal relaxation times (T_1) were determined by standard inversion−recovery experiments, with a 2 s relaxation delay and a spectral width of 99.7582 ppm.

Synthesis of *N*-bis[(pyridin-2-yl)methyl][1*H*-pyrazol-3-yl)-methyl]amine (HNpy$_2$pz). *N*,*N*-bis(pyridin-2-ylmethyl)amine (2.2 g, 11 mmol) was added dropwise to a solution of pyrazole-3-carbaldehyde (1 g, 11 mmol) in 50 mL of dried ethanol. A white suspension was obtained which was refluxed for 5 h. The solution was then cooled to 0 °C, and the reaction mixture was acidified with CF_3COOH to pH 5.5. The solution was cooled again to 0 °C, and 0.418 g of $NaBH_4$ was added; then the mixture was stirred for 10 h. The resulting solution was filtered off, and the ethanol evaporated under reduced pressure. The residual yellow oil was extracted by CH_2Cl_2 from the aqueous phase (pH 7), and the organic phase was dried over $MgSO_4$. The $MgSO_4$ was filtered off, and the CH_2Cl_2 removed under vacuum to give a yellow oil. Yield: 2.2 g (72%). Anal. Calcd for $C_{16}H_{17}N_5$: C, 68.79; H, 6.13; N, 25.07. Found: C, 68.96; H, 5.80; N, 25.69. ^1H NMR ($CDCl_3$, 300 MHz): δ 8.42 (m, 2H), 7.86 (m, 2H), 7.76 (s, 1H), 7.53 (m, 4H), 6.33 (s, 1H), 4.37 (s, 2H), 3.80(m, 4H). IR (film, cm^{-1}): ν(N−H) 3180−3230, ν(CH_2) 3008−2852, ν(C═N/C═C) 1652−1458, (aromatic skeleton vibrations) 1400−600. MS (*m*/*z*): $[M + H]^+ = 280.89$, 100.

Synthesis of $[Cu(Npy_2pz)]_2(ClO_4)_2 \cdot 2CH_3CN$ (1). A solution of THF (2 mL) containing HNpy$_2$pz (307 mg, 1.1 mmol) and Et_3N (112 mg, 1.1 mmol) was added to a solution of acetontrile/THF (1:3, 4 mL) containing $Cu(ClO_4)_2 \cdot 6H_2O$ (420 mg, 1.1 mmol). The slow diffusion of hexane into the resulting green solution leads to the formation of green crystals in 2 days. The crystals were collected by filtration, washed with hexane, and dried under vacuum. Yield: 54% (638 mg). Anal. Calcd for $C_{36}H_{38}Cl_2Cu_2N_{12}O_8$: C, 44.82; H, 3.97; N, 17.42. Found: C, 45.13; H, 4.26; N, 17.12. IR (cm^{-1}): ν(C═N) 1606, 1566 cm^{-1}, ν(ClO_4^-) 1084, 619.

X-ray Crystallographic Analysis and Data Collection. Intensity data for single crystals of **1** were collected using Mo Kα radiation ($\lambda = 0.71073$ Å) on a Nonius KappaCCD diffractometer. The intensity data were corrected for Lorentz and polarization effects and for absorption (ψ-scan absorption correction) and extinction. The absorption correction was done with the SADABS

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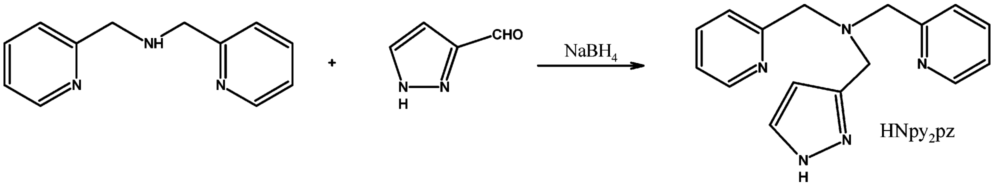

Figure 1. Synthesis of the HNpy$_2$pz ligand.

multiscan correction. The data reduction was done with EcalCCD. The structures were solved by direct methods. The programs DIRDIF99[28] and SHELXL-97[29,30] were used for data reduction and structure solution and refinement, respectively. The refinement of F^2 was done against all reflections. The weighted R factor, wR, and goodness of fit, S, are based on F^2. The conventional R factors are based on F, with F set to zero for negative F^2. The hydrogen of water molecules were taken from difference Fourier map and were independently refined. All other hydrogens were placed at calculated positions and were refined riding on the parent atoms. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 264661. Geometric calculations and molecular graphics were performed with the PLATON package.[31]

Results and Discussions

Synthesis and Spectroscopic Characterization. The tripodal N4-donor ligand, HNpy$_2$pz, was prepared by reacting 3-pyrazolecarbaldehyde with *N*,*N*-bis(pyridin-2-ylmethyl)-amine in a 1:1 molar ratio in ethanol, followed by in situ reduction with NaBH$_4$ (Figure 1). The ligand is a yellow oil, which was obtained, in a good yield (72%), in a pure state by extraction with dichloromethane. HNpy$_2$pz is a versatile ligand because it provides flexibility with the two pendant pyridyl arms, while the pyrazole arm can bind to one metal center or bridge two metal ions. The reaction of $Cu(ClO_4)_2\cdot 6H_2O$ with HNpy$_2$pz in the presence of 1 equiv of triethylamine results in the formation of a dinuclear bis-(pyrazolato)-bridged Cu(II) compound, $[Cu(Npy_2pz)]_2(ClO_4)_2\cdot 2CH_3CN$ (**1**). Crystals suitable for single-crystal X-ray diffraction studies were obtained by slow diffusion of hexane into an acetonitrile/THF solution. Attempts to prepare the mononuclear copper(II) complex of the non-deprotonated HNpy$_2$pz ligand by direct synthesis were unsuccessful, despite the large variety of reaction conditions used.

The infrared spectrum of the compound **1** is dominated by the characteristic bands of the ligand HNpy$_2$pz. The absence of the ν_{N-H} stretching vibration in the 3100−3300 cm^{-1} range indicates that the N−H acidic group is deprotonated by coordination to the copper(II) ion. The presence of the perchlorate counterion is indicated by the bands at 1084 and 619 cm^{-1}. The solid-state ligand field spectrum of **1** shows a low-energy absorption band at 838 nm with a high-energy shoulder at 710 nm, characteristic for trigonal-bipyramidal copper(II) complexes, corresponding to the d−d transition of Cu(II) ions. In acetonitrile solution, a weak band at 814 nm (ϵ = 147 M^{-1} cm^{-1}) with a shoulder at 676 nm (ϵ = 96 M^{-1} cm^{-1}) is observed; this is typical for trigonal bipyramidal copper(II).[32] The polycrystalline powder of **1** is EPR silent at room temperature and 77 K, thus suggesting a strongly antiferromagnetically coupled dinuclear compound.

Table 1. Crystallographic Data for $[Cu(Npy_2pz)]_2(ClO_4)_2\cdot 2CH_3CN$ (**1**)

chemical formula	$C_{36}H_{38}Cl_2Cu_2N_{12}O_8$
mol wt	964.78
cryst syst	triclinic
space group	$P\bar{1}$
a (Å)	11.0520(5)
b (Å)	11.4473(5)
c (Å)	16.7726(6)
α (deg)	98.987(4)
β (deg)	93.439(4)
γ (deg)	104.730(3)
V (Å^3)	2015.99(15)
Z	2
D_{calcd} (mg m^{-3})	1.589
μ(Mo Kα) (mm^{-1})	1.255
cryst size (mm)	0.07 × 0.14 × 0.19
T (K)	208
data collected	73345
unique Data	9253
R_{int}	0.062
R(F) [$I > 2\sigma(I)$]	6688
wR(F^2)	0.0490
S	1.03
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å^{-3})	−0.93, 0.93

Description of the Crystal Structure. Table 1 lists the crystallographic data for complex **1**, which crystallizes as green single crystals that belong to the triclinic system, space group $P\bar{1}$. The unit cell of **1** contains two nearly identical dinuclear cations $[Cu(Npy_2pz)]_2^{2+}$, both located on an inversion center. Figure 2 shows an ORTEP view of one of the independent molecules. The main angles and bond distances are presented in Table 2. The coordination geometry around the copper(II) atoms is trigonal bipyramidal, with the copper ions being surrounded by two pyrazolato nitrogens, two pyridine moieties, and the aliphatic nitrogen atom of the Npy$_2$pz$^-$ ligand. The copper(II)−nitrogen bond lengths fall in the range of 1.933(3)−2.140(3) Å with the equatorial copper−nitrogen bond lengths slightly longer than the corresponding axial copper−nitrogen bond lengths (Table 2). The axial positions of the trigonal bipyramid are occupied by aliphatic nitrogen N1 and nitrogen N32 of the pyrazolato bridge of the other ligand with an N2−Cu1−N32 angle of

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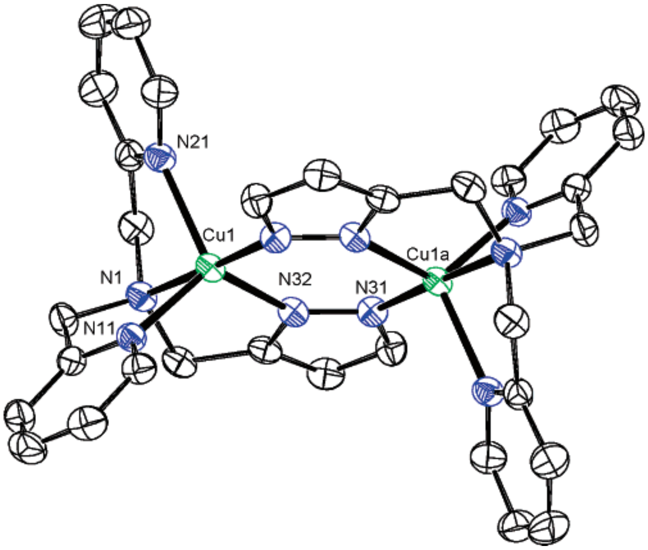

Figure 2. The crystal structure of the complex cation of **1**. Thermal ellipsoids are at 50% probability level. Hydrogen atoms, ClO_4^- ions, and CH_3CN molecules are not shown for clarity.

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for Compound **1**[a]

Cu1−N1	2.043(2)	Cu1−N11	2.077(2)
Cu1−N21	2.140(2)	Cu1−N32	2.013(2)
Cu1−N31a	1.933(2)		
N1−Cu1−N11	81.89(9)	N1−Cu1−O21	79.72(11)
N1−Cu1−O32	81.53(9)	N1−Cu1−N31a	178.38(10)
N11−Cu1−N21	110.63(9)	N11−Cu1−N32	122.11(10)
N11−Cu1−N31a	99.25(10)	N21−Cu1−N23	120.11(10)
N21−Cu1−O31a	98.78(11)	N32−Cu1−N31a	98.78(10)

[a] Symmetry operations: *x*, *y*, *z*; -*x*, -*y*, -*z*.

178.38(10)°. The angles around the copper(II) atom in the basal plane vary from 110.63(9)° to 122.11(10)°, indicating a slightly distorted TBP geometry. Such a distortion can be quantitatively characterized using the parameter τ as defined by Addison et al. ($\tau = 1$ for the trigonal bipyramid and 0 for the square pyramid).[33] The calculated value $\tau = 0.93$ indicates a small degree of distortion of the coordination polyhedron. In addition, the copper(II) atom slightly deviates from the equatorial plane by 0.008 Å in the direction of the aliphatic nitrogen. As imposed by the crystallographic restrictions, the two pyrazolato planes are strictly parallel. The bending angle of the pyrazole least-squares plane to the Cu1−N31−N32−Cu1a plane is 8.12(16)°. The Cu1⋯Cu1a distance is 3.9120(5) Å. Compared to those of related doubly pyrazolato-bridged copper(II) complexes, the Cu⋯Cu separation is much longer, probably as a result of the steric constraints induced by the pyridyl arms (Table 3).[34−37] A similar feature was observed in a closely related nickel(II) dinuclear compound.[38] No intermolecular stacking interactions are observed.

Magnetic Susceptibility Measurements. Magnetic susceptibility measurements of **1** have been recorded in the 2−300 K temperature range (Figure 3). At 300 K, the product of the molar susceptibility times the temperature ($\chi_m T$) equals 0.527 cm^3 mol^{-1} K, a value which is considerably lower than the theoretical value expected for two noncoupled Cu(II) centers with $S = 1/2$ (0.75 cm^3 mol^{-1} K). The $\chi_m T$ value decreases monotonically when the temperature is lowered to 2 K. This behavior is characteristic of dominant antiferromagnetic interactions. To estimate the exchange parameters in **1**, the experimental data were fitted to the Bleaney−Bowers equation for a dinuclear copper(II) complex

$$\chi_m T = \frac{2Ng^2\beta^2}{k[3 + \exp(-2J/kT)]}(1 - \rho) + \frac{Ng^2\beta^2}{2k}\rho$$

where J is the singlet−triplet energy gap (derived through the isotropic Hamiltonian $\hat{H} = -2J\hat{S}_1\hat{S}_2$) with $S_1 = S_2 = 1/2$ (interacting local spins) and N, g, β, and T have the usual meanings; ρ is the molar fraction of the noncoupled species.[39] A TIP (temperature-independent paramagnetism) of 60 × 10^{-6} cm^3 mol^{-1} was taken into account. The least-squares fitting led to the set of magnetic parameters $-2J = 188$ cm^{-1}, $g = 2.2$, and $\rho = 0.015\%$ with an agreement factor of $R = 1.4 \times 10^{-4}$ (R is defined as $\sum[(\chi_m)_{obsd-}(\chi_m)_{calcd}]^2/\sum[(\chi_m)_{obsd}]^2$).

In Table 3, the most relevant data for structural and magnetically characterized bis(pyrazolato) doubly bridged copper(II) dinuclear complexes are presented. The strength of the antiferromagnetic interaction in pyrazolato-bridged copper(II) complexes with pentacoordinate metal centers is expected to decrease as the distortion of the copper(II) geometry increases from square pyramidal (SP) toward TBP. In TBP geometry, the overlap of the magnetic d_{z^2} orbital is weaker and less effective than that in SP geometry with $d_{x^2-y^2}$, as the magnetic orbital and the bridging ligands are bonded in the *xy* plane. However, as shown in Table 3, no direct correlation is found between τ and the strength of the magnetic coupling. Magnetostructural correlations for bis(pyrazolato) doubly bridged copper(II) were considered by Bencini and co-workers[40] using extended Hückel molecular-orbital calculations. Their calculations predicted that deviation from the coplanarity of the two pyrazolato bridges has the largest effect on the exchange interaction and can in principle also change the sign of the interaction. The noncoplanarity of the copper coordination planes compensates for this effect.

If the J value obtained for compound **1** is compared with those reported for related systems, some considerations may be stated. It appears that the observed moderate antiferromagnetic coupling is related more to the effect of the binding angle of the pyrazole arm of the Npy$_2$pz$^-$ ligand and less to the coordination sphere around the copper(II) center: $\delta_{pz-bend}$

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Table 3. Relevant Structural and Magnetic Data for Bis(pyrazolato) Doubly Bridged Copper(II) Dinuclear Complexes[a]

compound	Cu···Cu (Å)	$\delta_{pz-bend}$ (deg)	δ_{pz-pz} (deg)	$\delta_{CuNN'}$ (deg)	τ	$-2J$ (cm^{-1})	ref
$[Cu_2(phen)_2(pz)_2(NO_3)(H_2O)](NO_3)$	3.335(3)	6.6	110.3	90.5	0.61	143	35
$[Cu_2(phen)_2(pz)_2(NO_3)_2]$	3.356(3)	2.4	106.9	90.8	0.63	166	35
$[Cu_2(phen)_2(4\text{-}Clpz)_2(NO_3)_2]\cdot 2CH_3OH$	3.266(2)	3.9	112.2	83.7	0.55	238	35
$[Cu_2(phen)_2(4\text{-}Brpz)_2(NO_3)_2]\cdot 2CH_3OH$	3.225(3)	4.5	113.1	83.7	0.54	227	35
$[Cu_2(bpy)_2(4\text{-}Mepz)_2(H_2O)_2](NO_3)_2$	3.3024(10)	9.6	88.3	87.7	0.10	244	35
$[Cu_2(phen)_2(4\text{-}Mepz)_2(H_2O)_2](NO_3)_2$	3.241(3)	4.1	100.7	87.1	0.14	268	35
$[Cu_2(phen)_2(pz)_2Cl_2]\cdot 2C_2H_5OH$	3.336(1)	nr	75.6(2)	nr	0.57	169	37
$[Cu_2(4\text{-}Br\text{-}3\text{-}CO_2mepz)_2(4\text{-}BrdmpzH)_2]$	3.924	nr	nr	98.6	0.70	148	36
$[Cu_2(Npy_2pz)_2](ClO_4)_2\cdot 2CH_3CN$	3.9120(5)	8.1	180	180	0.93	188	this work
$[Cu_2(L)_2](BPh)_2$	3.903(2)	nr	92	nr	0.15	240	34

[a] pz = pyrazolate, 4-Mepz = 4-methylpyrazolate, 4-Clpz = 4-chloropyrazolate, 4-Brpz = 4-bromopyrazolate, phen = 1,10-phenanthroline, bpy = 2,2′ − bipyridine, mepz = methylpyrazolate, 4-BrdmpzH = 4-bromo-3,5-dimethylpyrazole, L = 3,5-bis(2-diethylamino)ethylaminomethyl)pyrazole, nr = not reported.

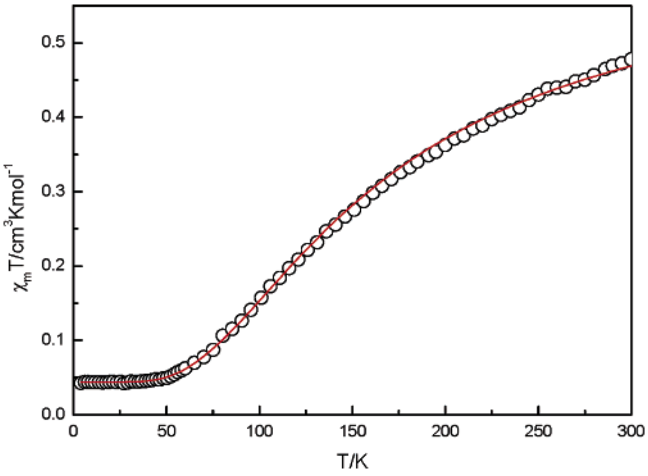

Figure 3. Plot of $\chi_m T$ vs temperature for compound **1**: (○) experimental values, (—) calculated values for $g = 2.2$, $-2J = 188\ cm^{-1}$, and $\rho = 0.015\%$.

$= 8.12°$, $\delta_{pz-pz} = 180°$, and $\delta_{CuNN'} = 180°$. The dihedral angle ($\delta_{pz-bend}$) of the least-squares plane of the pyrazole ring relative to the Cu−N(pz)−N(pz)−Cu plane is proposed to be the most important factor affecting the magnetic interaction; the $-2J$ value decreases as $\delta_{pz-bend}$ bending angle becomes larger because the magnetic d_{z^2} and $d_{x^2-y^2}$ orbitals give a much smaller overlap with the pyrazole ligand σ orbital when $\delta_{pz-bend}$ is large.[35] On the other hand, moderate to strong antiferromagnetic interactions, through the pyrazolato bridge, also occur when the dihedral angles between the planes of pyrazole molecules (δ_{pz-pz}) and the dihedral angles between the $CuN_{pz}N_{pz}'$ planes (δ_{CuNN}') are equal to 180°, as was also observed in the present case.[34,40] A strong effect of the geometry of the bridging ligand on the strength of the magnetic interaction has also been reported in the case of triazolato-bridged copper(II) complexes.[41]

Solution Chemistry Studies. To estimate the stability of the dicopper(II) core in solution, we have studied the behavior of **1** in solution by ESI-MS, UV/vis, EPR, and NMR spectroscopy, and we also studied it electrochemically. The plot of the absorption at 814 nm in an acetonitrile solution of **1**, in the concentration range of 0.3375−10 mM, versus the complex concentration gives a straight line ($R = 0.999$), suggesting that only one type of species is present in solution in the whole concentration range (Figure S1, Supporting Information). However, the positive-ion electrospray MS spectrum of a 1 mM acetonitrile solution of **1** is characterized by two peaks, corresponding to the mononuclear $[Cu(Npy_2pz)(CH_3CN)]^+$ ($m/z = 384.8$, $I = 100\%$) and dinuclear $[[Cu(Npy_2pz)]_2(ClO_4)]^+$ fragments ($m/z = 784.2$, $I = 20\%$). In the ESI-MS spectrum recorded in a 5 mM solution of **1** in acetonitrile, only one peak at $m/z = 784.2$ with a relative intensity, I, of 100%, corresponding to the dinuclear $[[Cu(Npy_2pz)]_2(ClO_4)]^+$ species, was found in the range $m/z = 200-1000$. A further indication of the presence of both the mononuclear and dinuclear species at equilibrium in the acetonitrile solution of **1** was obtained by EPR spectroscopy. The X-band EPR spectrum, recorded in a 5 mM solution of the complex, shows a superposition of two sets of signals (Figure S2, curve a, Supporting Information). The spectrum was reasonably well simulated, considering two noninteracting species, mononuclear and dinuclear, in the molar ratio 3.88:1. The best simulating parameters were for the **A** species (mononuclear): $g_x = 2.02$, $g_y = 2.08$, $g_z = 2.17$, $A_x = 27$ G, $A_z = 140$ G. Species **B** (dinuclear): $g_x = 2.06$, $g_y = 2.15$, $g_z = 2.11$, $A_z = 350$ G, zero-field splitting (D) = $0.05\ cm^{-1}$.

A cyclic voltammogram of a 1 mM solution of **1** in acetonitrile, recorded at room temperature with $TBAPF_6$ as the supporting electrolyte, shows the occurrence of a reversible reduction at $E_{1/2} = -0.73$ V vs Ag/AgCl (scan rate 20 mV/s), which can be attributed to the Cu^{II}/Cu^{I} redox couple of the mononuclear $[Cu(Npy_2pz)(CH_3CN)]^+$ species (Figure S3, Supporting Information). For a 5 mM solution of **1** in the same conditions, two irreversible ill-resolved reduction waves are present at $E_{pc}{}^1 = -0.63$ V and $E_{pc}{}^2 = -0.86$ V, which were tentatively assigned to the $Cu^{II}Cu^{II}/Cu^{II}Cu^{I}$ and $Cu^{II}Cu^{I}/Cu^{I}Cu^{I}$ redox couples of the dicopper(II) core (Figure S4, Supporting Information). After a first reduction−oxidation cycle, the shape of the cathodic peaks is altered, suggesting that the poor electrochemical behavior of the $Cu^{II}Cu^{II} \rightarrow Cu^{I}Cu^{I}$ is indicative of the accompanying structural changes being rate-limiting on the cyclic voltammetry time scale.

It is thus obvious that mononuclear and dinuclear species exist in equilibrium in acetonitrile solution. At low complex concentration, the complex dissociates into two mononuclear

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units, because of the poor bridging ability of the pyrazolate moiety, whereas at higher concentration levels, the mixture of two species is present in solution.

^{1}H NMR Studies. The moderate antiferromagnetic coupling between the two copper(II) ions, observed in the solid state, prompted us to attempt studying its solution properties by ^{1}H NMR spectroscopy. The slow electronic relaxation of Cu(II) ions usually results in large line widths and poor resolution of the spectra which makes their interpretation very difficult, if not impossible. However, if two antiferromagnetically coupled copper(II) ions are present in a complex, the situation is different. In antiferromagnetically coupled dicopper(II) systems, the ground state is a diamagnetic ($S = 0$) singlet. The energy separation between the ground state and the paramagnetic ($S = 1$) excited triplet state, which increases with the strength of the antiferromagnetic coupling, may lead to relatively sharp resonances, facilitating the interpretation of the spectra.[42]

The ^{1}H NMR spectrum of **1** was recorded in the temperature interval of 233−353 K in a concentrated CD_3CN solution. The resonances originating from the mononuclear species are believed to broaden beyond recognition, and only the peaks originating from the dinuclear species are observed in the spectrum. The resonances shift upfield as the temperature increases, so the complex shows Curie behavior, in full agreement with the antiferromagnetic coupling between the copper ions. Proton assignments have been carried out from a comparison with related complexes, integrations, and T_1 values. Only four broad resonances were found in the 0−60 ppm range, independent of the temperature (Figure S5, Supporting Information). This implies that the resonances corresponding to the protons of all three methylene groups, as well as the α-protons of the pyridine rings, are broadened beyond recognition because of the close proximity to the paramagnetic centers. Three resonances, 22.0, 21.8, and 9.7 ppm, integrate as 1:1:1 and were tentatively assigned to β, β', and γ protons of the pyridine rings. Earlier studies, published by Holz and co-workers,[43−45] argue that the dominant relaxation pathway in spin-coupled dicopper(II) complexes is a paramagnetic dipolar relaxation. In this case, the Cu−H distance, r, should be proportional to $T_1^{1/6}$. Using the equation $r_i = r_{\mathrm{ref}}(T_{1i}/T_{1\mathrm{ref}})^{1/6}$, in which r_i and T_i are the Cu−H distance and the relaxation time of proton i and r_{ref} and T_{ref} are the Cu−H distance and the relaxation time of the reference proton, the distances of each proton to the copper(II) centers can be calculated. As previously shown, the pyridyl resonances are usually subject to large isotropic shifts in the order $\alpha > \beta > \gamma$, on the basis of the fact that the shifts increase with closer proximity to the copper(II) center.[46] Therefore, if the least hyperfine-shifted resonance at 9.7 ppm is ascribed to the γ pyridine proton, as the most distant from the paramagnetic centers, and is used as a reference ($r_{\mathrm{ref}} = 5.748$ Å in this case, an arithmetic average of the Cu−H distances of two equivalent γ protons in the crystal structure was used), the Cu−H distances of 4.938 and 5.056 Å are obtained for the resonances at 22.9 and 21.9, respectively. The comparison of these values to the crystal structure data suggests that the resonance at 22.9 ppm should be assigned to the 3′ proton and the one at 21.9 ppm should be assigned to the 5′ proton of the pyridine rings. A very broad resonance at ca. 51 ppm, the exact integration of which is not certain because of its broadness, could correspond to the two protons of the pyrazolate moieties. However, an accurate assignment would be possible only by selective chemical substitution of the protons in question, which is not within the scope of the current investigation.

Conclusion

In summary, we have shown that the HNpy$_2$pz ligand enforces the assembly of a dinuclear structure with a high stability in the solid state and moderate stability in acetonitrile solution. Compound **1** represents the first example of a dinuclear copper(II) complex with only pyrazolato bridges and a nearly perfect TBP geometry around the metal centers, with all coordination sites being occupied by ligand donor atoms only. The pyrazolate bridges mediate a moderate antiferromagnetic coupling between the metal centers, the magnitude of which is believed to be defined by the effect of the binding angle of the pyrazole arm of the HNpy2pz ligand. The spectroscopic and electrochemical properties of the complex in CH_3CN solution are also reported and agree with a concentration-dependent mixture of mononuclear and dinuclear species.

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Supporting Information Available: Figures showing the plot of the absorption at 814 nm versus the concentration for an acetonitrile of **1**, the cyclic voltammogram curves of the complex in 1 and 5 mM acetonitrile solution, the recorded and simulated EPR spectrum of **1** in a 5 mM solution, and the ^{1}H NMR spectrum of **1** in CD_3CN and crystalloraphic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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