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Article

Novel Metal-Linked Face-to-Face Porphyrazine Dimer

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We report the synthesis and physical studies of a novel porphyrazine (pz) dimer {**1**[Ni,Cu]}$_2$, which has Ni(II) ions incorporated into the pz cores and is linked by two Cu(II) ions coordinated to bis(picolinamide) chelates attached to the pz periphery. {**1**[Ni,Cu]}$_2$ was prepared from precursor pz **2** with a selenodiazole ring fused to the pz core. This ring was deprotected to form the diamino-pz **3**, which reacted with 2 mol of picolinoyl chloride hydrochloride to form pz **1**[2H,2H], with peripheral bis(picolinamide) chelates; this was metalated to form {**1**[Ni,Cu]}$_2$. The crystal structures of **1**[2H,2H] and {**1**[Ni,Cu]}$_2$ are presented. The latter is a dimer in which parallel, face-to-face pz's with an average separation of 3.30 Å are linked through the peripheral picolinamide ligands by a pair of peripheral Cu(II) ions. Each Cu(II) is coordinated with distorted square-planar geometry by a picolinamide from each pz. In this report, we focus on the interaction of these two peripheral Cu(II) ions. We discuss the preparation and magnetic properties of the pz dimer complex {**1**[Ni,Cu]}$_2$ with two Cu(II) ions in the peripheral chelate but a diamagnetic metal ion Ni(II) in the pz core. Although {**1**[Ni,Cu]}$_2$ contains two Cu(II) ions ($S = {}^1/_2$), we could detect no electron paramagnetic resonance signal, which suggests very strong antiferromagnetic exchange between those two Cu(II) ions. Temperature-dependent magnetic susceptibility measurement gives an exchange splitting between the $S = 0$ ground state and the excited triplet state of $\Delta = 660$ cm^{-1}.

Introduction

There is considerable interest in the synthesis of dinuclear Cu(II) complexes because of their relevance as models for active sites of biomolecules[1] and also because of interest in the relationships between their magnetic properties and molecular structures.[2−5] More than 900 dimeric Cu(II) compounds have been structurally characterized and categorized by Melnik et al.[6] according to the type of bridge between the two Cu(II) atoms. Two types of bridges are most common: the first is the copper acetate type; the second has small anion (e.g., halide or hydroxy) bridging groups. There are few reports on dinuclear Cu(II) ions incorporated in electron-rich macrocycle ligand systems.

We recently showed that porphyrazines (pz's) can act as scaffolds on which to build complex peripheral chelating ligands.[7−10] We prepared pz's with bis(Schiff base) chelates appended and showed that the resulting complexes display intriguing core−periphery spin coupling. Here we report an alternate system in which bis(picolinamide) chelates are appended to the pz core. Vagg and co-workers prepared a series of bis(picolinamide) chelates that bind a metal ion by two central amido nitrogens and two terminal pyridyl nitrogens.[11] These ligands were used to prepare a range of transition-metal complexes, including several with Cu(II)

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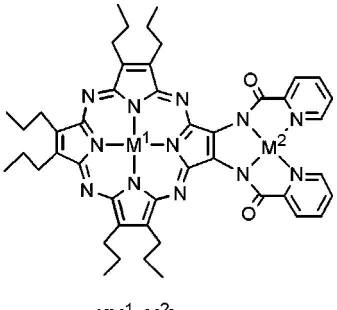
Chart 1



1[M^1, M^2]

ions.[12−22] We here have appended this ligand to the pz periphery so as to enable the formation of bimetallic complexes, **1**[M^1,M^2] (Chart 1). It was anticipated that M^2 = Cu(II) ions in the peripheral chelate would exhibit square-planar coordination[12] and would spin couple with the central M^1 metal ion, as in the Schiff base pz's.[8−10] However, the reaction of **1**[Ni,2H] with copper acetate surprisingly yields a face-to-face pz dimer in which parallel pz's are linked through the peripheral picolinamide ligands by a pair of peripheral M^2 = Cu(II) ions. With the appropriate metal ions bound in the pz core, such a structure, derived through a convenient high-yield synthesis, may well have future catalytic applications. Here we report the preparative scheme and discuss the magnetic properties of pz dimer complex {**1**[Ni,Cu]}$_2$ with two M^2 = Cu(II) ions in the peripheral chelate but diamagnetic metal ions M^1 = Ni(II) in the pz cores.

Experimental Section

Materials and Methods. All starting materials were purchased from Aldrich Chemical Co. and used as received, with the exception of picolinoyl chloride hydrochloride, which was purchased from TCI and used as received. All solvents were used as supplied. Silica gel used for chromatography was Whatman silica gel 60 Å (230−400 mesh) from VWR. Alumina gel used for chromatography was Brockmann I aluminum oxide 58 Å (∼150 mesh) from Aldrich. Pz **2** was prepared as previously reported.[23]

^{1}H NMR spectra were obtained using a mercury 400-MHz spectrometer. Electronic absorption spectra were recorded using a Hewlett-Packard HP8452A diode array spectrophotometer. Elemental analyses were performed by Quantitative Technologies Inc. (Whitehouse, NJ). Atmospheric phase chemical ionization mass spectra (APCI-MS) and electron spray ionization mass spectra (ESI-MS) were recorded using a Finnigan LCQ Advantage mass spectrometer. Electron paramagnetic resonance (EPR) spectra were measured by using a modified Varian E−4 X-band spectrometer. Solid-state magnetic susceptibility measurements were made by using a Quantum Design MPMS SQUID susceptometer operating in the temperature range 2−300 K and equipped with a 500-G field.

H$_2$[pz(A;B$_3$)] {A = Bis(picolinamide), B = (*n*-Propyl)$_2$; 1[2H,2H]}. To a solution of pz **2** (100 mg, 0.144 mmol) in 50 mL of pyridine was bubbled H_2S for 8 min, in which time the solution color changed from blue to violet. Picolinoyl chloride hydrochloride (513 mg, 7.2 mmol, 50-fold excess) was then added under anaerobic conditions. The reaction was allowed to stir at room temperature overnight. The solvent was removed under vacuum, and the residue was dissolved in 50 mL of chloroform and then stirred with saturated $NaHCO_3$(aq) for 0.5 h. The organic phase was collected and washed with water three times, after which it was dried by Na_2SO_4. The pz was chromatographed on silica gel using CH_3OH/CH_2Cl_2 (1:200) as the eluant. The major purple band was collected (70 mg, 60% yield based on **2**). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.26−1.34 (12H, m), 1.38 (6H, t, J = 6.6 Hz), 2.26−2.42 (8H, m), 2.46 (4H, q, J = 8 Hz), 3.81 (4H, t, J = 6.8 Hz), 3.94−4.06 (8H, m), 7.65 (2H, m), 8.01 (2H, m), 8.46 (2H, m), 8.95 (2H, m), 10.2 (2H, b). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 347 (4.74), 572 (4.48), 631 (4.18) nm. APCI-MS: calcd for $C_{46}H_{55}N_{12}O_2$ (M + H$^+$), *m/z* 807.5; found, *m/z* 807.6.

Ni[pz(A;B$_3$)] {A = Bis(picolinamide), B = (*n*-Propyl)$_2$; 1[Ni,2H]}. A mixture of pz **1**[2H,2H] (50 mg, 0.062 mmol), $NiBr_2$ (135 mg, 0.62 mmol, 10-fold excess), and 2,6-lutidine (2 mL) was dissolved in a stirred 1:1 tetrahydrofuran/toluene mixture (50 mL). The reaction was heated to reflux temperature for 8 h, after which time there was no free base form left. The solvents were removed under vacuum, and the residue was dissolved in methylene chloride (40 mL). A total of 4 mL of trifluroacetic acid (TFA) was slowly added to the solution, and the solution was stirred at room temperature for 1 h. The mixture was neutralized with dilute $NaHCO_3$(aq), washed with a large amount of water, and rotavaped. The pz was chromatographed on silica gel using CH_3OH/$CHCl_3$ (1:200) as the eluant. The major blue purple band was collected (51 mg, 96% yield based on **1**[2H,2H]). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 328 (4.67), 600 (4.64) nm. ESI-MS: calcd for $C_{46}H_{55}N_{12}O_2Ni$ (M + H$^+$), *m/z* 863.4; found, *m/z* 863.8.

{Ni[pz(A;B$_3$)]}$_2$ {A = Copper(II) Bis(picolinamide), B = (*n*-Propyl)$_2$; {1[Ni,Cu]}$_2$}. Pz **1**[Ni,2H] (100 mg, 0.116 mmol) and copper acetate (210 mg, 1.16 mmol, 10-fold excess) in a 1:1 mixture of chloroform and methanol were heated to reflux. The reaction was monitored by UV−vis and was stopped after there was no change in the optical spectra. The pz was chromatographed on alumina gel using CH_3OH/CH_2Cl_2 (1:50) as the eluant. The major purple band was collected (96 mg, 90% yield based on **1**[Ni,2H]). UV−vis (CH_2Cl_2): λ_{max} (log ϵ) 319 (5.04), 590 (4.85). ESI-MS: calcd for $C_{92}H_{101}N_{24}O_4Ni_2Cu_2$ (M + H$^+$), *m/z* 1849.6; found, *m/z* 1849.6. Anal. Calcd for $C_{92}H_{104}N_{24}O_6Ni_2Cu_2$ ({**1**[Ni,Cu]}$_2$ + $2H_2O$): C, 58.58; H, 5.56; N, 17.82. Found: C, 58.68; H, 5.30; N, 17.75.

X-ray Structure Determination. Single crystals suitable for X-ray data collection were grown from MeOH/CH_2Cl_2 for **1**[2H,2H] and MeOH/pyridine for {**1**[Ni,Cu]}$_2$. All measurements were made on a CCD area detector with graphite-monochromated Mo Kα radiation. A summary of the crystal data, data collection, and

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Table 1. Crystallographic Data for **1**[2H,2H] and {**1**[Ni,Cu]}$_2$

	1[2H,2H]	{**1**[Ni,Cu]}$_2$
formula	$C_{47}H_{56}O_2N_{12}$	$C_{101}H_{109}N_{24}O_7Cu_2Ni_2$
formula weight	891.94	2015.62
color, habit	purple, needle	dark red, needle
crystal size/mm	0.840 × 0.124 × 0.090	0.680 × 0.116 × 0.010
lattice type	triclinic	monoclinic
space group	$P\bar{1}$	Cc
a/Å	9.918(6)	14.254(3)
b/Å	14.017(10)	52.652(13)
c/Å	17.535(10)	13.443(2)
α/deg	100.04(4)	90
β/deg	91.68(6)	101.065(17)
γ/deg	105.88(10)	90
V/Å^3	2301(2)	9901(4)
Z	2	4
D_c/g cm^{-3}	1.287	1.352
F(000)	944	4212
T/K	153(2)	153(2)
$2\theta_{\max}$/deg	57.66	58.04
no. of total reflns measd	20464	45743
no. of obsvns	10535 ($R_{\text{int}} = 0.1735$)	22681 ($R_{\text{int}} = 0.0846$)
no. of variables	590	1249
R1^a	0.0782	0.0646
wR2^b	0.1865	0.1482

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.

refinement parameters for these two compounds is provided in Table 1. Both structures were solved by direct methods, expanded using Fourier techniques, and refined by full matrix least squares based on F^2. All of the non-hydrogen atoms of both complexes were refined anisotropically.

Results and Discussion

Synthesis and Structure of 1[2H,2H]. Attempts to prepare the bis(picolinamide)-pz **1**[2H,2H] by directly cocyclizing 2,3-dipropylmaleonitrile with bis(picolinamide)-maleonitrile were unsuccessful. We therefore utilized the procedure devised by Baum et al.[23] and employed in the preparation of the Schiff base pz's.[8−10] Diamine-pz **3** was formed in situ through reductive deselenation of pz **2** (Scheme 1) by treatment with H_2S in pyridine[24] and then anaerobically treated with 50-fold excess picolinoyl chloride hydrochloride to generate **1**[2H,2H] because **3** is unstable in air.

Purple needlelike crystals of **1**[2H,2H] were grown from MeOH/CH_2Cl_2, and the structure was solved. An ORTEP drawing of **1**[2H,2H] is presented in Figure 1. The pz core is planar to within 0.01 Å. Two picolinamide groups are linked to the pz macrocycle through amide bonds whose C−N bond lengths (1.36 Å for both) are comparable to those of typical amide bonds (1.33 Å). The carbonyl groups have a trans geometry with the N−H groups to alleviate steric interaction. The carbonyl and pyridyl groups of each picolinamide form a conjugated system and lie in a plane. These planes are rotated anti by angles of 32.2° and 49.4° relative to the pz macrocycle plane.

Synthesis and Structure of {1[Ni,Cu]}$_2$. The reaction of **1**[2H,2H] with $NiBr_2$ introduced Ni(II) into the pz core and the peripheral bis(picolinamide) chelate. The Ni(II) ion on the periphery is not stable in acidic conditions and was removed by treatment with TFA to afford **1**[Ni,2H]. We expected that peripheral metalation of **1**[Ni,2H] with Cu(OAc)$_2$ would yield the **1**[Ni,Cu] pz complex, which would show the EPR spectrum of a copper(II) bis(picolinamide) complex. However, we found the product to be EPR-silent and SQUID measurement showed it to have a very small susceptibility (see below), results incompatible with such an expectation. This anomaly was explained by crystallizing the product from MeOH/pyridine and determining its structure, which was revealed to be the dimer {**1**[Ni,Cu]}$_2$ (Figure 2). We believe the formation of the dimer is partially due to the poor solubility of **1**[Ni,2H], which caused it to dimerize in solution, as previously reported for copper(II) octathiomethyl-pz.[25]

The pz {**1**[Ni,Cu]}$_2$ dimer exhibits staggered, cofacially stacked pz's that are linked by two Cu(II) "linkers", with each Cu(II) coordinated by a picolinamide from each of the pz's, as showed in the top view of Figure 2. The two pz rings are almost parallel with a separation of 3.30 Å, while the Ni−Ni distance is 3.8 Å (side view of Figure 2). The four pyrrole nitrogen atoms of each of the macrocycles are coplanar within experimental error. The Ni(II) ion of each molecule lies in the least-squares plane defined by the inner pyrrolic nitrogen atoms. The Ni−N bond distances (1.87−1.89 Å) and angles (89.7−90.8°) are comparable to our previously reported values.[26−28] The peripheral Cu(II) ions are tetrahedrally coordinated with two amide and two pyridine nitrogen atoms. The bond distances of Cu(II)−N(amide) and Cu(II)−N(pyridine) are 1.94 and 1.98 Å, respectively. The dihedral angles defined by the picolinamide moieties bound to Cu(a) and Cu(b) are 45.3 and 42.9°, respectively; they would by 90° for tetrahedral coordination and 0° for square-planar coordination. Each Cu(II) ion coordinates one amide nitrogen atom from both upper and lower pz complexes to link these two pz macrocycles to form the dimer. The Cu−Cu distance is 4.82 Å.

UV−Vis Spectra. The UV−vis spectra of **1**[2H,2H], **1**[Ni,2H], and {**1**[Ni,Cu]}$_2$ are shown in Figure 3. The Ni(II) pz **1**[Ni,2H] exhibits an intense Soret band at $\lambda_{\max} = 328$ and 600 nm. The spectrum of the free-base pz **1**[2H,2H] with the same peripheral substituents is qualitatively similar but with the expected split Q band, $Q_x = 572$ nm and $Q_y = 631$ nm. The pz {**1**[Ni,Cu]}$_2$ has a Soret band at 319 nm, blue-shifted by 9 nm with respect to the corresponding monoporphyrazine **1**[Ni,2H]. The blue shift is the result of $\pi-\pi$ interactions and has been observed with

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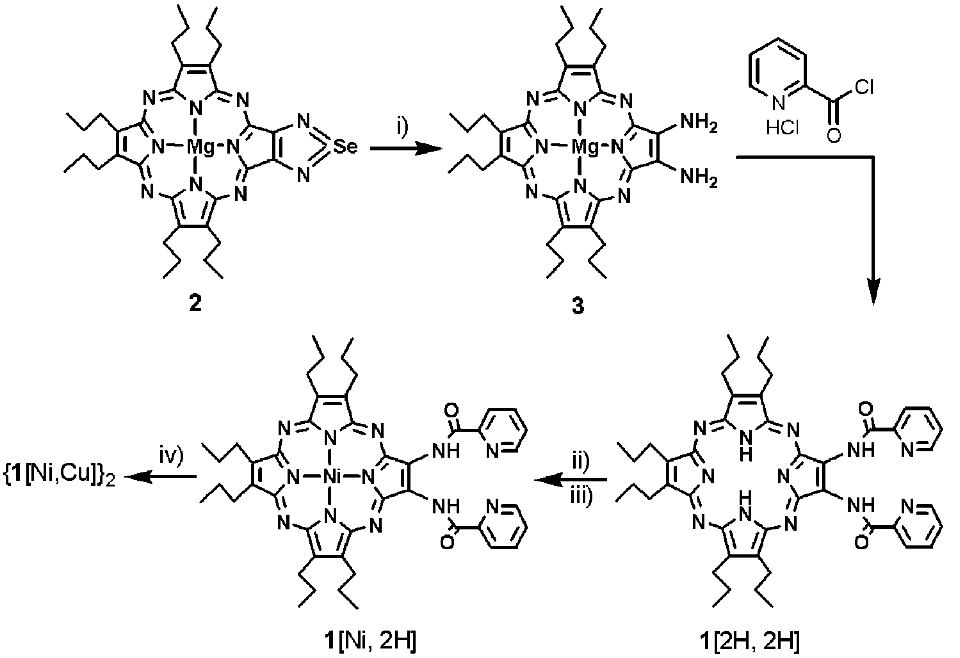
Scheme 1. Synthesis of $\{\mathbf{1}[\mathrm{Ni,Cu}]\}_2$[a]



[a] (i) H_2S, pyridine, room temperature. (ii) $NiBr_2$, dimethylformamide/chlorobenzene/lutidine. (iii) TFA, CH_2Cl_2, room temperature. (iv) $Cu(OAc)_2$, MeOH, $CHCl_3$, reflux.

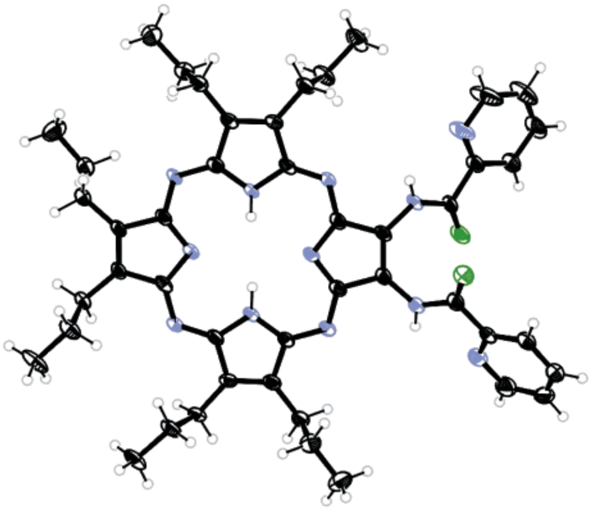


Figure 1. Molecular structure of $\mathbf{1}[2H,2H]$.

porphyrin sandwich complexes and cofacial porphyrin complexes.[29,30]

Magnetic Properties. The absence of a detectable EPR signal from $\{\mathbf{1}[\mathrm{Ni,Cu}]\}_2$, either in a fluid solution at 298 K or in a frozen glass at 77 K, implies that the two spins of the dimer are strongly antiferromagnetically coupled, with a diamagnetic $S = 0$ ground state and negligible thermal population of the corresponding triplet excited state.[31-33] To estimate the value of the singlet−triplet exchange parameter, J, the magnetic susceptibility of $\{\mathbf{1}[\mathrm{Ni,Cu}]\}_2$ was measured between temperatures of 2 and 300 K using a SQUID magnetometer. A plot of molar susceptibility versus temperature for $\{\mathbf{1}[\mathrm{Ni,Cu}]\}_2$ (Figure 4) was fitted to the

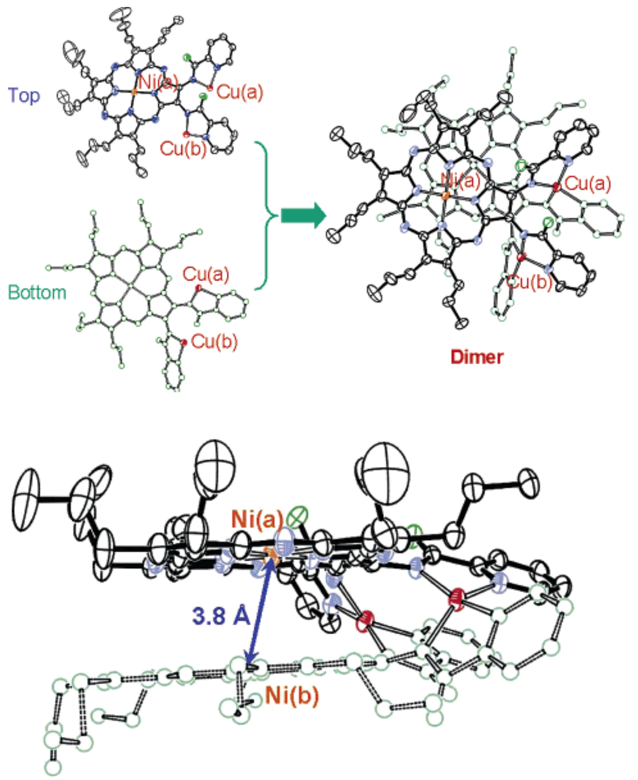


Figure 2. Top and side views of molecule $\{\mathbf{1}[\mathrm{Ni,Cu}]\}_2$. Atoms of the bottom part are represented by green circles for clarity.

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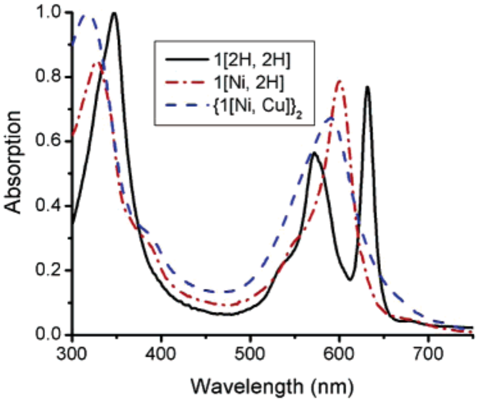

Figure 3. UV−vis spectra for pz's **1**[2H,2H], **1**[Ni,2H], and {**1**[Ni,Cu]}$_2$ in CH_2Cl_2.

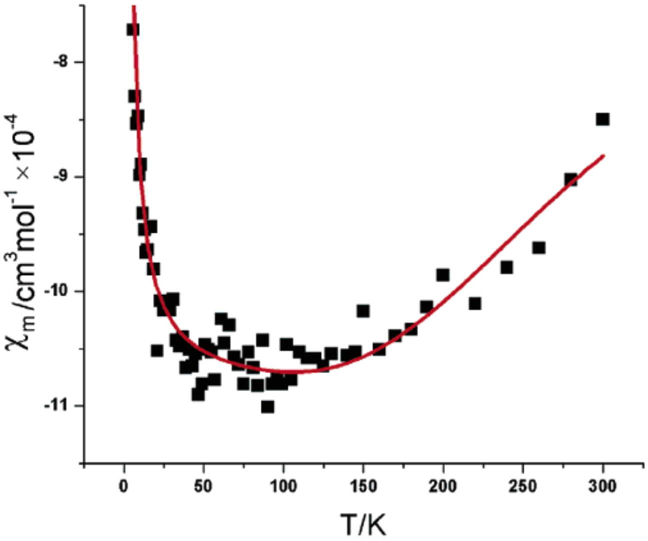

Figure 4. Plot of the molar magnetic susceptibility of a powdered sample of {**1**[Ni,Cu]}$_2$. The solid line was fit to the data by eq 1, with $g = 2.03$, $J = 660$ cm^{-1}, $\rho = 0.005$, and $N\alpha = -0.001$ cm^3 mol^{-1}.

Bleaney−Bowers equation (eq 1),[34] based on the zero-field

$$\chi_m = \frac{N\beta^2 g^2}{3kT}\left[1 + \frac{1}{3}\exp(J/kT)\right]^{-1}(1-\rho) + \frac{[N\beta^2 g^2]\rho}{4kT} + N\alpha \qquad (1)$$

spin Hamiltonian $H = JS_1S_2$ for two interacting $S = {}^1/_2$ centers, where χ_m is expressed per mole of copper atoms, ρ is the mole fraction of mononuclear impurity, $N\alpha$ corrects for the presence of temperature-independent paramagnetism, and the other symbols have their usual meanings. The sharp increase in χ_m at low temperature arises from a very small amount of paramagnetic impurity, $\rho \approx 0.5\%$.[35] The gentle increase in χ_m with temperature above ~100 K is described by eq 1 with $g = 2.03$ and $J = 660$ cm^{-1}.

Conclusion

In summary, a new ligand system, **1**[2H,2H], comprised of a pz peripherally functionalized with two picolinamide ligands, has been synthesized and structurally characterized. During metalation, this system surprisingly yields a novel face-to-face pz dimer, {**1**[Ni,Cu]}$_2$, with parallel pz's at an average separation of 3.30 Å, linked through the peripheral picolinamide ligands by two M^2 = Cu(II) ions. Here we have focused on the strong exchange coupling between the two peripheral, pseudotetrahedral Cu(II) ions that link the two pz's, finding strong antiferromagnetic coupling between them. The dimer structure, derived through a convenient high-yield synthesis, has the core metal ions at a distance that might be favorable for binding and reducing O_2 when M^1 = Mn, Fe, or Co. We plan to prepare those complexes and to test this possibility.[36−39]

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Supporting Information Available: X-ray crystallographic files in CIF format for compounds **1**[2H,2H] and {**1**[Ni,Cu]}$_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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