# Synthesis of a Spin-Coupled, Mixed-Metal Double Square Grid Complex $[(poap\text{-}H)_4Cu(II)_3Fe(III)(NO_3)]_2(ClO_4)_4(NO_3)_4\cdot 12H_2O$ (poap = $N^3$-(2-pyridoyl)-2-pyridinecarboxamidrazone) with an $S = 3$ Ground State, from a Mononuclear Fe(III) Precursor Complex

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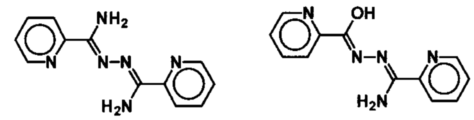
*Received August 11, 2000*

## Introduction

The synthesis of mixed-metal complexes can be achieved by the selective occupation of one polytopic ligand site by one metal, prior to occupancy of a second site by a different metal. Such bridging ligands as oxalate, oxamide, and their derivatives,[1−4] oximes,[5] and polyfunctional ligands derived from phenolic substrates[6−9] have been successfully metalated in this fashion, leading to heterodinuclear complexes. Producing higher nuclearity heteronuclear clusters is more difficult, but there have been some successes.[10] The polyfunctional diazine ligands pahap (picolinamide azine) and poap ($N^3$-(2-pyridoyl)-2-pyridinecarboxamidrazone) (Chart 1) provide several different dinucleating bonding motifs with cis and trans conformations about the single N−N bond,[11] and also oxygen-bridged structures (poap).[12] The magnetic properties vary as a function of the rotation of the magnetic planes about the N−N bond.[11]

This report outlines an unusual reaction between a mononuclear Fe(III) complex $[Fe(Hpoap\text{-}H)(NO_3)(H_2O)_2](NO_3)_2$ (**1**) with a "vacant" coordination pocket and $Cu(ClO_4)_2$ to produce a square $[Cu_3Fe]_2$ gridlike dimeric octanuclear cluster, $[(poap\text{-}H)_4Cu_3Fe(NO_3)]_2(ClO_4)_4(NO_3)_4\cdot 12H_2O$ (**2**), with only alkoxide bridges between the metal centers. Structural and magnetic properties will be discussed in the light of the magnetic orbital connections within the cluster.

**Chart 1**




pahap poap

## Experimental Section

**Physical Measurements.** Electronic spectra were recorded as Nujol mulls and in solution using a Cary 5E spectrometer. Infrared spectra were recorded as Nujol mulls using a Mattson Polaris FTIR instrument. C, H, N, and metal analyses on vacuum-dried samples (24 h) were performed by the Canadian Microanalytical Service, Delta, B.C., Canada. Variable temperature magnetic data (2−300 K) were obtained with a Quantum Design MPMS5S SQUID magnetometer operating at 0.1−5 T. Calibrations were carried out with a palladium standard cylinder, and temperature errors were determined with $[H_2TMEN][CuCl_4]$ ($H_2TMEN = (CH_3)_2HNCH_2CH_2NH(CH_3)_2^{2+}$).[13]

**Synthesis of $[(poap\text{-}H)_4Cu_3Fe(NO_3)]_2(ClO_4)_4(NO_3)_4\cdot 12H_2O$ (2).** $Cu(ClO_4)_2\cdot 6H_2O$ (0.18 g, 0.50 mmol) dissolved in methanol (10 mL) was added to a solution of $[Fe(Hpoap\text{-}H)(NO_3)(H_2O)_2](NO_3)_2$ (**1**)[14] (0.26 g, 0.5 mmol) and triethylamine (0.05 g, 0.5 mmol) in methanol (25 mL). The dark-green solution was stirred at room temperature for 30 min, filtered, and allowed to stand at room temperature for 2 weeks. Dark-green crystals of **2** suitable for structural analysis formed (yield, 0.17 g, 85% based on poap) after 2 weeks. IR (Nujol mull, $cm^{-1}$): 3555 (m) ($\nu(H_2O)$); 3328 (m) ($\nu(NH_2)$); 1737 (w) ($\nu_1 + \nu_4(NO_3)$); 1671 (s) ($\nu$(C=N)); 1086 ($\nu_3(ClO_4)$); 1018 (m) ($\nu$(py)); Vis (Nujol mull) $\lambda$ (nm): 615. Vis ($H_2O$) $\lambda$ (nm) ($\epsilon$ ($M^{-1}\ cm^{-1}$)): 616 (1830). Anal. Calcd for $[Cu_3Fe(C_{12}H_{10}N_5O)_4(NO_3)](ClO_4)_2(NO_3)_2\cdot 6H_2O$: C, 33.90; H, 3.08; N, 18.95; Cu, 11.21; Fe, 3.28. Found: C, 33.81; H, 2.76; N, 18.69; Cu, 11.10; Fe, 3.21. A similar monomeric complex, $[(poap\text{-}H)_4Cu_3Fe(H_2O)_2](ClO_4)_5\cdot H_2O$ (**3**), was produced with essentially the same method except that the reaction mixture was heated.[24] Anal. Calcd for [Cu3-

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10.1021/ic000923v CCC: $20.00 
Published on Web 04/12/2001

**Table 1.** Crystallographic Data for $[Fe(Hpoap-H)(NO_3)(H_2O)_2](NO_3)_2$ (**1**) and $[(poap-H)_4Cu_3Fe(NO_3)]_2(ClO_4)_4(NO_3)_4 \cdot 12H_2O$ (**2**)

| | | |
|---|---|---|
| formula | $C_{12}H_{15}N_8O_{12}Fe$ | $C_{48}H_{50}N_{23}O_{26}Cl_2Cu_3Fe$ |
| space group | $P2_1/c$ | $P2_1/n$ |
| fw | 519.17 | 1682.45 |
| $T$ (K) | 150(2) | 193(1) |
| $a$ (Å) | 8.4517(3) | 14.5592(7) |
| $b$ (Å) | 19.6456(6) | 32.753(2) |
| $c$ (Å) | 12.6511(4) | 14.9417(6) |
| $\beta$ (deg) | 109.400(1) | 116.3010(10) |
| $V$ (Å$^3$) | 1981.3(1) | 6387.5(5) |
| $Z$ | 4 | 4 |
| $\lambda$ (Å) | 0.710 73 | 0.710 73 |
| $\rho_{calcd}$ (g cm$^{-3}$) | 1.74 | 1.749 |
| $\mu$ (cm$^{-1}$) | 8.45 | 13.94 |
| GOF | 1.085 | 1.29 |
| R1($R$) [a] | 0.0462 | 0.052 |
| wR2($R_w$) [a] | 0.0754 | 0.051 |

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[w(|F_o|^2)^2]]^{1/2}$. $R = \sum||F_o| - |F_c||/\sum|F_o|$. $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)]^{1/2}$.

$Fe(C_{12}H_{10}N_5O)_4](ClO_4)_5 \cdot H_2O$: C, 33.47; H, 2.46; N, 16.26. Found: C, 33.44; H, 2.66; N, 16.39.

**X-ray Crystallography.** Diffraction data for a black, rectangular prism of **1** of dimensions 0.13 mm × 0.20 mm × 0.32 mm were collected using a Siemens Smart three-circle diffractometer equipped with a CCD area detector using graphite-monochromatized Mo Kα radiation and controlled by a Pentium based PC running the SMART software package.[15] Raw frame data were integrated using the SAINT[16] program. The structure was solved by direct methods.[17] An empirical absorption correction was applied to the data using the program SADABS.[18] The structure solution and the refinement were based on $F^2$. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms bonded to carbon atoms were fixed at idealized positions with isotropic $U$ values set 1.2$U$ (atom connected) and not refined. Hydrogen atoms bonded to N and O atoms were located from difference Fourier maps and refined. Abbreviated crystal data are listed in Table 1.

Diffraction data were collected for a black, irregular crystal of **2** of dimensions 0.52 mm × 0.20 mm × 0.05 mm using a Bruker P4/CCD system with graphite-monochromatized Mo Kα X-radiation and a rotating anode generator. The data were corrected for Lorentz and polarization effects, but no decay correction was applied. The structure was solved by direct methods[19] and expanded using Fourier techniques.[20] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were fixed at idealized positions with isotropic $U$ values set 1.2$U$ (atom connected) and not refined. Neutral atom scattering factors were taken from Cromer and Waber,[21] and all calculations were performed using teXsan.[22] Abbreviated crystal data are listed in Table 1.

## Results and Discussion

**Structures.** The structure of **1** is illustrated in Figure 1, and important bond distances and angles are listed in Table 2. The mononuclear Fe(III) center has a seven-coordinate pentagonal-bipyramidal structure, and the tridentate ligand poap has a planar trans conformation. The equatorial pentagonal plane comprises an $N_2O$ donor set from the ligand and a tightly bound bidentate nitrate. Fe−ligand distances in the equatorial plane fall in the range 2.05−2.23 Å, while the axial contacts are quire short (<2.014 Å). This structural arrangement is stabilized by hydrogen-bonding contacts from nitrate oxygen O(12) to hydrogen atoms bonded to N(2) and protonated nitrogen N(5) (N(5)−O(12) 2.836 Å, N(2)−O(12) 2.380 Å; N(5)−H−O(12) 163.6°, N(2)−H−O(12) 174.7°) and leads to a situation where there are three potentially open coordination sites in this trans conformation (N(2), N(4), and N(5)). This presents an opportunity for the complex to behave as a ligand. Further hydrogen-bonding contacts through N(2) link subunits together in the $y$ direction (N(2)−O(8) 2.954 Å; N(2)−H−O(8) 176.6°).

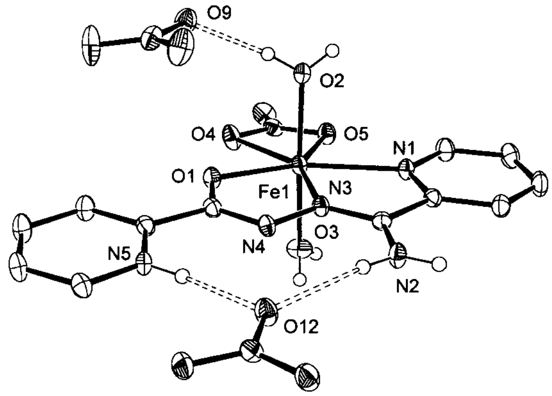


**Figure 1.** Molecular structure of $[Fe(Hpoap-H)(NO_3)(H_2O)_2](NO_3)_2$ **(1)**. Hydrogen atoms are omitted for clarity.

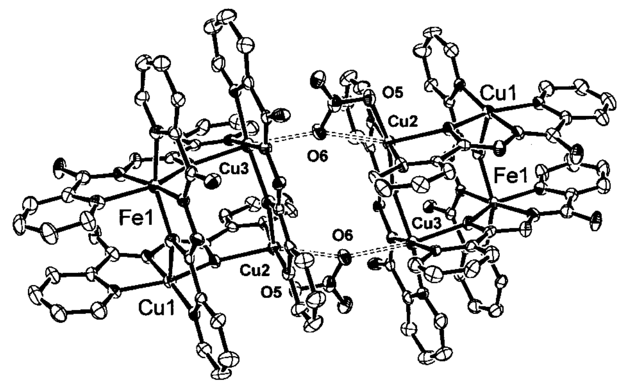


**Figure 2.** Molecular structure for $[(poap-H)_4Cu_3Fe(NO_3)]_2(ClO_4)_4(NO_3)_4 \cdot 12H_2O$ (**2**). Hydrogen atoms are omitted for clarity.

**Table 2.** Selected Bond Lengths (Å) and Angles (deg) for $[Fe(Hpoap-H)(NO_3)(H_2O)_2](NO_3)_2$ (**1**)

| | | | |
|---|---|---|---|
| Fe(1)−O(1) | 2.0174(17) | O(3)−Fe(1)−N(3) | 90.72(9) |
| Fe(1)−O(2) | 2.009(3) | O(4)−Fe(1)−O(5) | 58.30(7) |
| Fe(1)−O(3) | 2.013(3) | O(4)−Fe(1)−N(1) | 137.50(8) |
| Fe(1)−O(4) | 2.228(2) | O(4)−Fe(1)−N(3) | 150.12(8) |
| Fe(1)−O(5) | 2.1632(18) | O(5)−Fe(1)−N(1) | 79.22(7) |
| Fe(1)−N(1) | 2.250(2) | O(5)−Fe(1)−N(3) | 151.10(8) |
| Fe(1)−N(3) | 2.052(2) | N(1)−Fe(1)−N(3) | 72.26(8) |
| O(1)−Fe(1)−O(2) | 91.17(9) | O(2)−Fe(1)−O(3) | 172.97(9) |
| O(1)−Fe(1)−O(3) | 93.69(9) | O(2)−Fe(1)−O(4) | 88.93(8) |
| O(1)−Fe(1)−O(4) | 75.34(7) | O(2)−Fe(1)−O(5) | 88.44(8) |
| O(1)−Fe(1)−O(5) | 133.64(7) | O(2)−Fe(1)−N(1) | 88.84(10) |
| O(1)−Fe(1)−N(1) | 147.14(7) | O(2)−Fe(1)−N(3) | 95.45(8) |
| O(1)−Fe(1)−N(3) | 75.03(8) | O(3)−Fe(1)−O(4) | 87.39(8) |
| | | O(3)−Fe(1)−O(5) | 84.53(8) |
| | | O(3)−Fe(1)−N(1) | 89.83(10) |

The structure of **2** is illustrated in Figure 2, and important bond distances and angles are listed in Table 3. The complex consists of a dimeric entity with two heterotetranuclear subunits associated via a weak nitrate-bridging contact. Each subunit has an unusual square, tetranuclear gridlike arrangement of two nominally six-coordinate copper(II) centers, one square-pyramidal copper(II) center, and one six-coordinate iron(III) center, bridged by four poap ligands via their deprotonated oxygen centers. The square grid structure is very similar to homotetranuclear $Cu_4$ and $Ni_4$ square grids of poap and related ligands already reported.[23] The ligands are arranged in parallel pairs above and below the metal pseudoplane, with $NH_2$ ends pointing toward Fe(1), Cu(3), and Cu(1). The fifth and sixth sites at Cu(2) are occupied by oxygen atoms O(5) and O(6)

**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for $[(poap\text{-}H)_4Cu_3Fe(NO_3)]_2(ClO_4)_4(NO_3)_4\cdot 12H_2O$ (**2**)

| | | | |
|---|---|---|---|
| Cu(1)−O(1) | 2.014(4) | Cu(3)−N(8) | 1.893(5) |
| Cu(1)−O(4) | 2.240(4) | Cu(3)−N(15) | 1.972(5) |
| Cu(1)−N(1) | 2.037(6) | Fe(1)−O(3) | 2.004(5) |
| Cu(1)−N(3) | 1.907(5) | Fe(1)−O(4) | 2.002(4) |
| Cu(1)−N(20) | 1.986(5) | Fe(1)−N(11) | 2.162(6) |
| Cu(2)−O(1) | 2.233(4) | Fe(1)−N(13) | 2.022(6) |
| Cu(2)−O(2) | 2.007(4) | Fe(1)−N(16) | 2.139(6) |
| Cu(2)−O(5) | 2.004(5) | Fe(1)−N(18) | 2.019(5) |
| Cu(2)−N(5) | 1.977(6) | Cu(1)−Cu(2) | 3.976(3) |
| Cu(2)−N(10) | 1.959(5) | Cu(2)−Cu(3) | 3.917(3) |
| Cu(3)−O(2) | 2.135(4) | Cu(3)−Fe(1) | 3.902(2) |
| Cu(3)−O(3) | 2.234(4) | Cu(1)−Fe(1) | 3.923(3) |
| Cu(3)−N(6) | 2.059(5) | | |
| O(1)−Cu(1)−O(4) | 97.2(2) | O(4)−Fe(1)−N(18) | 75.2(2) |
| O(3)−Cu(3)−N(15) | 78.1(2) | O(1)−Cu(2)−N(10) | 106.3(2) |
| O(1)−Cu(1)−N(1) | 159.3(2) | N(11)−Fe(1)−N(13) | 74.3(2) |
| N(6)−Cu(3)−N(8) | 79.8(2) | O(2)−Cu(2)−O(5) | 163.2(2) |
| O(1)−Cu(1)−N(3) | 79.4(2) | N(11)−Fe(1)−N(16) | 95.1(2) |
| N(6)−Cu(3)−N(15) | 97.6(2) | O(2)−Cu(2)−N(5) | 97.8(2) |
| O(1)−Cu(1)−N(20) | 100.5(2) | N(11)−Fe(1)−N(18) | 96.5(2) |
| N(8)−Cu(3)−N(15) | 177.4(2) | O(2)−Cu(2)−N(10) | 83.1(2) |
| O(4)−Cu(1)−N(1) | 89.8(2) | N(13)−Fe(1)−N(16) | 104.8(2) |
| O(3)−Fe(1)−O(4) | 93.5(2) | O(5)−Cu(2)−N(5) | 87.4(2) |
| O(4)−Cu(1)−N(3) | 110.5(2) | N(13)−Fe(1)−N(18) | 170.8(2) |
| O(3)−Fe(1)−N(11) | 149.1(2) | O(5)−Cu(2)−N(10) | 90.3(2) |
| O(4)−Cu(1)−N(20) | 77.9(2) | N(16)−Fe(1)−N(18) | 74.8(2) |
| O(3)−Fe(1)−N(13) | 74.8(2) | N(5)−Cu(2)−N(10) | 174.8(2) |
| N(1)−Cu(1)−N(3) | 79.9(2) | O(2)−Cu(3)−O(3) | 90.6(2) |
| O(3)−Fe(1)−N(16) | 93.5(2) | O(2)−Cu(3)−N(6) | 157.4(2) |
| N(1)−Cu(1)−N(20) | 100.0(2) | O(2)−Cu(3)−N(8) | 77.6(2) |
| O(3)−Fe(1)−N(18) | 114.3(2) | O(2)−Cu(3)−N(15) | 105.0(2) |
| N(3)−Cu(1)−N(20) | 171.6(2) | O(3)−Cu(3)−N(6) | 94.0(2) |
| O(4)−Fe(1)−N(11) | 94.0(2) | O(3)−Cu(3)−N(8) | 102.3(2) |
| O(1)−Cu(2)−O(2) | 99.0(2) | Cu(1)−O(1)−Cu(2) | 138.8(2) |
| O(4)−Fe(1)−N(13) | 105.7(2) | Cu(2)−O(2)−Cu(3) | 142.0(2) |
| O(1)−Cu(2)−O(5) | 97.6(2) | Cu(3)−O(3)−Fe(1) | 134.0(2) |
| O(4)−Fe(1)−N(16) | 149.4(2) | Cu(1)−O(4)−Fe(1) | 135.2(2) |
| O(1)−Cu(2)−N(5) | 78.6(2) | | |

from bidentate nitrate N(21) (Cu(2)−O(5) 2.004(5) Å, Cu(2)−O(6) 2.685(5) Å) with short and long contacts, respectively, and the dimer interaction occurs as a result of weak Cu(3)−O(6) (2.709(5) Å) bridging contacts. The iron center is coordinated to two ligands via contiguous NNO donor segments, generating a *cis*-$N_4O_2$ chromophore. Cu(1), Cu(2), and Cu(3) have $N_3O_2$, $N_2O_4$, and $N_3O_3$ chromophores, respectively. The equatorial planes of Cu(2) and Cu(3) are connected via O(2) with a short (Cu(2)−O(2) 2.007(4) Å) and a longer (Cu(3)−O(2) 2.135(4) Å) contact. Cu(2) and Cu(1) are connected through O(1) by a long (2.233(4) Å) and a short (2.014(4) Å) connection, respectively, and Cu(1) and Cu(3) are connected to Fe(1) via O(4) and O(3) with long Cu−O contacts (2.234(4) and 2.240(4) Å, respectively). This sets up orthogonal connections between Cu(1) and Cu(3) and Fe(1), and an equatorial connection between Cu(2) and Cu(3) via the oxygen bridges. The $Cu_3FeO_4$ framework has a distorted boat shape (Figure 3) with the four metals forming a slightly twisted square. Metal−metal distances are quite long (3.90−3.98 Å), and oxygen bridge angles are large (134−142°).

A preliminary X-ray structural study on **3** revealed the same pseudosquare $Cu_3Fe$ gridlike arrangement with no evidence for dimer association. The equivalent coordination sites on Cu(2) and Cu(3) are occupied by water molecules.[24] Two water molecules are lost on vacuum-drying (see Experimental Section).

**Synthesis.** Repeated syntheses of **2** and **3** produce the same compounds with no evidence of other mixed-metal clusters with different combinations of copper and iron centers. Similar $M_4O_4$, oxygen-bridged square $M(II)_4$ complexes (M = Mn(II), Co(II), Ni(II), Cu(II))[23,24] and 2:2 mixed-metal $(Fe(III)_2M(II)_2$ (M = Mn(II), Co(II), Ni(II)) derivatives of poap have also been prepared, with the heteronuclear complexes produced in the same way by reaction of **1** with the appropriate metal salt.[24] It is of interest to note that only copper produces a 3:1 derivative. The iron remains coordinated to three original donors (NNO) of one ligand, but unexpectedly a second ligand also binds to this six-coordinate center with a comparable bonding arrangement, generating a *cis*-$N_4O_2$ chromophore. This second ligand to iron, and the involvement of two other iron-free ligands, must have resulted from partial decomplexation of **1** during the reaction with $Cu(ClO_4)_2$ and from significant molecular rearrangement prior to the formation of **2** and **3**, which are clearly the thermodynamically favored products. It is perhaps significant that there is no evidence for the formation of any $Cu_4$ cluster in these reactions and that no tetranuclear Fe(III) complexes of poap or related ligands have been produced so far.

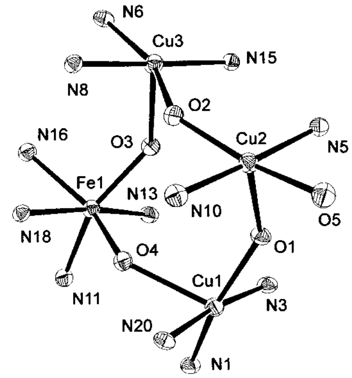

**Figure 3.** Core structure of **2**.

**Magnetic Properties.** The variable temperature magnetic properties of a powdered sample of **2** are most unusual, with a room-temperature magnetic moment ($\mu_{mol}$) of 6.68 $\mu_B$, dropping to a minimum value of 6.38 $\mu_B$ at 35 K, followed by a sharp rise at lower temperatures with a value of 7.20 $\mu_B$ at 2.0 K (Figure 4). The initial drop is consistent with intramolecular antiferromagnetic exchange and is reasonably associated with the equatorial Cu(2)−Cu(3) bridging connection and the large oxygen bridge angle (Cu(2)−O(1)−Cu(3); 142.0°),[25] despite the rather long Cu(3)−O(2) contact (2.135(4) Å). All other oxygen connections involving copper are orthogonal and so would not be expected to cause significant antiferromagnetic coupling. The pronounced rise in moment below 30 K indicates the presence of an intramolecular ferromagnetic term, and this is reasonably assumed to be associated with the Cu(1)−O(4)−Fe(1) connection because at low temperature the Cu(2)−Cu(3) interaction would lead to dominant occupation of a singlet ground-state term. Given this situation, a reasonable model would involve two effectively "isolated" dinuclear halves (Cu(2)−Cu(3) and Fe(1)−Cu(1)). The variable temperature magnetic data were therefore fitted to an exchange equation derived from the sum of two dinuclear components based on the spin Hamiltonians $H = -J_1S_{Cu2}S_{Cu3}$ and $H = -J_2S_{Fe1}S_{Cu1}$, with corrections for paramagnetic impurity ($\rho$), TIP, and intermolecular coupling ($\theta$). An excellent fit was obtained, and Figure 4 shows the experimental and calculated $\mu_{mol}$ values for $g_{ave} = 2.04(1)$, $J_1 = -54.0(2)$ cm$^{-1}$, $J_2 = 0.8(1)$ cm$^{-1}$, $\theta = 0.6$ K, $\rho = 0.03$, and TIP = 0.00016 cm$^3$ mol$^{-1}$. These parameters are consistent with the structure. The moderately large negative $J_1$ value is associated with the equatorial Cu(2)−O(2)−Cu(3) connection, due to direct copper magnetic orbital overlap via the oxygen

(25) Merz, L.; Haase, W. *J. Chem. Soc., Dalton Trans.* **1980**, 875.

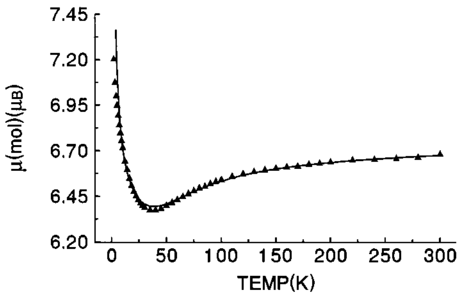


**Figure 4.** Variable temperature magnetic data for **2**. Solid line was calculated using $g_{ave} = 2.04(1)$, $J_1 = -54.0(2)$ cm$^{-1}$, $J_2 = 0.8(1)$ cm$^{-1}$, $\theta = 0.6$ K, $\rho = 0.03$, and TIP $= 0.000\,16$ cm$^3$ mol$^{-1}$.

bridge, while the small positive $J_2$ value indicates the presence of weak ferromagnetic coupling between Cu(1) and Fe(1), consistent with the orthogonal bridge. The small positive Weiss-like correction ($\theta$) indicates a weak intermolecular association, which is reasonably associated with the orthogonal connection between the two dinuclear halves. The dimer association via O(6) is likely to be a much weaker intermolecular component.

The variable temperature magnetic data were also fitted to a complete exchange model based on a spin Hamiltonian ($H = -J_1S_{Cu2}S_{Cu3} - J_2S_{Fe1}S_{Cu1} - J_3S_{Fe1}S_{Cu3} - J_4S_{Cu1}S_{Cu2}$) with four different $J$ values. The fit required that $J_3$ and $J_4$ be set close to zero and was dominated by variations in $J_1$ and $J_2$. To avoid overparametrizing the fit, $J_3$ and $J_4$ were set to zero, and a good fit of the data was obtained with $g = 2.04$, $J_1 = -61.5$ cm$^{-1}$, $J_2 = 1.1$ cm$^{-1}$, and TIP $= 0.000\,150$ cm$^3$ mol$^{-1}$. This result is entirely consistent with the previous analysis and strongly supports the simplified, isolated dimer model. The magnetic models suggest an $S = 3$ spin ground state at low temperature, in agreement with the observed moments below 30 K. A magnetization ($M/H$) study was carried out at 2 K in the field range 0−50000 Oe (Figure 5). Experimental data (●) were compared with the theoretical Brillouin function (−) calculated at 2 K for $g = 2.04$ and $S = {}^6/_2$, clearly confirming the $S = 3$ ground state.

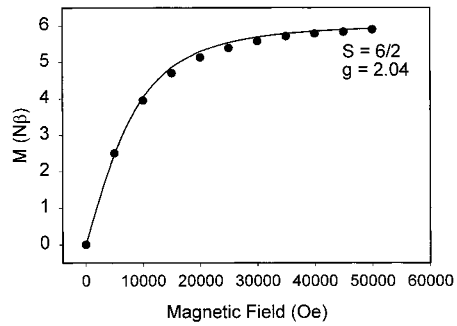


**Figure 5.** $M/H$ data for **2** (●); theoretical line using $g = 2.04$, $T = 2$ K (−).

**Acknowledgment.** This research was supported by NSERC (Natural Sciences and Engineering Research Council of Canada) and EPSRC (U.K.). We thank Dr. R. McDonald (University of Alberta) for structural data on compound **2**.

**Supporting Information Available:** X-ray crystallographic files in CIF format for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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