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Triangular, Ferromagnetically-Coupled Cu^{II}_3–Pyrazolato Complexes as Possible Models of Particulate Methane Monooxygenase (pMMO)

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Magnetic susceptibility and EPR studies show that trinuclear Cu^{II}–pyrazolato complexes with a $Cu_3(\mu_3\text{-}X)_2$ core (X = Cl, Br) are ferromagnetically coupled: $J_{Cu-Cu} = +28.6\ cm^{-1}$ (X = Cl), +3.1 cm^{-1} (X = Br). The orderly transition from an antiferromagnetic to a ferromagnetic exchange among the Cu centers of $Cu_3(\mu_3\text{-}X)$ complexes, X = O, OH, Cl, Br, follows the change of the Cu–X–Cu angle from 120° to ~80°. The crystal structures of $[Bu_4N]_2[Cu_3(\mu_3\text{-}Br)_2(\mu\text{-}pz^*)_3Br_3]$ (pz* = pz (**1a**) or 4-O_2N-pz (**1b**), pz = pyrazolato anion, $C_3H_3N_2^{1-}$) are presented.

Multimetallic systems with ferromagnetic ground states are attracting attention because of their potential application as single molecule magnets.[1] Ferromagnetically coupled trinuclear Cu^{II} complexes in particular are of further interest because they may relate to the active sites of pMMO. The latter enzyme, in its fully oxidized form, has been proposed to have an $S = {}^3/_2$ ground state, attributed to ferromagnetically coupled trinuclear Cu^{II} centers.[2] In the extensive Cu^{II} chemistry, there are only four examples of ferromagnetic trinuclear copper complexes: one linear, two angular, and one triangular.[3]

We have recently described a triangular Cu^{II}_3−pyrazolate that provides a stable metallacyclic framework for the pH-dependent exchange of μ_3-O, μ_3-OH, and $(\mu_3\text{-}Cl)_2$ bridging ligands.[4] We have further shown that the planar $Cu_3(\mu_3\text{-}O)$ species is strongly antiferromagnetic, while its protonated, pyramidal $Cu_3(\mu_3\text{-}OH)$ analogues are known weakly antiferromagnetic systems.[4,5] Continuing our investigation of this system, we describe here the synthesis and crystal structures of $[Bu_4N]_2[Cu_3(\mu_3\text{-}Br)_2(\mu\text{-}pz^*)_3Br_3]$ (pz* = pz (**1a**) or 4-O_2N-pz (**1b**), pz = pyrazolato anion, $C_3H_3N_2^{1-}$), as well as the magnetic susceptibility studies of **1b** and the chloro complex $[Bu_4N]_2[Cu_3(\mu_3\text{-}Cl)_2(\mu\text{-}pz)_3Cl_3]$, **2**. Complexes **1** and **2** are rare examples of triangular, ferromagnetically coupled Cu^{II} complexes.[3d] This discovery demonstrates that the pH-controlled interconversion of the $Cu_3(\mu_3\text{-}O)$, $Cu_3(\mu_3\text{-}OH)$, and $Cu_3(\mu_3\text{-}X)_2$ motifs (X = Cl, Br) is accompanied by an orderly switch from antiferro- to ferromagnetic coupling of the three Cu^{II} centers.

Complexes **1a** and **1b** are prepared from $CuBr_2$ and pzH or 4-O_2N-pzH, respectively, in the presence of a base, following the established procedure[4] for the synthesis of the chloride complex **2**.[6] Single crystal X-ray structure determinations of **1a** and **1b** show them to consist of approximately planar copper pyrazolato trimers capped on either side by two μ_3-Br ligands (Figure 1).[8] The three Cu atoms of **1b** define an approximately equilateral triangle with Cu−Cu distances of 3.428(1)−3.443(1) Å, while those of **1a** are more disparate, 3.424(1) and 3.510(1) Å. Two axial pyrazolates and three equatorial bromides define the distorted trigonal-bipyramidal environment of the five-coordinate Cu atoms. Two capping bromides are loosely held by the three copper atoms of **1a** and **1b** at average Cu−(μ_3-Br) distances of 2.763 and 2.698 Å, respectively, much longer than the bond lengths of the terminal bromide ligands. The Cu−(μ_3-Br) distances fall into the range of the corresponding Cu−

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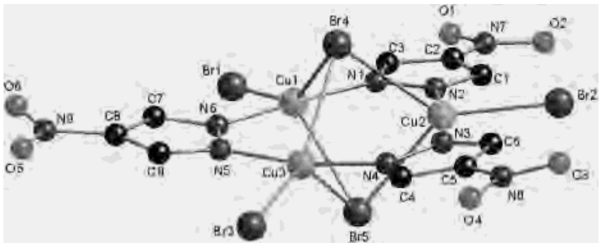

Figure 1. Structure of the **1b** anion. Selected bond lengths (Å) and angles (deg): Cu···Cu = 3.428(1)−3.443(1), Cu−Br = 2.408(2)−2.425(1), Cu−(μ_3-Br) = 2.638(1)−2.806(2), Cu−N = 1.917(7)−1.959(7), N−Cu−N = 170.6(3)−176.3(3), Br(4)−Cu−Br(5) = 84.20(4)−86.23(4), Br−Cu−(μ_3-Br) = 125.96(7)−148.59(6), Cu−(μ_3-Br)−Cu = 77.41(4)−81.07(4). The corresponding bond lengths and angles for **1a** are not significantly different from the above.

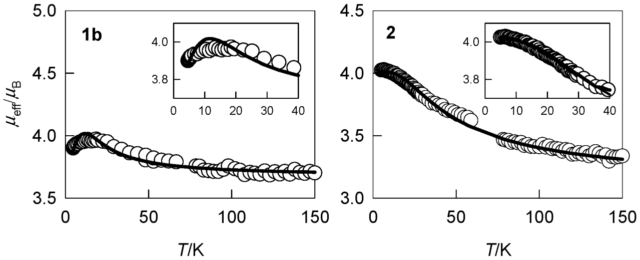

Figure 2. Temperature dependence of the effective magnetic moment for **1b** and **2**: open circles (○), experimental data; solid line (—), best-fit.[9]

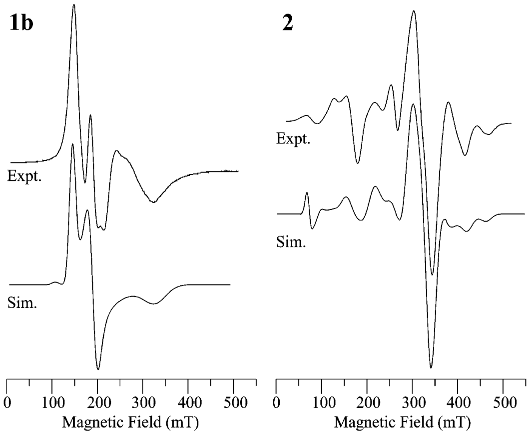

Figure 3. Solid sample and simulated X-band EPR spectra of **1b** and **2**, at 77 K. For **1b**, $g_\perp = 2.01(2)$, $g_{||} = 2.08(2)$; for **2**, $g_\perp = 2.05(5)$, $g_{||} = 2.11(5)$.[10]

(μ_3-Cl) distances reported for **2**, 2.241(2)−3.056(2) Å, but the average values are longer for the bromide than the chloride (2.574 Å).[4] This results in a slightly more acute average Cu−X−Cu pyramidal angle for X = Br, 79.1°, than for X = Cl, 80.9°. While the crystallographic symmetry is lower than 3-fold, the magnetic equivalence of the three pyrazole rings, evident by the presence of a single paramagnetically shifted ^{1}H NMR resonance for **1b**, indicates average D_{3h} molecular symmetry in solution.

The analysis of the magnetic susceptibility measurements[9] shows (Figure 2) that a ferromagnetic exchange operates in **1b** and **2**: the effective magnetic moment increases gradually on cooling from its high-temperature limit to a μ_{eff} value of about 4.0 μ_B at 4 K. Its slope for **1b** is evidence of a considerable zero-field splitting. The experimental magnetic susceptibility data are best fitted with the set of magnetic parameters $g_z = 2.42$, $g_x = g_y = 2.46$, $J = +3.1$ cm^{-1}, and $D_{3/2} = \pm 20$ cm^{-1} for **1b** and $g_{\text{iso}} = 2.07$ and $J = +28.6$ cm^{-1} for **2**. The zero-field splitting parameter for **1b** means that there are ground and nearest excited state Kramers doublets separated by a 2D energy gap. A pair of degenerate doublets lies at $(^3/_2)J$ above the barycenter of the quartet states.

Consistent with the $S = {}^3/_2$ spin-state are the X-band EPR spectra[10] at 77 K of powder **1b** and **2** (Figure 3). EPR simulations using the standard spin Hamiltonian for $S = {}^3/_2$ successfully reproduce the overall pattern observed for these samples. It is difficult to reproduce exactly the line width and intensity, since these magnetically nondilute systems include unresolved ^{63,65}Cu hyperfine splitting as well as "strain" effects, as discussed in EPR studies of pMMO.[2] Compound **1b** is characterized by $D \gg h\nu$ ($|E/D| \sim 0.09$); $g_\perp = 2.01(2)$, $g_{||} = 2.08(2)$.[11] Compound **2** is quite different,

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(6) Synthetic details for $(Bu_4N)_2[Cu_3(\mu_3\text{-}Br)_2(\mu\text{-}4\text{-}NO_2\text{-}pz)_3Br_3]$ (**1b**) follow. $CuBr_2$ (653 mg, 2.92 mmol), 4-nitro-pyrazole (330 mg, 2.92 mmol), NaOH (117 mg, 2.92 mmol), and Bu_4NBr (656 mg, 2.03 mmol) are stirred in 10 mL of CH_2Cl_2 for 2 days at ambient temperature. The green solution is filtered, evaporated to one-half, crashed out with 80 mL of Et_2O, and washed with chilled EtOH and Et_2O. Yield: 1.28 g (93%). Mp 204 °C. Recrystallization from hot EtOH 95% affords **1b** as shiny green plates suitable for X-ray diffraction. Anal. Calcd for $C_{41}H_{78}Br_5Cu_3N_{11}O_6$: C, 34.89; H 5.58; N 10.92%. Found: C, 34.95; H, 5.59; N, 10.81%. IR (KBr pellet, cm^{-1}): 3143m, 2963s, 2934m, 2875m, 1515s, 1484m, 1438m, 1408s, 1382m, 1321w, 1287s, 1172m, 1029s, 1006m, 887m, 817s, 756m, 739w, 599w, 566w, 495w. UV−vis (CH_2Cl_2, cm^{-1}): 14150. ^{1}H NMR (d_6-acetone, ppm): 93.74 (6H, $w_{1/2} = 1.4$ kHz). Compound **1a** is prepared similarly, using pyrazole instead of 4-nitro-pyrazole, or from **2** by stirring with excess NaBr in CH_2Cl_2. The crystal structure of **1a** shows one pyrazole partially brominated (40%) at the 4-position; similar unexpected chlorination of a pyrazole ligand under mild conditions has been observed elsewhere.[7]

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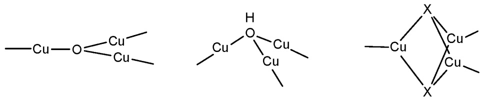
(8) X-ray diffraction data were collected with a Bruker AXS SMART 1K CCD diffractometer, graphite-monochromated Mo Kα radiation at 295 K, and corrected for Lorentz and polarization effects. Structure solution was performed by direct methods and refinement by full-matrix least-squares refinement based on F^2. For **1a** ($C_{41}H_{80.6}Br_{5.4}Cu_3N_8$): $M_r = 1307.86$, monoclinic, space group $C2/c$, $a = 17.578(3)$ Å, $b = 16.378(3)$ Å, $c = 19.488(3)$ Å, $\beta = 95.498(4)°$, $V = 5584.7(2)$ Å^3, $Z = 4$, $\rho_{\text{calcd}} = 1.556$ g/cm^3, $2\theta_{\max} = 46.62°$, 12023 reflections measured (4031 independent, R(int) = 0.0454), R1 = 0.0519 and wR2 = 0.1254 for 2311 reflections with $I > 2\sigma(I)$ (0.0983 and 0.1446 for all data) and 289 parameters. For **1b** ($C_{41}H_{78}Br_5Cu_3N_{11}O_6$): $M_r = 1411.31$, triclinic, space group $P\bar{1}$, $a = 9.939(1)$ Å, $b = 12.722(2)$ Å, $c = 25.515(3)$ Å, $\alpha = 81.138(3)°$, $\beta = 81.202(3)°$, $\gamma = 68.948(2)°$, $V = 2958.4(7)$ Å^3, $Z = 2$, $\rho_{\text{calcd}} = 1.584$ g/cm^3, $2\theta_{\max} = 46.56°$, 13162 reflections measured (8478 independent, R(int) = 0.0434), R1 = 0.0559 and wR2 = 0.0960 for 3923 reflections with $I > 2\sigma(I)$ (0.1493 and 0.1192 for all data) and 603 parameters.

(9) The isothermal differential magnetic susceptibility has been recorded with the alternating current susceptometer (LakeShore 7221) with the following field parameters: $H_{AC} = H_{DC} = 800$ Am^{-1}, $f_{AC} = 222$ s^{-1}. Data were corrected to a signal of the free sample holder and underlying diamagnetism, and fitted to an isotropic exchange model of three $S = {}^1/_2$ centers. For **1b**, an additional asymmetric exchange has been accounted for, giving rise to the molecular-state value of the zero-field splitting parameter $D_{3/2}$. The exchange Hamiltonian, $\hat{H} = -J\vec{S}_1 \cdot \vec{S}_2$.

(10) Modified Varian E4 spectrometer, 9.23 GHz for **1b**, 9.10 GHz for **2**.

(11) The discrepancy between g-values determined by EPR or magnetic susceptibility for **1b** is attributed to the different nature of those measurements; all populated states contribute to bulk magnetic susceptibility, while fast-relaxing states are not observable by EPR.

Scheme 1

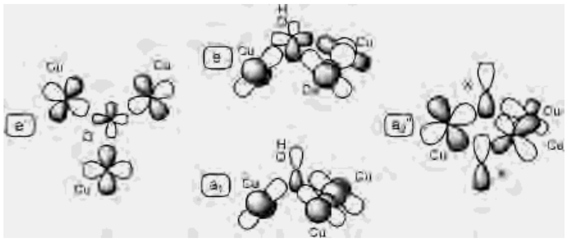


Cu - X - Cu, (°):	120 (X = O), **3**	110-115 (X = OH), **4**	81 (X = Cl), **2** 79 (X = Br), **1b**
Ground State:	S = 1/2	S = 1/2	S = 3/2
$J_{Cu\text{-}Cu}$, (cm^{-1}):	-500 (Ref. 4)	-140 - (-200) (Ref. 5b)	+28.6 (X = Cl) (this work) +3.1 (X = Br) (this work)

with $D < h\nu$, so that multiple fine structure transitions are observed, allowing accurate determination of the spin Hamiltonian parameters: $D = 0.075(5)$ cm^{-1}, $E = 0.008(2)$ cm^{-1}, $g_\perp = 2.05(5)$, and $g_{||} = 2.11(5)$ ($g_{iso} = 2.07$, in agreement with magnetic data). Such EPR spectra are the first reported for an exchange coupled trinuclear Cu^{II} cluster.

In dinuclear Cu^{II} complexes, the dependence of the sign and magnitude of the magnetic exchange on the Cu−(μ-E)−Cu angle, ϕ, (E = O, OH) has been clearly established and is now well understood: antiferromagnetic coupling occurs at $\phi > 92°$, while at $\phi < 92°$ the coupling is ferromagnetic. The magnitude of the coupling constant, J, increases with increasing $|\phi - 92|°$.[12] A similar critical value of ϕ has been established for a different dinuclear Cu system.[13] The present work demonstrates that the same principles apply to trinuclear systems, with an orderly progression from strongly antiferro- to ferromagnetic exchange accompanying the change of the Cu−(μ_3-X)−Cu angle (X = O, OH, halogen) from 120° to ~80° (Scheme 1). A qualitative interpretation of the antiferromagnetic character of $[Cu_3(\mu_3\text{-}O)(\mu\text{-}pz)_3Cl_3]^{2-}$ (**3**) and $[Cu_3(\mu_3\text{-}OH)(\mu\text{-}pz)_3Cl_3]^{1-}$ (**4**) versus the ferromagnetic **1b** and **2** is provided by orbital complementarity arguments describing the symmetry of the magnetic orbitals, $d_{x^2-y^2}$, of the three Cu^{II} atoms in the HOMO of each complex. Within the planar $Cu_3(\mu_3\text{-}O)$ core of **3** (D_{3h}), the in-plane degenerate p_x and p_y (e′) O-orbitals form the predominant interaction with the e′ combination of the three $d_{x^2-y^2}$ orbitals, bringing about their antiferromagnetic coupling (Scheme 2), and the oxygen p_z orbital remains nonbonding. In the pyramidal $Cu_3(\mu_3\text{-}OH)$ of **4** (C_{3v}), there are both a diminished $e[p_x, p_y] - e[d_{x^2-y^2}]$ as well as an $a_1[p_z] - a_1[d_{x^2-y^2}]$ bonding interaction; the former is, evidently, the predominant one, as **4** remains antiferromagnetically coupled, but with a smaller magnitude J-value than **3**.[14] In contrast, the geometry of the trigonal bipyramidal $Cu_3(\mu_3\text{-}X)_2$ core of **1** and **2** (D_{3h}) allows only the overlap of the metal $a_2''[d_{x^2-y^2}]$ and the $(\mu\text{-}X)_2$ $a_2''[p_z, p_z]$ SALC-AOs, consistent with the ferromagnetic exchange among the three Cu-centers.[15]

Scheme 2



Materials that switch reversibly between two different magnetic states in response to a change of their chemical environment constitute the basic unit of a magnetochemical sensor. Dinuclear chromium and vanadium complexes that switch between ferro- and antiferromagnetic ground states upon protonation/deprotonation of the μ-O ligand have been reported by Wieghardt et al.[16]

The results presented here suggest that a triangular Cu^{II} cluster, capped on one or both sides (i.e., by an alkoxide group), elongated along the 3-fold symmetry axis, is a possible structural motif of the ferromagnetic form of the pMMO active site.

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Supporting Information Available: X-ray crystallographic data in CIF format (S1, S2) and ORTEP diagrams for **1a** and **1b** (S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) Besides the shorter Cu−O(H)−Cu, the longer Cu−N−N−Cu path also contributes to the magnetic exchange among the Cu $d_{x^2-y^2}$ orbitals in **3** and **4**. As the $[Cu-N-N]_3$ framework remains invariant in those complexes, the weaker contribution of the μ-pz* ligands is considered constant and ignored in the present discussion.

(15) (a) The equatorial $d_{x^2-y^2}$ orbitals are the magnetic orbitals in **1b** and **2** as $g_{||} > g_\perp$. Other trigonal bipyramidal Cu centers with a $d_{x^2-y^2}$ ground state are known, i.e.: Gupta, M.; Mathur, P.; Butcher, R. J. *Inorg. Chem.* **2001**, *40*, 878. (b) The SALC-AOs for the three Cu $d_{x^2-y^2}$ and two Cl, Br p_z orbitals in D_{3h} symmetry are the following: $a_2'' + e''$ and $a_2'' + a_1'$, respectively.

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