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High-Spin [2 × 2] [$Fe^{III}_2Ni^{II}_2$] Heterometallic Square Grid with an $S = 3$ Ground State

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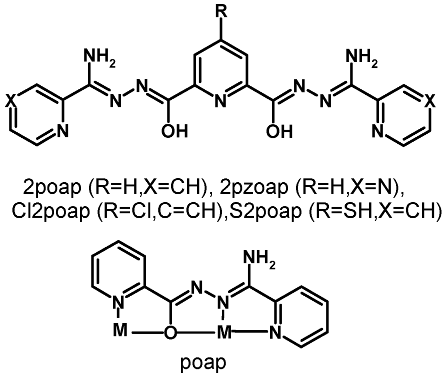
A [2 × 2] heterometallic [$Fe^{III}_2Ni^{II}_2$] ferrimagnetic, square-grid complex has been synthesized by the self-assembly reaction of a mononuclear Fe^{III} precursor with $Ni(NO_3)_2$. Intramolecular antiferromagnetic exchange through the resulting hydrazone O-bridging framework (M–O–M 133.3–136.4°) leads to an $S = 3$ ground state. Structural and magnetic properties are discussed.

Self-assembly strategies have seen increasing use in recent years as logical ways of constructing novel molecular architectures in simple one-step processes, where the products have some rational design based on the bonding features of the constituents. "Ditopic" ligands, e.g., poap (Chart 1), are coordinatively versatile, and can bridge metal ions via μ-O or μ-N−N connections.[1a,b] Homometallic, spin-coupled [2 × 2] [M_4-(μ-O)$_4$] (M = Mn^{II}, Ni^{II}, Cu^{II}, Co^{II}) square grids are well-documented examples.[1a−c] Mononuclear derivatives can also be produced, and [Fe(Hpoap-H)(NO_3)(H_2O)$_2$](NO_3)$_2$·2H_2O (**1**)[2] is a novel example (Figure 1; Hpoap-H represents a formally neutral ligand with O1 deprotonated and N5 protonated) with Fe^{III} bound on one side of the ligand to an N_2O coordination pocket, thus leaving two possible options for further coordination: (1) binding to the tridentate pocket N2−N4−N5, creating a μ-N−N bridge to a second metal ion, or (2) binding to N5 and O1 to form a μ-O bridge (the pyridine ring would rotate 180°). In one previously reported case, the reaction of **1** with $Cu(ClO_4)_2$ produced the 3:1 heterometallic [2 × 2] square-grid complex [(poap-H)$_4$-$Cu^{II}_3Fe^{III}$(NO_3)]$_2$(NO_3)$_4$(ClO_4)$_4$·12H_2O (**2**), which contains two [$FeCu_3$(μ-O)$_4$] subunits involving hydrazone O bridges between adjacent metal centers.[2] While the Fe^{III} center retains

Chart 1



2poap (R=H,X=CH), 2pzoap (R=H,X=N),
Cl2poap (R=Cl,C=CH),S2poap (R=SH,X=CH)

poap

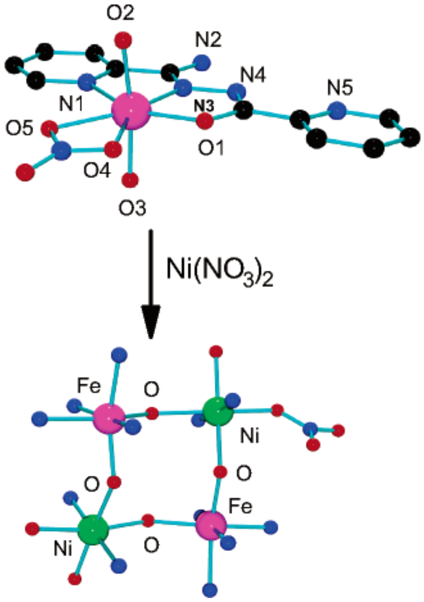


Figure 1. POVRAY structural representation of complex **1** and self-assembly scheme to form **3** (core structure).

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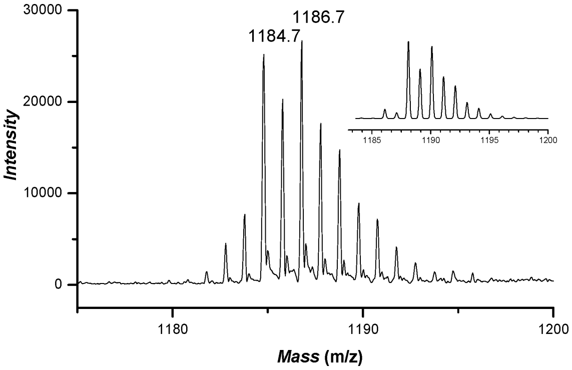

Figure 2. MALDI-TOF mass spectrum of the complex **3** cation and its calculated isotopic mass distribution (inset).

its original N_2O coordination to one ligand, the presence of two Cu centers with their own independent ligands implies that a dynamic situation exists in solution involving ligand dissociation/association and that transmetalation of the Fe precursor occurred during the reaction. However, despite this rearrangement, the [2 × 2] grid structure, common to ligands in this class, persists, implying that the coordination information programmed into the ligand dominates the self-assembly process. A combination of antiferromagentic (Cu−Cu) and ferromagnetic (Fe−Cu) behavior within the same molecule leads to an $S = 3$ ground state.[2]

In the current report, we describe a different 2:2 heterometallic [2 × 2] grid system starting with **1** as the source of Fe^{III}. The square-grid complex $[Fe_2Ni_2(poap\text{-}H)_4(NO_3)(H_2O)_3](NO_3)_5\cdot 2.5H_2O\cdot 1.75CH_3OH$ (**3**) was produced by the reaction of **1** with $Ni(NO_3)_2\cdot 6H_2O$ in $MeOH/CH_2Cl_2$ as a green complex in moderate yield (Figure 1).[3]

Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometry (Figure 2) for **3** indicated the presence of a tetranuclear complex ion in solution ($MeOH/CH_3CN$) (m/z calculated for $C_{48}H_{35}N_{20}O_4Fe_2Ni_2$, inset), consistent with the structural formula and elemental analysis.[3]

The structure of the cation in **3** (Figure 3) reveals a [2 × 2] square grid, with four ligands arranged in two parallel groups and two Fe^{III} and two Ni^{II} centers bridged by deprotonated hydrazone O atoms (see Chart 1 for the binding mode). Each Fe^{III} atom is bonded to two N_2O ligand pockets, completing a *cis*-N_4O_2 coordination sphere. The Ni atoms occupy the remaining NO sites of the ligands and require additional donors (H_2O and NO_3^-) to fill the octahedral *trans*-N_2O_4 coordination spheres. Averaged M−L distances for all metal ions are comparable (2.069−2.083 Å), with distances for the Fe^{III} centers being slightly shorter than those for Ni^{II}. Compound **1** has an average Fe−L distance of 2.084 Å if the long bond to nitrate oxygen O4 is ignored. The Fe^{III} center in **2** has a similar *cis*-N_4O_2 coordination sphere, with an average Fe−L distance of 2.058 Å. M−O−M angles in **3** fall in the range 133.3−136.4°, typical for square grids in this class, and M−M separations fall in the range 3.79−3.86 Å. Bond valence sum (BVS) analyses were performed using the parameters provided by O'Keefe and Brese.[4] The oxidation-state determination by the BVS method is in accordance with the presence of Fe^{III} and Ni^{II} centers (BVS values: Fe2, 3.088; Fe4, 3.102; Ni1, 1.999; Ni3, 2.042).

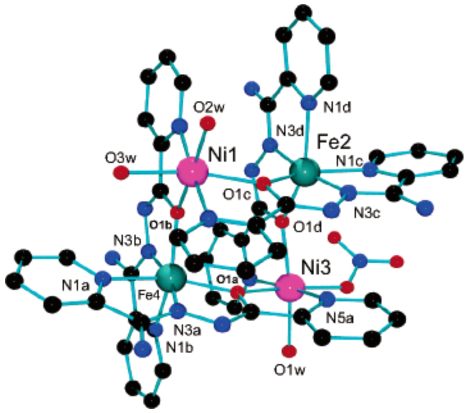

Figure 3. POVRAY projection of complex **3** (blue, N; red, O; black, C). Important bond lengths (Å) and angles (deg): Ni1−N 2.065−2.068, Ni1−O 2.068−2.105, Ni3−N 2.045−2.066, Fe2−N 2.000−2.176, Fe2−O 2.038−2.051, Fe4−N 2.006−2.170, Fe4−O 2.016−2.044, M−O−M 133.3−136.4.

The Fe^{III} binding site in **1** (N_2O) would be considered to be less labile than, e.g., a comparable site with Ni^{II}, and it is of interest to note that a bis-ligand complex $[(poap)_2Fe^{III}](ClO_4)_3\cdot H_2O$ (**4**) results upon the reaction of $Fe^{III}(ClO_4)_3\cdot 6H_2O$ with poap.[5] The structure of **4** (Figure S1 in the Supporting Information) shows a *cis*-N_4O_2 coordination sphere similar to those observed in **2** and **3**, indicating the preference of the Fe^{III} center for the N_2O portion of the ligand. What is somewhat surprising, however, is that upon the reaction of **1** with the $Ni(NO_3)_2\cdot 6H_2O$ ligand scrambling must have occurred to some extent because no additional ligand was added but, nevertheless, the Fe^{III} center seems to preferentially seek out two N_2O sites, in keeping with its hard Lewis acid character.

The magnetic properties of **3** are shown in Figure 4 as a plot of μ_{mol} as a function of temperature. The drop in the moment as the temperature decreases to 30 K is indicative of intramolecular antiferromagnetic exchange, which can reasonably be associated with the large O bridge angles between the metal ions. The sharp rise at low temperature is typical of a system involving noncompensation of spins in an antiferromagnetically coupled heterometallic cluster, as illustrated with recent examples involving [2 × 2] V^{IV}/Mn^{II} [6] and Mn^{II}/Co^{II} [7] grids, and is associated with spin

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(3) Synthesis. $[Fe(Hpoap\text{-}H)(NO_3)(H_2O)_2](NO_3)_2\cdot 2H_2O$ (**1**; 0.5 mmol) and $Ni(NO_3)_2\cdot 6H_2O$ (0.5 mmol) were reacted together in the presence of NEt_3 (0.6 mmol) in MeOH (20 mL). CH_2Cl_2 (2 mL) was added and the solution filtered. Dark-green crystals of **3** (30%) formed upon standing. An air-dried sample gave the following elemental analysis. Elem anal. Calcd for $(C_{12}H_{10}N_5O)_4Fe_2Ni_2(NO_3)_6(H_2O)_8$ (**3**): C, 33.79; H, 3.31; N, 21.34. Found: C, 33.42; H, 3.22; N, 21.52. Crystal data for $[Fe_2Ni_2(poap\text{-}H)_4(NO_3)(H_2O)_3](NO_3)_5\cdot 2.5H_2O\cdot 1.75CH_3OH$ (**3**): $C_{49.75}H_{62}N_{26}O_{29.25}Fe_2Ni_2$, $M = 1721.37$, $P2_1/n$, $a = 22.6313(10)$ Å, $b = 13.7104(13)$ Å, $c = 23.899(13)$ Å, $\beta = 115.101(4)°$, $V = 6720.1(9)$ Å^3, $T = 120(2)$ K, $Z = 4$, $F(000) = 3538$, μ(Mo Kα) $= 1.083$ mm^{-1}, 39 729 reflections, 11 831 unique ($R_{int} = 0.050$), R1 = 0.0546, and wR2 = 0.1420.

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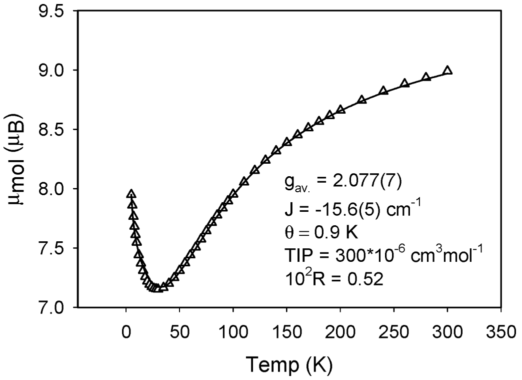

Figure 4. Magnetic data [μ_{mol}/T (K)] for **3**. The solid line corresponds to fitted data (see the text and inset).

states with smaller S values and slightly higher in energy than the ground-state itself, which are populated above 2 K. The magnetic data for **3** were fitted to an isotropic exchange expression, based on the simple exchange Hamiltonian (eq 1) ($S_1 = S_3 = {}^5/_2$; $S_2 = S_4 = {}^2/_2$). The small range of M−O−M angles in **3** suggests that a simple square model involving one J value is reasonable. The total spin states

$$H_{ex} = -J\{S_1\cdot S_2 + S_2\cdot S_3 + S_3\cdot S_4 + S_1\cdot S_4\} \qquad (1)$$

and their energies were calculated by the normal vector addition approach and substituted into the Van Vleck equation within the software package *MAGMUN4.1*[8] to generate theoretical susceptibility data based on this model. Fitting of the experimental data gave $g_{av} = 2.077(7)$, $J = -15.6(5)$ cm^{-1}, TIP = 300 × 10^{-6} cm^3 mol^{-1}, and $\theta = 0.9$ K ($10^2R = 0.52$; $R = [\sum(\chi_{obs} - \chi_{calc})^2/\sum\chi_{obs}{}^2]^{1/2}$; θ = Weiss-like corrective term; TIP = estimated temperature-independent paramagnetism). The excellent fit is illustrated by the solid line in Figure 4. The J value is comparable with values observed for structurally similar [2 × 2] homometallic Ni^{II}_4 complexes.[1a]

Magnetization vs field data at 2 K (Figure 5) show M rising steeply to a value of 6.4 Nβ at 5 T. The solid line in Figure 5 is the result of a fit to the appropriate Brillouin function for $g_{av} = 2.06$ and $S = 3$ (2 K), in agreement with the ground state calculated from the vector coupling scheme for the grid and consistent with the analysis of the variable-temperature magnetic data.

New routes to novel magnetic grids and clusters are important in the search for new materials with potentially useful properties. The creation of mixed-spin-state systems provides a unique opportunity to "mix and match" different spin sites in specific locations within a self-assembled structural motif. In a separate study, it has been found that site-specific metal ion oxidation can be achieved successfully with [3 × 3] Mn^{II}_9 square grids, based on site-specific differences in coordination environments, and different ground-state situations can be created.[9−11] In one novel case, a [3 × 3] $Mn^{III}_4Mn^{II}_5$ grid complex only has the corner sites oxidized, thus creating an antiferromagnetically coupled system with an $S = {}^1/_2$ ground state.[11] Such mesoscopic systems are of fundamental importance in the search for robust spin "qubit" subunits, which can store and process quantum information.[12] The demonstrated stability of these grid systems in general and their ability to spontaneously assemble on surfaces, e.g., Au(111), in organized monolayer arrays, augers well for their use as molecular-based "devices".[10,13] Recent studies have shown that site differences in the [3 × 3] Mn^{II}_9 grids can also be exploited directly to produce mixed-metal systems by heterometal substitution.[14] Further studies on the [2 × 2] heterometallic systems with ditopic ligands, and also tritopic ligands such as 2poap and its variants, are in progress. Preliminary results indicate that the reaction of **1** with $Mn^{II}(NO_3)_2$ produces a [2 × 2] [$Fe^{III}_2Mn^{II}_2$] square grid with a similar structure and with $Co^{II}(NO_3)_2$ a [2 × 2] [$Fe^{II}_2Co^{III}_2$] rectangular grid, in which a novel intramolecular redox reaction has occurred.[5]

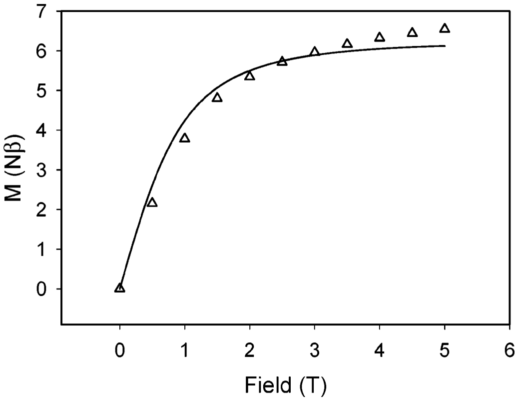

Figure 5. Magnetization vs field plot at 2 K for **3** (solid line; see text for parameters).

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Supporting Information Available: Crystallographic details in CIF format and Figure S1 showing the structure of **4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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