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A $S = 7$ Ground Spin-State Cluster Built from Three Shells of Different Spin Carriers Ferromagnetically Coupled, Transition-Metal Ions and Nitroxide Free Radicals

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The synthesis of new magnetic molecular objects possessing a high-spin ground state and a high anisotropy became a challenge for chemists a few years ago when the dodecanuclear mixed-valence manganese-oxo cluster with acetate ligands, Mn_{12} acetate, demonstrated experimental evidence for a single-molecule magnet behavior below 4 K[1] and quantum phenomena such as thermal-assisted tunneling.[2] Search for other examples of such behavior resulted in the octanuclear iron(III) oxo−hydroxo cluster, Fe_8, which exhibits ground-state tunneling[3] and quantum phase interference.[4] These polynuclear clusters possess strong intramolecular interactions between the metallic centers, very week intermolecular interactions, and electronic and structural anisotropy.

Although highly isotropic, nitroxide free radicals are useful paramagnetic building blocks[5] which offer opportunities to design high-spin anisotropic molecules in two different ways: (i) They have demonstrated their bridging capabilities when adequately substituted.[6] In that case a ground spin-state of high multiplicity would result from a ferrimagnetic structure. (ii) They might play the role of terminal ligands and increase the multiplicity of the ground state. The latter strategy is virtually applicable to every existing system whose structure includes an anisotropic core.

We took advantage of the well understood ferromagnetic interactions between paramagnetic centers in μ-cyano bimetallic complexes when the magnetic orbitals are orthogonal[7−9] and of the ferromagnetic behavior of Ni(II)−imino nitroxide complexes,[10] (relying also on the orthogonality of magnetic orbitals) to perform the synthesis of the discrete pentanuclear complex **1** including two Fe(III) and three Ni(II) ions in addition to six (2-pyridyl)-substituted imino nitroxide ligands (IM-2Py).[11]

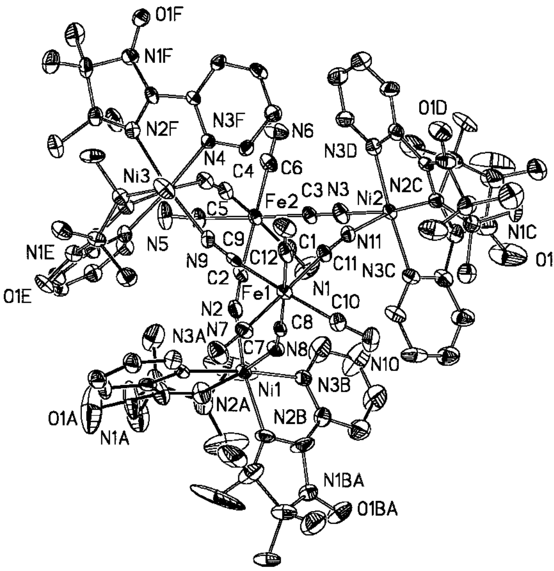

Figure 1. Molecular structure of cluster **1a**. Only one position of the statistically disordered IM-2Py ligands on Ni1 is shown, and the molecules of water are omitted. Selected bond lengths (Å, av) and angles (deg, av) are as follows for **1a**: Fe1−Fe2 = 6.59, Fe−Ni = 5.06, Ni−Ni = 6.62, Fe−C = 1.945, Ni−N (CN) = 2.039, Ni−N (L) = 2.118, N−O (nitroxyl) = 1.250; Ni−Ni−Ni = 60, Ni−Fe−Ni = 82.2, Fe−Ni−Fe = 81.3.

Such a stoichiometry is similar to that already described for other sterically hindered chelating diamines[12] which, in contrast to ethylenediamine, give clusters instead of extended structures.[13,14] The synthesis was performed in a water−methanol mixture and, depending upon the content of water, two neutral solvates were obtained, **1a**, $[Fe_2(CN)_{12}Ni_3(IM\text{-}2Py)_6]\cdot 4H_2O$ and **1b**, $[Fe_2(CN)_{12}Ni_3(IM\text{-}2Py)_6]\cdot 2MeOH\cdot 2H_2O$. Compound **1a** was unambiguously characterized by single-crystal X-ray diffraction.[15] The structure consists of two $[Fe(CN)_6]$ octahedral fragments connected via three CN−Ni(IM-2Py)$_2$−NC bridges in a *fac* arrangement (Figure 1). Although the quality of the single-crystals of **1b** that we were able to grow were not suitable for a full X-ray diffraction determination, it was sufficient to establish the discrete nature of the compound and a similar Fe_2Ni_3 pentanuclear arrangement. In **1a** (H_2O solvate) one of the three Ni(II) fragments exhibits a statistical disorder involving the *gem*-dimethyl groups of the IM-2Py ligands. All three Ni(II) coordination spheres are *cis* and exhibit identical chirality within each molecule but the crystals are inactive since the space group ($P2_1/c$) is centrosymmetric.

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(11) Synthesis. A typical experiment involved 117 mg of IM-2Py and 59 mg of $Ni(ClO_4)_2\cdot 6H_2O$ in a mixture of 5 mL of H_2O and 2.5 mL of methanol. On adding 55 mg of $Fe(CN)_6K_3$ in 1.5 mL of H_2O, precipitation of **1b** occurred as a powder (23 mg). On standing, the solution afforded crystals of **1b** (34 mg). Slow evaporation of the filtrate resulted in formation of **1a** (78 mg) which was not obtained as single crystals if methanol is not used in the synthesis. IR ν(CN) (cm^{-1}): 2164 (bridging), 2123 (nonbridging). Satisfactory elemental analyses were obtained.

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(15) Crystal data. **1a**, (dark brown crystals, $T = 19$ °C): $C_{84}H_{104}Fe_2N_{30}Ni_3O_{10}$, M = 1980.8, monoclinic, space group $P2_1/c$, $a = 22.4567(3)$ Å, $b = 20.8822(3)$ Å, $c = 20.3466(1)$ Å, $\beta = 90.535(1)°$, $Z = 4$, $\rho = 1.380$ g cm^{-3}, Mo Kα graphite monochromated, 13645 data, 1217 parameters, $R(F) = 0.079$, wR(F^2) = 0.1588.

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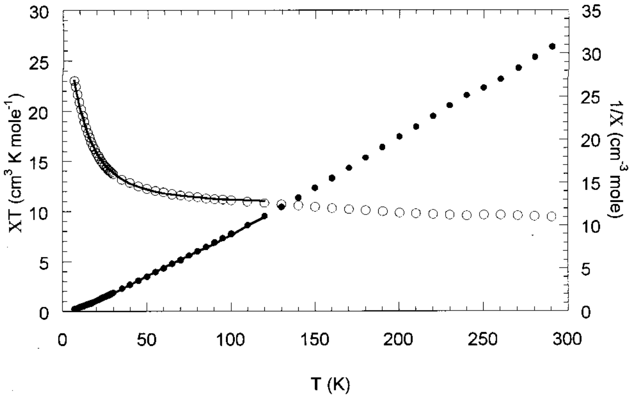

Figure 2. Temperature dependence of $\chi_M T$ and $1/\chi_M$ for **1a**. Solid lines between 120 and 5 K are calculated with parameters reported in the text.

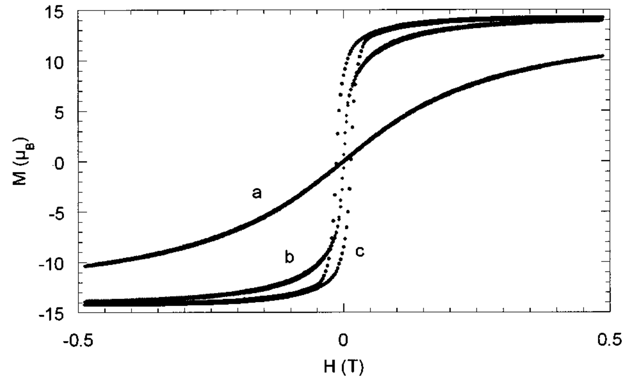

Figure 3. Field dependence of the magnetization for **1a** at 3 (a), 1.5 (b), and 1 (c) K. The field is aligned with the 001 direction of the crystal cell, and the sweeping rate of the field is 0.014 T s^{-1}.

The uncoordinated oxyl groups of the IM-2Py ligands are not engaged in intermolecular close contacts with each other as often observed in related compounds.[16] However, one of them (O1F) does experience hydrogen bonding (O(oxyl)−O(water) = 2.83 Å) with one (Ow3) water molecule also connected to one of the free CN groups of a neighboring molecule. This arrangement results in chains of clusters running along the *c* axis. A similar hydrogen bond network connecting the clusters is probably also present in **1b**. Although inter-nitroxide magnetic interactions mediated by hydrogen bonds are not strong,[17] from the magnetic point of view the neutral clusters are probably not very well isolated.

The magnetic behavior of both clusters is almost identical. Within the 5−300 K temperature range (Figure 2), on decreasing the temperature, $\chi_M T$ increases from 9.2 cm^3 K mole^{-1} to 24 cm^3 K mole^{-1}. The room-temperature value is much higher than anticipated for independent spin carriers ($<$7 cm^3 K mole^{-1}) but it is close to that expected for three $S = 2$ and two $S = {}^1/_2$ independent spins (∼10 emu K mole^{-1}) corresponding to three [Ni(IM-2Py)$_2$]$^{2+}$ and two low-spin [Fe(CN)$_6$]$^{3-}$ fragments. Indeed, a strong metal-radical ferromagnetic interaction ($2J = +200-300$ cm^{-1}) is well documented in Ni(II)-imino nitroxide species[10] (orthogonality of Ni(II) and nitroxide magnetic orbitals), but depopulation of $S = 0$ and 1 excited states in the *cis*-Ni(IM-2Py)$_2$ fragments is not complete at room temperature, a situation which accounts for the observed smaller value of $\chi_M T$. Since the ferromagnetic nature of Fe(III)−Ni(II) interactions mediated by cyano bridges is also well established, the expected ground spin-state of the cluster is $S = 7$. In agreement with this expectation, $\chi_M T$ increases monotonically as the temperature decreases and a positive value of θ (+ 2.9 K) is obtained through linear fitting of $1/\chi_M$ in the 300−10 K temperature range. To estimate the Fe(III)−Ni(II) interaction, the low temperature ($5 < T < 120$ K) magnetic data were modeled considering that the Fe(III) ions were interacting with identical *cis*-Ni(IM-2Py)$_2$, $S = 2$, fragments. These calculations[18] resulted in the following parameters: $g = 2.03(1)$, $J = +3.4(2)$ cm^{-1} ($H = -2J\mathbf{S}_i\mathbf{S}_j$); the quality of the agreement is only slightly improved if one considers a weak antiferromagnetic coupling $J_{Ni-Ni} = -0.20(1)$ cm^{-1} between Ni(II) centers. A $S = 7$ (14 μ_B) high ground spin-state is confirmed by the measurement of the magnetization at 4 K in the 0−5.5 T field range which saturates at 14.2 μ_B and is fairly well described by a Brillouin function for $S = 7$ and $g = 2.03$.

A related pentanuclear (Fe$_2$−Ni$_3$) cluster involving diamagnetic ligands instead of nitroxide free radicals was characterized by Murray.[12] In this $S = 4$ cluster heptaaquo solvate, an extensive study of the magnetic properties has ascertained the role of hydrogen bonds in intermolecular coupling and phase transition to a bulk ordered state. Since compound **1a** (and probably **1b**) displays a similar hydrogen bond network, we did not expect a low-temperature magnetic behavior corresponding to that of a single-molecule magnet. Indeed, we investigated the low-temperature behavior of single crystals of the two samples in the 5−0.5 K temperature range by use of a homemade microSQUID machine.[19] The few curves displayed in Figure 3 for **1a** show that an hysteresis loop opens below 1.2 K (1.3 K for **1b**). Relaxation measurements below 1.2 K showed a time dependence which is not exponential (logarithmic for $t > 50$ s) and more importantly, the relaxation process is temperature dependent down to 0.05 K. This behavior is in full contradiction with the presence of quantum effects and confirms the absence of single-molecule behavior.[2−4]

This study shows that nitroxide ligands are well suited for increasing the ground spin-state of a cluster leading to a rare onion-like structure where three shells of different spin bearers are ferromagnetically coupled. Nevertheless, close-packing of the clusters due to their neutrality and the presence of a intermolecular network of hydrogen bonds impede observation of a single-molecule magnet behavior. A single-molecule magnet based on this strategy should be designed in such a way as to minimize intermolecular magnetic interactions. Work along this line includes synthesis of charged clusters well separated by large organic counterions or/and incorporation of another shell of peripheral protecting diamagnetic ligands. Such attempts are currently under way.

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Supporting Information Available: Tables of crystal data, structure solution and refinement, atomic coordinates, bond lengths and angles, and anisotropic thermal parameters for **1a** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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