Inorganic Chemistry
Communication

Inorg. Chem. **2010**, *49*, 1–3 1
DOI: 10.1021/ic901747w

An Undecanuclear Fe^{III} Single-Molecule Magnet

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Received September 2, 2009

The undecanuclear complex in $[Fe^{III}_{11}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_4(L)_3(\mu\text{-}O_2CCMe_3)_{12}]Cl\cdot 5MeCN$ has been synthesized and characterized by single-crystal X-ray crystallography. Mössbauer spectroscopy and bulk susceptibility studies reveal that the complex has an $S = {}^{13}/_2$ spin ground state and exhibits single-molecule-magnet behavior.

While clusters containing Mn^{III} ions represent the largest source of single-molecule magnets (SMMs),[1] Fe^{III} has long been recognized as being less isotropic than is usually imagined[2] and polynuclear homovalent Fe^{III} compounds are an alternative source of interesting magnetic molecules, with several reported as SMMs in the literature.[3]

We and others recently reported the structurally related compounds $[Fe^{III}_7(\mu_3\text{-}O)_3(L)_3(\mu\text{-}O_2CCMe_3)_6(\eta^1\text{-}O_2CCMe_3)_3(H_2O)_3]$ (**1**) and $[Fe^{III}_8(\mu_4\text{-}O)_3(\mu_4\text{-tea})(teaH)_3(O_2CCMe_3)_6(X)_3]$ (**2**) (L = dianion of triethanolamine or N-substituted diethanolamine; X = N_3 or SCN).[4] The $\{Fe^{III}_7\}$ motif found in **1** corresponds to the theoretical model of a frustrated Heisenberg star, one of the very few solvable models in frustrated quantum-spin systems,[5] and is related to the motif found in some $[Fe^{III}_4]$ SMMs.[6] Elucidation of its magnetic properties should help in the understanding of the magnetic behavior of larger ferric systems. With this in mind, we have extended this work using diethanolamine ($deaH_2$) as the ligand, which results in the formation of a new undecanuclear SMM, $[Fe^{III}_{11}(\mu_4\text{-}O)_3(\mu_3\text{-}O)_4(dea)_3(\mu\text{-}O_2CCMe_3)_{12}]Cl\cdot 5MeCN$ (**3**), structurally related to **1** and **2**.

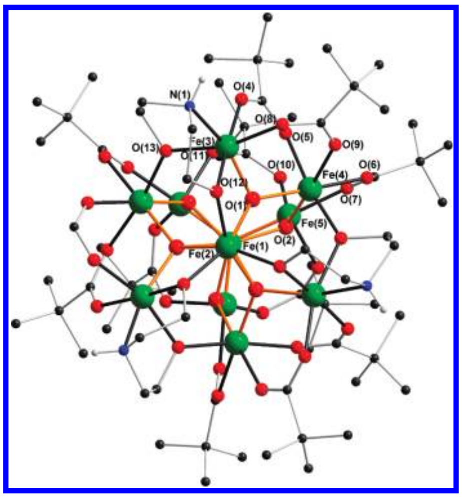

Figure 1. Molecular structure of **3** viewed along the C_3 axis. Organic H atoms and minor disorder of the *tert*-butyl groups were omitted for clarity; bonds to oxo ligands are shown as orange.

The reaction of $FeCl_3\cdot 6H_2O$ and HO_2CCMe_3 with $deaH_2$ in MeCN afforded dark-brown crystals of **3** in 60% yield. **3**

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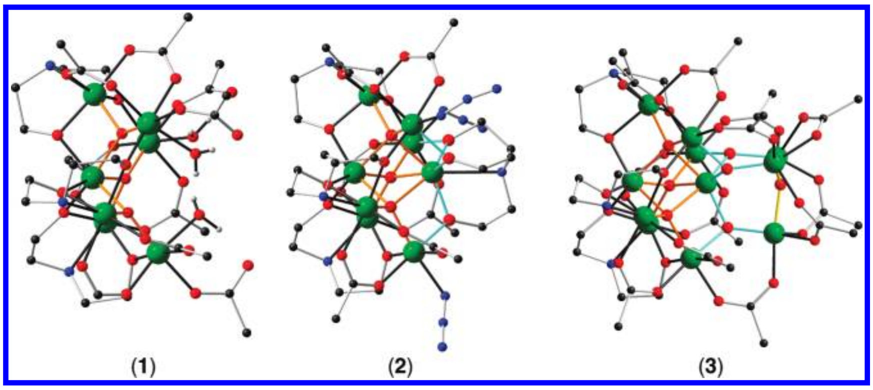

Figure 2. Structural relationship (see text) of compounds **1**−**3** (pivalate CH_3 groups, N substituents, and H atoms were omitted for clarity).

crystallizes in the space group $P\bar{3}c1$ with the Fe_{11} molecule on a 3-fold site.[7] The structure of the $[Fe_{11}]$ cluster in **3** (Figures 1 and 2) consists of an $[Fe^{III}{}_{11}(O)_7]^{19+}$ core with three μ_4-O^{2-} and four μ_3-O^{2-} bridges. Peripheral coordination is provided by 12 bridging pivalates and 3 chelating $(dea)^{2-}$ ligands. The deprotonated O atoms of these form μ-alkoxo bridges to other Fe^{III} centers.

The central Fe ions, Fe(1) and Fe(2), lie on the C_3 axis, and both show significant trigonal distortions in the octahedral FeO_6 environments. The respective $FeNO_5$ or FeO_6 environments of Fe(3) and Fe(4) are much closer to regular octahedral. By contrast, Fe(5) has a trigonal-bipyramidal FeO_5 coordination sphere consisting of three carboxylate O atoms from three different pivalate ligands and two $(\mu_3\text{-O})^{2-}$ oxides. The latter occupy one axial site and one equatorial site, leading to a rather unsymmetrical environment. The Fe−N and Fe−O bond distances are as expected for diethanolamine ligand coordination to Fe^{III},[4a] with mean bond lengths of 2.263 and 1.997 Å, respectively. The chloride counteranion and lattice MeCN are mutually disordered about a 3-fold axis in the crystal lattice. Compound **3** is a new addition to the small family of undecanuclear Fe^{III} complexes,[8] which all present different topologies and magnetic properties.

The structure of **3** is closely related to those of **1** and **2** (Figure 2). As was previously noted, **1** and **2** are related with a mononuclear {Fe(tea)} unit in **2** displacing the three aqua ligands in **1** and the conversion of the $(\mu_3\text{-O})^{2-}$ bridges in **1** to $(\mu_4\text{-O})^{2-}$ in **2** (orange bonds) and formation of three new alkoxo bridges (blue bonds).[4a] In **3**, we can see an analogous displacement of the aqua ligands in **1** by a tetranuclear $\{Fe_4O_4(piv)_3\}$ unit or as a replacement of the $(tea)^{3-}$ and azide ligands in **2** by a triangular $\{Fe_3O_4(piv)_6\}$ moiety. Either way, the three alkoxo bridges in **2** are replaced in **3** by three $(\mu_3\text{-O})^{2-}$ bridges (blue), with a fourth $(\mu_3\text{-O})^{2-}$ bridge between the three new Fe centers (yellow bonds).

The ^{57}Fe Mössbauer spectra of **3** (Figures 3 and S2−S4 in the Supporting Information, SI) indicate that **3** is paramagnetic between 293 and 30 K but exhibits typical spectra of correlated spins at 3.15 K. The paramagnetic spectra can be fitted with three doublets in a 2:6:3 ratio, assigned to the trigonally distorted Fe(1) and Fe(2), the less distorted octahedral Fe(3) and Fe(4), and the trigonal-bipyramidal Fe(5), respectively; the resulting hyperfine parameters are typical for Fe^{III} (Table S2 in the SI). Below 30 K, the Mössbauer spectra show that intermediate relaxation phenomena (Figure 3) become dominant, followed below 10 K by the development of magnetic hyperfine lines superimposed on the absorption envelope at the center of the spectrum. Although the spectra in the paramagnetic region could be fitted with a superposition of three doublets, a good fit for the spectrum at 3.15 K could only be achieved with five sextets, reflecting the five crystallographically different Fe centers, each with different directions of their electronic spin density. This results in an overlap of five nonequivalent six-line patterns at 3.15 K, with the effective hyperfine fields B_{eff} at the iron nuclei of 44.2, 35.6, 48.0, 41.4, and 27.4 T for Fe(1), Fe(2), Fe(3), Fe(4), and Fe(5), respectively (Figure S5 in the SI). In view of the magnetically dilute nature (the average distance between centroids is ∼16 Å) of the clusters found in **3**, the magnetic ordering effects observed at 3.15 K are likely due to magnetic coupling between the Fe^{III} spins in the complex rather than the long-range magnetic order.

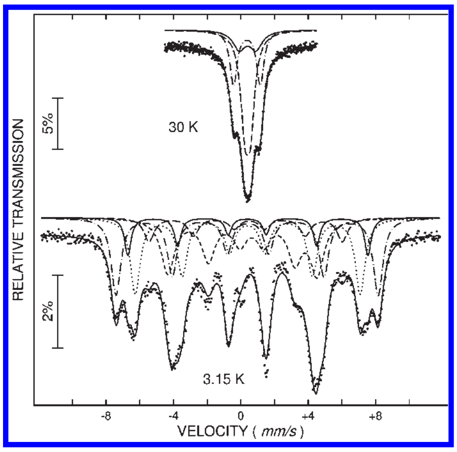

Figure 3. ^{57}Fe Mössbauer spectra of **3** at indicated temperatures.

Magnetic susceptibility data were collected over a range of 1.8−300 K under a field of 0.1 T (Figure 4) after the immediate isolation of the polycrystalline powder of **3** by filtration. The room temperature χT value is 18.5 $cm^3 \cdot K/mol$, which is much less than the value 48.125 $cm^3 \cdot K/mol$ expected for 11 uncoupled $S = {}^5/_2$ centers with $g = 2$, indicating strong antiferromagnetic interactions between the Fe^{III} ions. The χT product

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[7] **3**: $C_{82}H_{150}ClFe_{11}N_8O_{37}$, 2489.90 g/mol, trigonal, $P\bar{3}c1$, a = 15.5135(5) Å, c = 51.3543(17) Å, V = 10703.5(6) $Å^3$, T = 100 K, Z = 4, ρ_c = 1.545 g/cm^3, μ(Mo Kα) = 1.550 mm^{-1}, $F(000)$ = 5188, 46327 data, 7314 unique (R_{int} = 0.0326). wR2 = 0.1418, S = 1.235 (all data), R1 = 0.0459 [6277 with $I > 2\sigma(I)$]. CCDC 746368.

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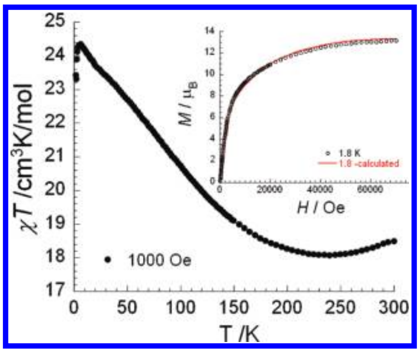

Figure 4. Temperature dependence of the χT product for **3** at 0.1 T (with $\chi = M/H$). Inset: Field dependence of the magnetization for **3** at 1.8 K; the red solid line is the fit discussed in the text.

decreases slightly between 300 and 240 K, reaching 18.1 cm^3·K/mol, but, upon further cooling, increases continuously to reach 24.4 cm^3·K/mol at 5 K, followed by a slight final decrease to 23.4 cm^3·K/mol at 1.8 K. Compound **3** can therefore be described as an uncompensated (sometimes described as ferrimagnetic) spin system, in which the magnetic behavior is similar to that reported for many Fe clusters showing SMM behavior.[3,8a,9] The final decrease of the χT product below 5 K is probably the result of magnetic anisotropy and/or intermolecular interactions. Considering the presence of 11 $S = {}^5/_2$ spins, the ground state of the complex can take any value between ${}^1/_2$ and ${}^{55}/_2$. From the χT product at 5 K of 24.4 cm^3·K/mol, the value for **3** is ${}^{13}/_2$ (24.375 cm^3·K/mol), which is likely also supported by the field dependence of the magnetization at low temperatures (Figures 4 and S6 in the SI), which saturates at 13.2 μ_B at 7 T. To confirm this spin ground state, magnetization data collected at temperatures in the range of 1.8−7 K and with fields up to 7 T were fitted using ANISOFIT.[10] As mentioned in the structural description, this molecule has a 3-fold symmetry, indicating the presence of uniaxial anisotropy D only. Furthermore, assuming that only the ground state is populated, simultaneous least-squares fittings to all data lead to $S = {}^{13}/_2$, $g = 2.09$, and $D = -0.25$ cm^{-1} (Figures S6 and S7 in the SI). It is worth noting that the sign of D is always under question using M vs H data, but the slow relaxation of the magnetization observed in **3** (vide infra) confirms the uniaxial nature of the anisotropy (i.e., a negative D value). Frequency-dependent in-phase (χ') and out-of-phase (χ'') alternating-current (ac) susceptibilities were found below 4 K (Figure S8 in the SI), showing that **3** exhibits slow relaxation of the magnetization. The frequency dependence of the ac susceptibility under an applied direct-current field was measured at 1.8 K (Figure S9 in the SI), and it appears that at around 10 Hz and above 1500 Hz two relaxation modes are present, maybe indicative of small interactions between [Fe$_{11}$] complexes.

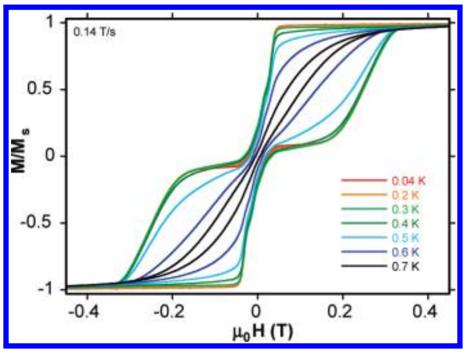

Figure 5. Hysteresis loops of the normalized magnetization for a single crystal of **3** oriented in its easy direction of magnetization at a field sweep rate of 0.14 T/s.

To confirm the SMM behavior for **3**, low-temperature (0.7−0.04 K), single-crystal magnetic measurements were performed using a micro-SQUID. Hysteresis loops were observed, for which the coercivity increases with both decreasing T and increasing scan rate (Figures 5 and S10 in the SI), confirming that **3** is a SMM. Slow relaxation is seen at $H = 0$; however, very broad steps could only be observed at 0.04 K, and it was not possible to obtain suitable magnetization versus time decay data to construct a reliable Arrhenius plot. Close examination of the hysteresis loops reveals a double-S shape around $H = 0$, indicative of very small intermolecular magnetic dipolar interactions, in agreement with the Mössbauer and magnetic data and with the lack of obvious intermolecular exchange pathways in the crystal structure. This is in contrast to the $S = {}^{13}/_2$ Fe$^{III}_9$ aggregate, where magnetic hysteresis can be attributed to significant intermolecular interactions.[11]

In conclusion, the cluster in **3** possesses a novel core topology and a ground spin state of $S = {}^{13}/_2$ and displays SMM behavior. A comparative Mössbauer study aimed at elucidating the magnetic structures of **1**−**3** is in progress.

Acknowledgment. DFG (CFN and SPP 1137), MAGMANet (NMP3-CT-2005-515767), Conseil Regional d'Aquitaine, GIS Advanced Materials in Aquitaine (COMET Project), Université de Bordeaux, and CNRS are thanked for financial support.

Supporting Information Available: Synthetic details, crystal data (CIF and additional structural data), and additional Mössbauer and magnetic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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