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Intensely Colored Mixed-Valence Iron(II) Iron(III) Formate Analogue of Prussian Blue Exhibits Néel N-Type Ferrimagnetism

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The presence of mixed-valence iron(II) and iron(III) imparts important properties to minerals such as magnetite (Fe_3O_4) and pigments such as Prussian Blue (PB) ($Fe^{III}_4[Fe^{II}(CN)_6]_3 \cdot xH_2O$), which has been called the first coordination compound.[1] An extensive body of research in recent years on PB and its transition-metal analogues has been motivated by their properties, including high-temperature molecular magnetism.[2] There is a comparable level of interest in coordination polymers utilizing larger multitopic ligands to obtain larger cavities in open-framework structures,[3] a good portion of which have been obtained using metal carboxylates.[4] Mixed-valence polyiron(II,III) oxalates $A[Fe^{II}Fe^{III}(C_2O_4)_3]$ ($A = R_4N^+$ cation) have been shown by Day and co-workers[5] to exhibit Néel N-type ferrimagnetism with some cations but not others. The rare negative magnetization observed in the two-dimensional (2D) polyiron(II,III) oxalates has not been seen in 3D molecular-based network magnets[6] until the present work.

The reported framework structures of the anionic divalent formates $A[M^{II}(HCOO)_3]$ (**1**) [$A = NH_4^+$, $Me_2NH_2^+$, $(Me_2enH_2^{2+})_{1/2}$; M = Mn, Co, Ni][7] and neutral trivalent formates, $[M^{III}(HCOO)_3] \cdot X$ (**2**) (M = Mn,[8] Fe,[9] Al,[8] Ga,[8] In;[8] X = HCOOH, CO_2) are remarkably similar, with cations in the cavities of the former and small neutral molecules such as formic acid or CO_2 in those of the latter. This suggests that it should be possible to isolate mixed-valence structures of iron(II) and iron(III) related to PB as well as 3D anionic polymetal(II,III) oxalates.

Reactions of $Fe_3(HCOO)_6 \cdot DMF$ in a combination of DMF and concentrated formic acid afford mixtures of colorless crystals of $(Me_2NH_2)[Fe(HCOO)_3]$ (**1**) and $Fe_3(HCOO)_6$ (orthorhombic form) and black crystals of $(Me_2NH_2)[Fe_2(HCOO)_6]$ (**3**).[10] These have to be mechanically separated. An alternative synthetic approach that affords pure crystalline samples of **3** involves heating the mixed-valence cluster $[Fe_3O(CH_3COO)_6(H_2O)_3]$ (**4**)[11] at 110 °C in a mixture of DMF and concentrated formic acid.

The colorless iron(II) formates encountered in this work are isomorphous to formates of other divalent transition metals.[12,13] The intensely colored crystals, on the other hand, are unprecedented mixed-valence polyiron(II,III) framework formate materials. Whereas the anionic iron(II) formate **1** crystallizes in the rhombohedral space group $R\bar{3}c$ with $Z = 6$, compound **3** crystallizes in the trigonal space group $P\bar{3}c1$ with $Z = 2$.

There are two independent iron atoms in the asymmetric unit of **3** (Figure 1). Bond valence sum (BVS) calculations[14] indicate that Fe(1) is iron(II) (BVS 2.12, FeO_6 octahedral volume of 12.6 Å^3) and Fe(2) is iron(III) (BVS 3.08, FeO_6 volume of 10.7 Å^3). The formates bridge each Fe(1) to six different Fe(2) atoms in the anti−anti bonding mode. This results in a structure composed of alternating layers of Fe(II) with $Me_2NH_2^+$ cations and Fe(III) perpendicular to the unique *c* axis (Figure 2).

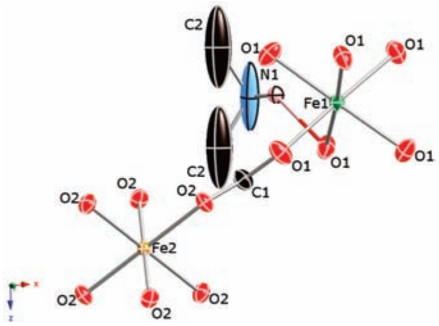

Figure 1. Thermal ellipsoid plot of $(Me_2NH_2)[Fe^{II}Fe^{III}(HCOO)_6]$ (**3**). The cation is disordered about a D_3 site, and only one N−H···O hydrogen bond is shown. Fe(1)−O(1), 2.119(1) Å; Fe(2)−O(2), 2.0049(9) Å; Fe(1)···Fe(2), 5.89 Å.

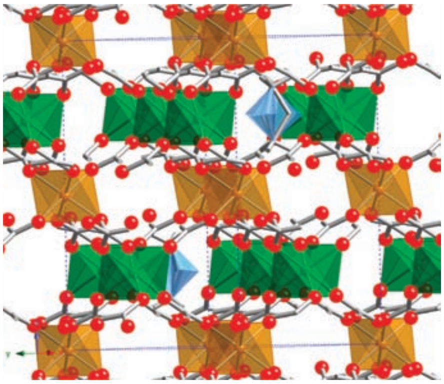

Figure 2. Polyhedral representation of the layered structure of **3**, with Fe(II) in green, Fe(III) in ocher, and N in blue (only two representative cations are shown).

The structure of **1** is very similar to that of **3** except that there is only one crystallographic iron site and all of the cavities are occupied by $Me_2NH_2^+$. The volume and Fe−O bond lengths are 13.0 Å^3 and 2.1362 (7) Å, respectively, in the $Fe^{II}O_6$ octahedra in **1** and 10.6 Å^3 and 1.997(2) Å, respectively, in the $Fe^{III}O_6$ octahedra of **2**.

The 3D network in **3** consists of Fe(III) surrounded by an octahedral arrangement of six nearest-neighbor Fe(II), while six Fe(III) form a trigonal prism about each octahedral Fe(II). The Fe···Fe distances are 6.04 Å in **1**, 5.89 Å in **3**, ~5.5 Å in $[Fe^{II}Fe^{III}(C_2O_4)_3]^-$, and 5.08 Å in PB. The 2D and 3D polymetal oxalates have only three neighboring metals.

The observed parameters in the room temperature (298 K) Mössbauer spectrum of **3** (Figure 3) support the structural data and are indicative of high-spin Fe(II) and Fe(III) with oxygen coordination.[10,15] The magnetic susceptibility data (Figure 4) indicate that Fe(II) and Fe(III) are noninteracting at room temper-

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10.1021/ja901093b CCC: $40.75

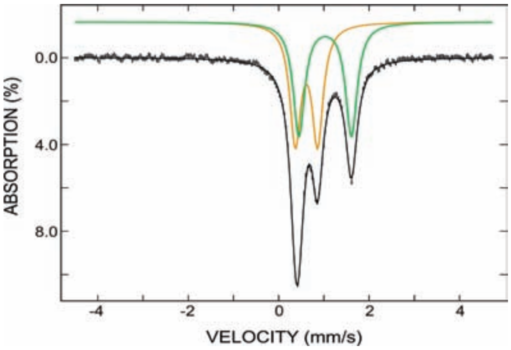

Figure 3. Room-temperature Mössbauer spectrum (hatched marks) of powdered crystals of **3**. The spectrum can be decomposed into two components, with Fe(II) in green [isomer shift (δ) = 1.03 mm/s, quadrupole splitting (ΔE_Q) = 1.16 mm/s, line width (Γ) = 0.31 mm/s] and Fe(III) in ocher (δ = 0.62 mm/s, ΔE_Q = 0.49 mm/s, Γ = 0.30 mm/s). The black solid line is the composite spectrum.

ature but that spontaneous magnetization occurs at low temperature, including negative magnetization that has been seen in only Day and co-workers' anionic polyiron(II,III) 2D magnets.[5,16]

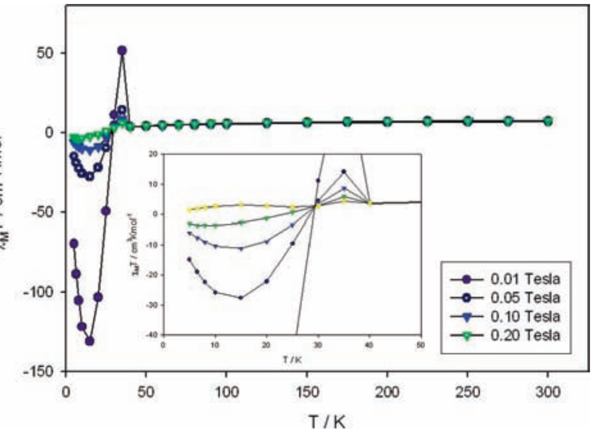

Figure 4. Plot of $\chi_M T$ vs T for powdered crystals of **3**.

The black crystals, which appear dark-purple when powdered, exhibit a very broad intervalence charge-transfer (IVCT) band ($\lambda_{max} \approx 520$ nm $\approx 19\,200$ cm^{-1}) that covers the whole visible spectrum (Figure S1 in the Supporting Information) and a more intense peak at 280 nm. The intense color is bleached when the material is dissolved in water or DMF. The polyiron(II,III) oxalates do not exhibit an IVCT band, although Lippard and co-workers' valence-delocalized diiron(II,III) paddlewheel carboxylates do (Fe···Fe 2.7 Å).[17] The physical properties of this framework material indicate class II mixed-valence behavior in the Robin−Day classification scheme.[18]

Acknowledgment. We thank the University Research Committee and Chemistry Department of Emory University, the NIH (GM47295 to B.H.H.), and the NSF (CHE 0414555 to G.C.) for financial support and the NSF [CHE-9974864 (single-crystal) and CHE-0541752 (powder)] and NIH (S10-RR07323 and S10-RR13673) for support of the X-ray Crystallography Center.

Supporting Information Available: Synthetic details, UV−vis and IR spectra, and thermogravimetric and X-ray powder diffraction data for **3** and details of the crystal structures of **1** and **3** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) (a) (Me$_2$NH$_2$)[Fe(HCOO)$_3$] (**1**): rhombohedral; $R\bar{3}c$; $Z = 6$; $T = 173$ K; $a = b = 8.2310(5)$ Å, $c = 22.399(3)$ Å; $V = 1314.2(2)$ Å^3; R$_1$ = 0.020, wR$_2$ = 0.054. (b) (Me$_2$NH$_2$)[Fe$_2$(HCOO)$_6$] (**3**): trigonal; $P\bar{3}c1$; $Z = 2$; $T = 173$ K; $a = b = 8.251(5)$ Å, $c = 13.846(3)$ Å; $V = 816.4(2)$ Å^3; R$_1$ = 0.028, wR$_2$ = 0.077.
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JA901093B