Magnetic properties of a metal-organic network Fe(N₃)₂(4,4′-bpy)

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The results of magnetic susceptibility, isothermal magnetization, and heat capacity measurements on a newly discovered iron complex with mixed ligands Fe(N₃)₂(4,4′-bpy) (4,4′-bpy = 4,4′-bipyridine) are reported. The study of high-temperature magnetic susceptibility data indicates antiferromagnetic correlation of the Fe²⁺ moments. However, the results of low-temperature measurements reveal a ferromagnetic transition for this compound, and the Curie temperature is determined from the Arrott plot with Tᵥ = 20 K. The large jump in the heat capacity data confirms the magnetic phase transition and the transition temperature. © 2002 American Institute of Physics. [DOI: 10.1063/1.1456426]
nomic nature of the Fe\(^{2+}\) interaction at high temperature is also evidenced in the \(\chi \cdot T\) vs \(T\) plot shown in Fig. 2 and its insert. As temperature \(T\) is lowered, the \(\chi \cdot T\) data decreases its value from \(\sim 3\) emu K/mol at room temperature, which is expected for a free Fe\(^{2+}\), to a minimum of \(\sim -2\) emu K/mol at \(T = 31\) K. Such variation of \(\chi \cdot T\) vs \(T\) is expected for an antiferromagnetic coupling. However, as \(T\) is further decreased from 31 K, which is still well above \(T_C\) of 20 K, \(\chi \cdot T\) starts to increase, until it reaches its maximum value at \(\sim 16\) K. \(\chi \cdot T\) decreases as \(T\) decreases from 16 to 0 K, due to the Fe\(^{2+}\) saturation at low \(T\). The increase in \(\chi \cdot T\) upon cooling in the \(16 < T < 31\) K range indicates that a positive exchange coupling of Fe\(^{2+}\) is dominant at temperatures below 31 K and it could be responsible for the ferromagnetlike phase transition at 20 K. Similar sign changing for the exchange coupling from “−” at high \(T\) to “+” at low \(T\) was previously observed in an isostructural compound \([\text{Mn}(4,4'-\text{bpy})(\text{N}_3)_2]_n\) and in two other metal-azido networks with 2D networks, \([\text{Mn}(4-\text{acpy})_2(\text{N}_3)_2]_n\)\(^{14}\) and \([\text{Mn(py)}_2(\text{N}_3)_2]_n\).\(^{15}\) However, the turning point for \(\chi \cdot T\) in these systems are all very close to the transition temperatures of the long range magnetic ordering characterized as an antiferromagnetic kind with canting phenomena. This is very different from what is observed in our system, i.e., the turning point for \(\chi \cdot T\) is at 31 K, 11 K higher than \(T_C\).

Figure 3 illustrates the \(M(H)\) data measured at 2 K on I. At the low field region, the \(M(H)\) curve behaves somewhat like a ferromagnet. A sizable hysteresis loop is observed as shown in the insert of Fig. 3. The coercivity is found to be \(H_c = 900\) G. The \(M(H)\) value continues to increase with a rather large slope, as the field increases from 30 kG and above. At the largest field of 250 kG, \(M(H)\) reaches \(13 \times 10^3\) emu/mol, which is 2.33 \(\mu_B\) per Fe\(^{2+}\), and shows no clear sign of changing slope. In contrast to \(M(H)\) of the isostructural compound \([\text{Mn}(4,4'-\text{bpy})(\text{N}_3)_2]_n\), for which a canting antiferromagnetic structure that produces weak ferromagnetism was proposed, the \(M(H)\) of I is very suggestive that the ground state magnetic structure is ferromagnetic, if one argues that the large slope and the nonsaturation behavior of the \(M(H)\) curve could be explained by the possible existence of a large anisotropy energy in this compound. Yet, we could not exclude the possibility that such behavior is due to the fact that the ground state magnetic structure is not a truly ferromagnetic one. In other words, there could exist a certain kind of canting structure that would produce a ferromagnetic component in a particular direction, though for most of the cases involving canting phenomena, the \(M(H)\) values would not reach as high as that of I.

The thermal evolution of \(M(H)\) was investigated. In an “Arrott plot” (not shown), it was seen that a mean-field approximation for ferromagnetism at the small field region agreed with the experimental data quite reasonably, and the transition temperature \(T_C\) was determined to be 20 K. The data of molar heat capacity \(C(T)\) measured in zero field and a field of 35 kG are presented in Fig. 4. A cusplike anomaly with a peak value of 32 J/mol K at \(T = 20\) K is clearly seen for the zero field \(C(T)\) data set, consistent with the spontaneous ferromagnetic phase transition observed in the magnetization measurements. The Curie temperature \(T_C\), determined from \(C(T)\) measurements, is consistent with that determined from for the \(\chi(T)\) measurements and the Arrott plot. In the \(C(T)\) of 35 kG data set the peak is shifted to 21.5 K and the anomaly is spread out to a much wider range of \(T\). The shift towards to a higher temperature of the \(C(T)\) anomaly under an applied field is typical for ferromagnetic systems, thus the result of \(C(T)\) measurements strongly supports the ferromagnetic ground state exhibited in I. Due to lack of a knowledge of the phonon contribution to the total heat capacity, magnetic entropy removal \(\Delta S_m\) was estimated by integrating the \(\Delta C(T)/T\) vs \(T\) curve from 15 to 21.5 K.
where $\Delta C(T)$ is the difference between the measured $C(T)$ curve and a smooth curve $C'(T)$, obtained by extrapolating the $C(T)$ data at far below and far above the anomalous region. The estimated $\Delta S_m$ is 3.2 J/mol K, which is about 24% of 13.5 J/mol K, a value calculated from $\Delta S_{cal} = Nk_B \ln(2s+1)$, assuming $s = 2$ for Fe$^{2+}$. It is also interesting to note that the shape of the zero field $C(T)$ anomaly is not that of a typical second order transition, in that the slopes on both sides of the cusp are rather symmetric, which is different from the asymmetric $\lambda$-like shape predicted by a mean-field theory. Further investigations are on the way to see whether a crystalline structure transformation also occurs in the vicinity of $T_C$, participating in the overall $C(T)$ anomaly, in addition to the anomaly that originates from the magnetic phase transition.

The magnetic interactions of Fe$^{2+}$ in the network of I are achieved mainly via the $\mu-(1, 3)$ bridging azido ligands. Because the $\mu-(1, 3)$ bridging is expected to be antiferromagnetic, the unique network of I involving the two types of helical pathways would produce a very interesting arrangement for the Fe$^{2+}$ moments when ordered: For the Fe$^{2+}$ lining along both the [010] (the direction for both helices) and [100] direction, their moments, oriented, or at least a component of their moments, would be in the same direction. In effect, this would be true for the Fe$^{2+}$ moments lining along the 4,4' -bpy axial as well. The complex antiferro-ferromagnetic magnetic correlation observed in both [Mn(4,4' -bpy)(N$_3$)$_2$], and Fe(N$_3$)$_2$(4,4' -bpy) systems may have originated from this topological uniqueness. However, this alone cannot explain the overwhelming ferromagnetic interaction of the Fe$^{2+}$, which leads to the long range ferromagnetic ordering with rather high $T_C$ in the Fe(N$_3$)$_2$(4,4' -bpy) system, in contrast to the weak ferromagnetic behavior exhibited in the Mn isostructural compound. Orbital contribution to the Fe$^{2+}$ moment, especially at low temperatures, should be considered because of its distorted octahedral site. Low-temperature structural information will also be crucial. Our ongoing investigations using complementary experimental techniques will further reveal the true nature of this organometallic magnet.

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