A Nearly Ideal One-Dimensional $S = 5/2$ Antiferromagnet FeF$_3$(4,4′-bpy) (4,4′-bpy =4,4′-bipyridyl) with Strong Intrachain Interactions

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S *Supporting Information*

ABSTRACT: An ideal one-dimensional (1D) magnet is expected to show exotic quantum phenomena. For compounds with larger S (S = 3/2, 2, 5/2, ...), however, a small interchain interaction J' tends to drive a conventional long-range ordered (LRO) state. Here, a new layered structure of FeF$_3$(4,4′-bpy) (4,4′-bpy = 4,4′-bipyridyl) with novel S = 5/2 (Fe^{3+}) chains has been hydrothermally synthesized by using 4,4′-bpy to separate chains. The temperature-dependent susceptibility exhibits a broad maximum at high as 164 K, suggesting a fairly strong Fe−F−Fe intrachain interaction J. However, no anomaly associated with a LRO is seen in both magnetic susceptibility and specific heat even down to 2 K. This indicates an extremely small J' with $J'/J < 3.2 \times 10^{-5}$, making this new material a nearly ideal 1D antiferromagnet. Mössbauer spectroscopy at 2.7 K reveals a critical slowing down of the 1D fluctuations toward a possible LRO at lower temperatures.

Low-dimensional antiferromagnetic (AFM) systems, in particular one-dimensional (1D) Heisenberg spin chains, have been extensively investigated because of their intriguing phenomena, such as reduced magnetic moment, spin-charge separation, and quantum disordered state.[1] Experimental investigations on the 1D AFM Heisenberg spin chain system are quite active, in particular since Haldane conjectured that integer and half-integer spin chains possess different types of quantum disordered ground states: a spin-singlet state with an energy (Haldane) gap and a magnetic state with gapless excitations, respectively.[2] In a real material, however, there inevitably exists an interchain interaction J', which provides a crucial influence on the magnetic properties. It is theoretically shown that, with increasing S, the quantum disordered state is significantly destabilized. For example, the Haldane gap is reduced from $E_g \sim 0.411|J|$ for S = 1 to $E_g < 0.1|J|$ for S = 2.[3] One can therefore expect that for a larger-S chain even a small interchain interaction induces a long-range ordered (LRO) state. Indeed, Haldane-gap compounds have been realized mostly for S = 1 including [Ni(en)$_2$(NO$_2$)]ClO$_4$[4] and AgVP$_2$S$_6$.[5] For S = 2 only Mn(2,2′-bpy)Cl$_3$ (2,2′-bpy =2,2′-bipyridyl) is reported.[6] Likewise, spin-Peierls transitions predicted for half-integer S have

been exclusively limited to S = 1/2 systems such as TTF-MS$_4$C$_4$(CF$_3$)$_4$ (TTF = tetrathiafulvalene, M = Cu^{2+}, Au^{2+})[7] and CuGeO$_3$.[8] For better understanding of the nature of a large-S chain, it would be crucial to explore new materials having a more ideal chain with $J'/J \ll 1$. Bi$_2$Fe(SeO$_3$)$_2$OCl$_3$[9] and FeSeO$_3$F[10] with S = 5/2 are recently reported as such candidates, but the values of J'/J are relatively large, 0.08 and ~0.33, respectively.

Recently, a diverse range of hybrid compounds has been studied for solar cell applications, geometrical spin frustration, quantum tunneling in magnetization, and so on.[11] In comparison with purely inorganic compounds (e.g., oxides), hybrid systems are advantageous in terms of weakening interchain interactions. For example, 4,4′-bipyridyl (4,4′-bpy), 2,2′-bithiazol (bt), and 1,4-bis(imidazol-1-yl)benzene (bib) were used to separate divalent transition-metal chains [ML$_2$L′ (M = Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, etc.; L$_2$ = F$_2^{2-}$, Cl$_2^{2-}$, (N$_3$)$_2^{2-}$, C$_2$O$_4^{2-}$, etc.), L′ = 4,4′-bpy, bt, bib, etc.].[11b,12] The structure of these hybrids is characterized by doubly bridging M−L$_2$−M octahedral chains that are covalently connected by L′. The edge-sharing connectivity of octahedra, unfortunately, gives relatively weak AFM (or even ferromagnetic) intrachain interactions according to the Goodenough−Kanamori rule.[13] As a result, magnetic order can be easily achieved in these hybrids.[11b,12b,c,e,14] In order to increase J (decrease J'/J), the corner-sharing octahedral chains with 180° bridging angle are desirable, but few hybrids with corner-sharing octahedral chains are reported to date. In particular, for metal-(4,4′-bpy) hybrids, only V^{3+} (S = 1)[15] and Mn^{3+} (S = 2)[16] systems exit. However, the magnetic susceptibility χ of the former sample has a serious contribution of impurity or defects. In the latter, the χ−T curve shows a 1D character with its maximum at $T(\chi_{max})$ = 68 K, but the Mn−F−Mn angle largely varies with temperature.[15,16] Thus, both compounds are not suitable systems as large-S chains. Here, we report on the hydrothermal preparation of the iron analogue FeF$_3$(4,4′-bpy) **1** with S = 5/2 (Fe^{3+}). The magnetic measurements indicate an excellent 1D nature with $J'/J < 3.2 \times 10^{-5}$.

The title compound **1** was hydrothermally synthesized with Fe$_2$O$_3$, 4,4′-bpy, and HF$_{aq}$ (*caution!*), as used in Poeppelmeier group.[17] Experimental details and crystallographic data are described in Supporting Information (SI). The phase purity was

examined by X-ray diffraction (XRD) pattern of ground crystals (Figure S1). Compound **1** crystallizes in a layered structure with the space group $I222$ [a = 3.8900(3) Å, b = 10.7997(9) Å, c = 11.3951(8) Å]. As shown in Figure 1, the layers are stacked along
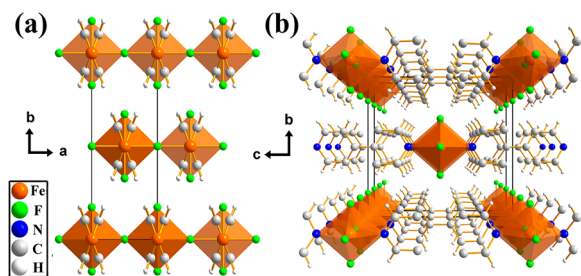

Figure 1. Crystal structure of **1** along (a) the c and (b) the a axes.

the b axis with a distance of 5.3999(5) Å (half of the b axis) and stabilized by hydrogen-bonding interactions through $C_2-H_2\cdots F_1$ between layers ($H_2\cdots F_1$ = 2.3080(1) Å, $\angle C_2-H_2-F_1$ = 164.0°). The Fe$\cdots$Fe distance between layers is 8.0872(4) Å. Within the layer, the iron-centered FeF_4N_2 octahedra share trans-F atoms to form a linear magnetic chain (i.e., $\angle$Fe$-$F$-$Fe = 180°) along the a axis (see Figure 1). Along the c axis, the chains are bridged to each other by the 4,4′-bpy groups, where the two pyridine rings are twisted by an angle of 41.0°. For the FeF_4N_2 octahedron, Fe$-$F$_2$(trans-F), Fe$-$F$_1$(terminal-F), and Fe$-$N bond lengths are, respectively, 1.9450(2) Å, 1.8596(2) Å, and 2.1606(1) Å (Table S2). The single-crystal XRD at 123 K provided no evidence for structural modulation, as opposed to MnF_3(4,4′-bpy).[16]

The oxidation state of +3 in iron is confirmed by bond valence sums (BVS) calculations (Table S2).[18] Moreover, the Mössbauer spectrum of compound **1** at 297 K (Figure 2) consists of a sharp doublet, which is consistent with the single iron site from XRD. The value of isomer shift (IS), 0.382 mms^{-1}, is typical for a trivalent iron in a high spin state. The full width at half-maximum (fwhm) is 0.31 mms^{-1}, which is close to the instrumental
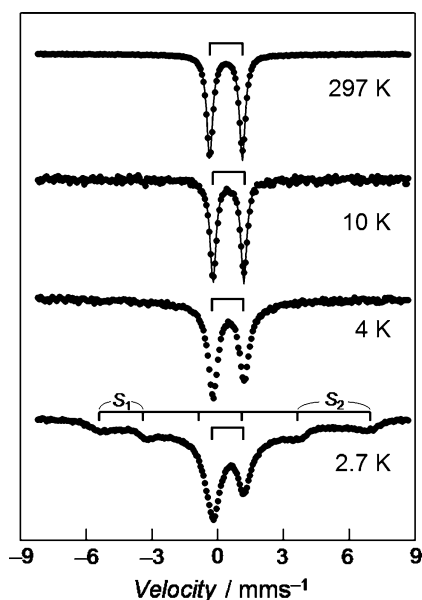

Figure 2. ^{57}Fe Mössbauer spectra of compound **1** at various temperatures. The circles and the solid lines represent experimental and fitting curves, respectively.

resolution (see Table S3). To further verify the structure and composition of **1**, TG-DTA was performed in air (Figure S3). The sample started to decompose around 250 °C to Fe_2O_3, accompanied by an exothermic peak. The weight loss of 29.8% corresponds mostly to the loss of 4,4′-bpy, in excellent agreement with the calculated value of 29.7%.

From the determined crystal structure, **1** is likely to show a 1D magnetic behavior with predominant intrachain superexchange AFM (Fe$-$F$-$Fe) interactions J along [100]. In the ac layer, the interchain Fe$\cdots$Fe distance mediated by 4,4′-bpy along [001] is 11.3951(8) Å, much longer than the intrachain Fe$\cdots$Fe distance of 3.8900(3) Å along [100]. Thus, the interchain interaction J' should be much smaller. Besides, one can consider the Fe$-$Fe interaction J'' between layers (Figure 1b). Although a shorter Fe$\cdots$Fe distance of 8.0872(4) Å is found between layers (than that along [001]), the Fe^{3+} ions are not chemically bonded. Also, the staggered arrangement of chains induces a magnetic frustration. From these considerations, the magnetism of **1** should be well described by the S = 5/2 AFM chains. Figure 3
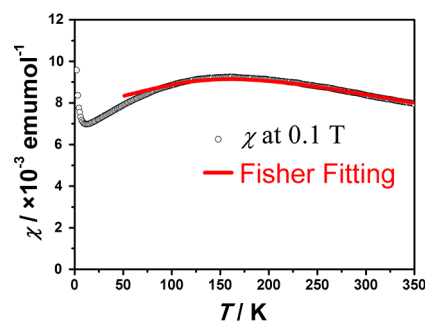

Figure 3. $\chi(T)$ for **1** measured at 0.1 T. The red curve is a fitting by Fisher classical spin model at 50−350 K.

shows the temperature-dependent magnetic susceptibility for **1** measured up to 350 K. The most notable feature is a very broad maximum centered around $T(\chi_{max})$ = 164 K. Undoubtedly, this broad maximum in the $\chi-T$ curve is originated from well-developed spin−spin correlations or short-range order (SRO) along the chain. The high $T(\chi_{max})$ assures fairly strong AFM intrachain interactions. No signature of LRO is seen down to 2 K. A slight increase of $\chi(T)$ below 15 K is ascribed to a tiny amount of free paramagnetic spins (at most 0.15% of high-spin Fe^{3+}, Figure S5), referred often as Curie tail.[19] The system is not purely paramagnetic up to 350 K reflecting short-range spin−spin correlations. Upon temperature cooling (Figure S4), the χT starts to decrease even from 350 K, thereby reinforcing the interpretation that the AFM intrachain interaction is strong. The temperature-dependent magnetic susceptibility was fitted by a Fisher classical model of $\chi = [Ng^2\mu_B^2 S(S + 1)/3k_BT]\cdot[(1 + u)/(1 - u)]$, where g = 2, S = 5/2, $u = \coth[2JS(S + 1)/k_BT] - k_BT/2JS(S + 1)$, and J is defined negative for AFM coupling from the Hamiltonian $H = -2J\sum S_iS_{i+1}$.[19a,20] As shown in Figure 3, the best fit to the experimental data between 50 and 350 K gave J/k_B = −19.2(1) K, which is close to −16.6 K simply estimated from a relation $T(\chi_{max})/(|J|/k_B) = 1.12S(S + 1) + 0.10$.[21] The agreement between experimental and theoretical curves is reasonably good, particularly at high temperatures. A slight discrepancy in the low-temperature regime may arise from the next-nearest-neighbor intrachain interaction and/or Dzyaloshinskii−Moriya interaction, which are not included in the model above and will be investigated in near future, combined with theoretical calcu-

lations. Note that more details of fittings including a mean-field approximation were given in Figure S5.

The temperature dependence of the specific heat is shown in Figure 4. Consistent with the susceptibility data, there is no sign
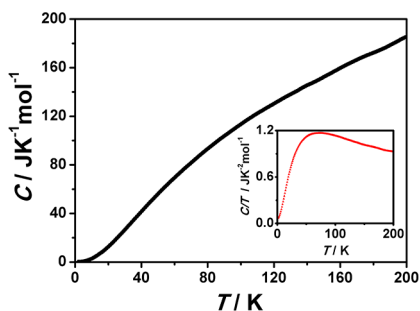

Figure 4. Specific heat for compound **1**. Inset shows specific heat divided by temperature.

of a phase transition down to 2 K. The $C/T-T$ curve, shown in the inset of Figure 4, has a broad maximum at around 74 K, suggesting the presence of SRO, which agrees with the susceptibility data. Low-temperature Mössbauer spectra are shown in Figure 2. The spectrum at 10 K stays a doublet, consistent with a paramagnetic state. It is rather surprising that the doublet is almost symmetric and is resolution limited, which indicates the excellent quality of the specimen as well as fast spin fluctuations despite well-developed 1D SRO. At 4 K, the doublet becomes slightly anisotropic and broader than those above 4 K, suggesting that spin relaxation is becoming slower and is within the time window for Mössbauer spectroscopy (10^{-11} to 10^{-6} s for ^{57}Fe). When temperature is further lowered to 2.7 K, the asymmetry of the doublet spectrum becomes much more pronounced with broadened peak widths. In addition, there appears another component featured by a broad sextet with a hyperfine field of 38 T. In low-dimensional magnetic systems, strong spin fluctuations often lead to novel phase separation as observed in La_2CuO_{4+y}, $(Cu_{1-x}Zn_x)GeO_3$ and $(CuCl)La-(Nb_{1-x}Ta_x)_2O_7$.[22] It may be possible that the enhanced one dimensionality in our compound gives an unusual phase separating behavior. It would be also possible that only a very small amount of defect induces a phase separation.

It should be pointed out that the static specific heat and susceptibility data down to 2 K did not show any anomaly associated with LRO, which appears to contradict with the result of dynamical Mössbauer measurement at 2.7 K. This fact and the fairly broad sextet subspectrum suggest that the observed (sextet) state is not a truly LRO state in a sense of thermodynamic equilibrium but a dynamical one with strong and slow fluctuations in a time domain of Mössbauer spectroscopy. In order to understand the ground state of this new material, further experimental study is necessary, particularly lower temperature experiments, which is in progress.

For a better estimation of interchain interaction J', we employed an equation $\exp[2|J|/(k_BT_N)] = (4 + z\eta)/(z\eta)$,[9,23] where η is J'/J and z is the number of nearest-neighboring chains ($z = 4$). This model was also used for the recently reported classical quasi-1D magnet $Bi_2Fe(SeO_3)_2OCl_3$, yielding $J'/J = 0.08$.[9] Since we have not reached the transition temperature in our compound **1**, we assumed here $T_N = 2.0$ K, which should provide a higher limit of J'/J. Remarkably, an exceedingly small value of $J'/J < 4.6 \times 10^{-9}$ is obtained for **1**. An alternate model based on Green function method, $k_BT_N/|J| = 4S(S + 1)/3I(\eta)$,

where $I(\eta) \approx 0.633/(\eta^{1/2})$ (when $\eta \ll 1$),[23,24] which is known more appropriate for small η (like the present case), gives a larger but still significantly small value of $J'/J < 3.2 \times 10^{-5}$.

In $FeF_3(4,4'-bpy)$, the susceptibility shows the broad maximum at $T(\chi_{max}) = 164$ K, and the intrachain interaction was calculated to be $J/k_B = -19.2(1)$ K. Despite the strong intrachain interaction along the Fe−F−Fe chain, **1** does not experience LRO even at 2 K, thanks to negligibly small interchain interactions J' ($J'/J < 3.2 \times 10^{-5}$). Interestingly, different behaviors are observed in the isostructural Mn and V compounds. In $MnF_3(4,4'-bpy)$ with $S = 2$, $T(\chi_{max})$ is much lower (68 K) and the intrachain interaction ($J/k_B = -11.2$ K) is almost half of that of **1**, which is possibly due to a larger energy difference between Mn^{3+} 3d and F^- 2p orbitals than that between Fe^{3+} 3d and F^- 2p orbitals.[16] In $VF_3(4,4'-bpy)$ with $S = 1/2$, no obvious broad maximum is seen possibly because of low sample quality and/or paramagnetic impurity. Furthermore, it exhibits a magnetic order at 8 K.[15,16] In spite of the high $T(\chi_{max})$, **1** remains paramagnetic even down to 2 K, giving $T_N/T(\chi_{max}) < 0.01$ ($T_N < 2.0$ K). This reflects the excellent one-dimensionality of **1** characterized by fairly strong intrachain interaction and very small interchain interactions. To the best of our knowledge, no compounds with $S = 5/2$ (Fe^{3+} or Mn^{2+}) 1D chains have such a low $T_N/T(\chi_{max})$; mostly the $T_N/T(\chi_{max})$ values are at least ∼10 times larger, e.g., 0.09, 0.10, and 0.11 for $N_2H_6FeF_5$,[25] $FeF_5(C_2H_{10}N_2)$,[26] and β-$FeF_3\cdot H_2O$[27] with Fe−F−Fe chains, 0.10 and 0.27 for $Bi_2Fe(SeO_3)_2OCl_3$[9] and $NaFe(WO_4)_2$[28] with Fe−O−Fe chains, 0.16 for $CsMnCl_3\cdot 2H_2O$[29] with Mn−Cl−Mn chains, 0.21 for $SrMn_2V_2O_8$,[30] with Mn−O−Mn chains, 0.8 for $CuMnVO_4$[31] with $Mn-O_2$-Mn chains. As far as the authors are aware, $[(CH_3)_4N]MnCl_3$ with triply bridging $Mn-Cl_3-Mn$ chains has a small value of $T_N/T(\chi_{max}) \approx 0.02$, but the energy scale is much smaller ($T(\chi_{max}) = 55$ K, $J/k_B = -6.3$ K, $T_N = 0.84$ K) than the title compound **1**.[32]

Given the current availability of experimental techniques at low temperatures, it is important to increase J, in addition of reducing J', for an ultimate observation of the spin-Peierls transition or other exotic phenomena in $S = 5/2$ AFM chains. Regarding J, corner-sharing metal octahedra with M−L−M bridging angle of 180° is ideal as formed in **1** rather than edge- and face-sharing ones. Furthermore, it is also necessary to consider metal−ligand type with matchable orbital levels for more effective superexchange coupling. For example, the Fe−F−Fe coupling in **1** seems more effective, compared to Mn−F−Mn coupling in isostructure $MnF_3(4,4'-bpy)$. Numerical calculation for orbital levels of different metal−ligands would definitely help in revealing an ideal combination of transition metal and ligand. In comparison with J, the optimization of J' is not straightforward, but there are a number of molecule groups or clusters that can be tested so as to separate chains. Particularly, long organic molecules would be promising like 4,4'-bpy used in **1**.

In conclusion, a new 1D $S = 5/2$ (Fe^{3+}) antiferromagnet $FeF_3(4,4'-bpy)$ with Fe−F−Fe chains has been hydrothermally synthesized. The temperature-dependent susceptibility shows a typical 1D behavior, featured by a broad maximum at 164 K, indicating a strong intrachain interaction ($J/k_B = -19.2(1)$ K). The susceptibility, specific heat, and Mössbauer experiments all indicate that the title compound stays paramagnetic at least down to 2 K. The interesting observation is a superficial discrepancy for the existence of the LRO around 2 K between the static measurements of susceptibility and specific heat and the dynamic one of Mössbauer spectroscopy. It suggests that the observed

Mössbauer sextet state at 2.7 K (coexisting with the doublet state) indicates a critical slowing down of the 1D fluctuations in a time window of Mössbauer spectroscopy. Considerably weak interchain interactions compared to strong intrachain interaction with $J'/J < 3.2 \times 10^{-5}$ make this new material a nearly ideal 1D antiferromagnet, which is rarely found in 1D classical spin chains (e.g., $S = 5/2$). Using specific molecules for syntheses of novel inorganic−organic hybrid structures is an effective and practical method to explore 1D or other magnetic frameworks for understanding further nature of magnetic properties.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b06120.

Additional details (PDF)

X-ray crystallographic file (CIF) for compound $FeF_3C_{10}H_8N_2$ (CCDC 1020227) (CIF)

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Notes

The authors declare no competing financial interest.

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