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Two Chain Compounds of $[M(N_3)_2(HCOO)][(CH_3)_2NH_2]$ (M = Fe and Co) with a Mixed Azido/Formato Bridge Displaying Metamagnetic Behavior

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Two new magnetic chain compounds, where the anionic $[M(N_3)_2(HCOO)^-]_n$ chains with a 3-fold bridge of two *end-on* azido and one *syn–syn* formato ligands are isolated by the cations of $[(CH_3)_2NH_2]^+$, exhibit metamagnetism because of the strong intrachain ferromagnetic coupling versus the weak interchain antiferromagnetic coupling.

1D magnetic chain systems have experienced continuous interest because of their importance in lower-dimensional magnetism.[1] The recent developments in the research of single-chain magnets (SCMs),[2] together with the singe-molecule magnets (SMMs),[3] provide the linkage between paramagnetism and 3D long-range-ordered magnetism and potential applications of data storage and quantum calculation. The lower-dimensional magnetism relies on the great difference of the magnetic coupling strength along different dimensionalities in the material.[1−3] For a magnetic chain, this means strong intrachain coupling but weak interchain coupling. When the former is ferromagnetic, uniaxial anisotropic, such as Ising like, and much stronger, namely, 4 orders, than the latter, SCM behavior will be expected.[2a,4] The strong and anisotropic intrachain coupling requires anisotropic ions, such as Co^{2+} and Mn^{3+}, and short bridging ligands, such as cyanide and azide, to be employed,[2] while the interchain interaction can be weakened by several approaches to well isolate the chains. Because most reported SCMs were constructed by utilizing bulky coligands,[2b−g] we want to explore whether utilizing bulky counterions can be another approach. Bulky protonated akylamine cations are a good choice because they were used ca. 30 years ago for constructing a series of magnetic chains[1,5] and in recent years they have been used as templates in constructing many molecular magnetic systems such as oxalates,[6] azides,[7] and formates.[8] On the other hand, azido and formato ions, as two versatile bridging ligands and effective magnetic coupling mediators, have been widely employed.[7−10] However, to the best of our knowledge, no magnetic materials containing both azido and formato bridges have been documented. We report here two new chainlike compounds

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of $[M(N_3)_2(HCOO)][(CH_3)_2NH_2]$ (**1Fe**, M = Fe; **2Co**, M = Co), consisting of chains of $[M(N_3)_2(HCOO)^-]_n$ isolated by the cations of $[(CH_3)_2NH_2]^+$. The adjacent metal ions within the chain are 3-fold bridged by two *end-on* (EO) azido and one *syn*−*syn* formato ligands, representing the first samples of a azido/formato triplet bridge. Both materials are metamagnets showing strong intrachain ferromagnetic coupling and weak interchain antiferromagnetic coupling.

Diffusion of the methanol solution of metal salts, $Fe(ClO_4)_2 \cdot 4H_2O$ for **1Fe** and $CoCl_2 \cdot 6H_2O$ for **2Co**, into the methanol solution containing formic acid, NaN_3, and dimethylamine afforded the column-shaped crystals of the two isomorphs.[11] X-ray analysis[12] revealed that the structure consists of the anionic chain of $[M(N_3)_2(HCOO)^-]_n$ and the countercation of $[(CH_3)_2NH_2]^+$. In the chain, the adjacent M^{2+} ions are linked by two EO azido and one *syn*−*syn* formato bridges (Figure 1a). The unique M^{2+} ion is octahedrally coordinated by four N atoms, each from one EO azido, in its equatorial positions and two O atoms of two formates at apical sites. The M−O bond lengths are pairs of 2.121(2) and 2.129(2) Å for **1Fe** and 2.100(2) and 2.106(2) Å for **2Co**, while slightly longer M−N bond lengths are observed in the range of 2.166(2)−2.172(2) Å for **1Fe** and 2.125(2)−2.139(2) Å for **2Co**. The M−N−M angles in pairs are 96.5(1) and 96.2(1)° for **1Fe** and 97.2(1) and 97.6(1)° for **2Co**, and the intrachain M···M distances are 3.232 and 3.205 Å for **1Fe** and **2Co**, respectively. Because of the *syn*−*syn* formato bridge, the adjacent edge-shared MN_4O_2 octahedra have their O−M−O axes tilted one toward another and their equatorial planes show a dihedral angle of 155.1° (**1Fe**) or 158.1° (**2Co**). The linear azido ions do not lie in the M−N−M plane, and the two unique out-of-plane shift angles are 8.4° and 31.5° (**1Fe**) or 10.9° and 34.7° (**2Co**).

In the lattice, the $[M(N_3)_2(HCOO)^-]_n$ chains run along the *c* direction. They are arranged roughly in a hexagonal closest packing (Figure 1b), with each trigonal channel of the stacking occupied by one array of $[(CH_3)_2NH_2]^+$. Therefore, each $[M(N_3)_2(HCOO)^-]_n$ chain is surrounded by six arrays of countercations and each cation array by three anionic chains, and the $[M(N_3)_2(HCOO)^-]_n$ chains are isolated quite well. The cations provide not only the charge balance but also the hydrogen bonds (Table S1 in the Supporting Information), both conventional and weak,[13] to glue the counterparts of the structure together. The shortest interchain M···M distances are 8.548 and 8.537 Å for **1Fe** and **2Co**, respectively, and the interchain M···M connections via hydrogen-bond bridges include six or eight diamagnetic atoms.

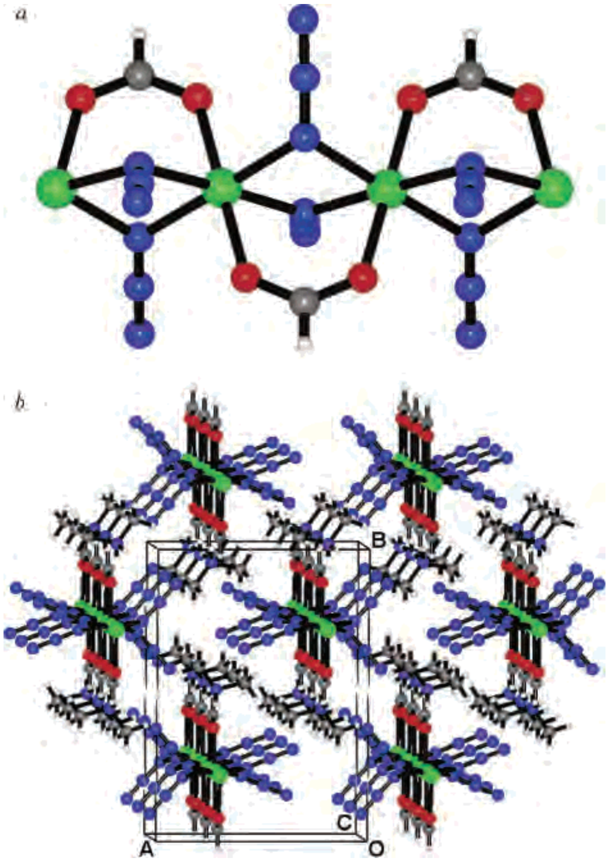

Figure 1. (a) Side view of the 1D $[M(N_3)_2(HCOO)^-]_n$ chain. (b) Packing of the 1D $[M(N_3)_2(HCOO)^-]_n$ chains and arrays of $[(CH_3)_2NH_2]^+$ in the crystal, viewed down the *c* axis. Color scheme: M, green; N, blue; O, red; C, gray; H, white.

Regarding the structural features of **1Fe** and **2Co**, showing strong intrachain but weak interchain interactions, lower-dimensional magnetism is expected for the two materials. Indeed, both compounds display similar metamagnetic properties (Figures 2 and S1 and S2 in the Supporting Information). At room temperature (Figure 2), the χT values are 4.27 $cm^3\ K\ mol^{-1}$ for **1Fe** and 3.52 $cm^3\ K\ mol^{-1}$ for **2Co**, being typical for isolated M^{2+} ions of high spin ($S = 2$ for Fe^{2+} and $S = {}^3/_2$ for Co^{2+}) in the octahedral coordination environment.[14] Upon cooling, the χT values increase slowly, and below 50 K, they increase more quickly, reaching very sharp maxima of 25.6 $cm^3\ K\ mol^{-1}$ at 9.3 K for **1Fe** and of 20.9 $cm^3\ K\ mol^{-1}$ at 7.6 K for **2Co**. After the maxima, they quickly decrease to low values of 1.19 and 2.36 $cm^3\ K\ mol^{-1}$ at 2.0 K for **1Fe** and **2Co**, respectively. The high-temperature data fit the Curie−Weiss law well and

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(11) **1Fe**: In a test tube, a 5 mL methanol solution of 0.10 M $Fe(ClO_4)_2 \cdot 4H_2O$ was layered carefully by 3 mL methanol and then a 10 mL methanol solution of 0.20 M formic acid, 0.20 M NaN_3, and 0.10 M dimethylamine. The tube was sealed and kept undisturbed. Tiny yellow-green columnlike crystals appeared overnight. Crystallization for 1 week produced crystals in a yield of 25% based on the metal salt. Anal. Calcd for $C_3H_9N_7O_2Fe$: C, 15.60, H, 3.93, N, 42.45. Found: C, 15.62, H, 3.98, N, 42.40. IR (cm^{-1}): 2062vs (N_3^-), 1578vs and 1350s ($HCOO^-$). **2Co**: A similar procedure was employed by using $CoCl_2 \cdot 6H_2O$ instead of $Fe(ClO_4)_2 \cdot 4H_2O$. Pink column crystals were obtained with a yield of 41% based on $CoCl_2 \cdot 6H_2O$. Anal. Calcd for $C_3H_9N_7O_2Co$: C, 15.39, H, 3.88, N, 41.89. Found: C, 15.42; H, 3.86; N, 41.87. IR (cm^{-1}): 2059vs (N_3^-), 1573s and 1352s ($HCOO^-$).

(12) Crystal data for **1Fe**: $M = 231.02$, monoclinic, space group $P2_1/c$, $a = 10.1584(4)$ Å, $b = 13.8447(5)$ Å, $c = 6.4644(2)$ Å, $\beta = 94.690(1)°$, $V = 906.11(6)$ Å^3, $Z = 4$, $D_c = 1.693$ g cm^{-3}, $\mu = 1.648$ mm^{-1}, 15 235 measured data, 2069 unique, $R_{int} = 0.0879$, R1 = 0.0331 for 1162 observations of $I \geq 2\sigma(I)$, wR2 = 0.0715 for all data, and GOF = 0.942. Crystal data for **2Co**: $M = 234.10$, monoclinic, space group $P2_1/c$, $a = 10.0878(5)$ Å, $b = 13.8377(5)$ Å, $c = 6.4100(2)$ Å, $\beta = 94.653(1)°$, $V = 891.84(6)$ Å^3, $Z = 4$, $D_c = 1.744$ g cm^{-3}, $\mu = 1.907$ mm^{-1}, 17 871 measured data, 2044 unique, $R_{int} = 0.0916$, R1 = 0.0343 for 1125 observations of $I \geq 2\sigma(I)$, wR2 = 0.0755 for all data, and GOF = 0.943. The intensity data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation ($\lambda = 0.710\ 73$ Å) at 293 K.

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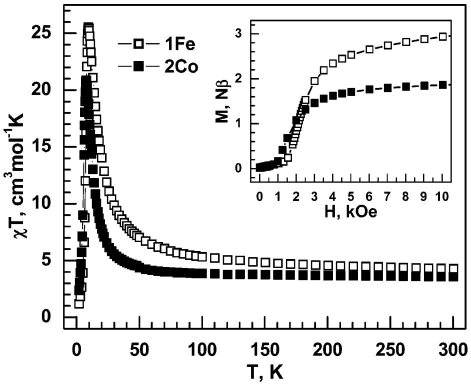

Figure 2. Temperature dependence of the magnetic susceptibility of **1Fe** and **2Co** under an applied field of 1 kOe. Inset: field-dependent magnetization of **1Fe** and **2Co** in the low-field region at 2.0 K.

give Curie and Weiss constants of $C = 4.12$ cm^3 K mol^{-1} and $\theta = 17.5$ K for **1Fe** and of $C = 3.46$ cm^3 K mol^{-1} and $\theta = 11.0$ K for **2Co**. Positive Weiss temperatures indicate that the ferromagnetic interaction is dominant in the two materials. Considering the structures and the fact that EO azido transmits ferromagnetic couplings,[9c] it is rational to say that the intrachain interactions are ferromagnetic. However, further magnetic investigation revealed that both materials are metamagnets. The field-cooled magnetizations under different fields are shown in Figure S1 in the Supporting Information. At 500 Oe, the two compounds showed maxima in their magnetizations, suggesting the occurrence of 3D antiferromagnetic ordering. Upon an increase in the field, the maxima moved to lower temperatures, became less prominent, and finally disappeared at 5.0 kOe for **1Fe** and 2.0 kOe for **2Co**, indicating a metamagnetic transition by the external field. The Neel temperatures (T_N), determined by the negative peaks of $d(\chi T)/dT$ of data in Figure 2, are 11.5 K for **1Fe** and 10.0 K for **2Co**. The sigmoidal shape of the field-dependent magnetizations at 2K (Figures 2, inset, and S2 in the Supporting Information) featured the field-induced transition from an antiferromagnetic state to a ferromagnetic state. Below 1 kOe, the magnetizations are small, while in the 1−3 kOe range, they increase very quickly, and above 5 kOe, the increase of magnetization slows down and is nearly linearly field-dependent. The critical fields for the metamagnetic transition are 2.0 and 1.3 kOe for **1Fe** and **2Co**, respectively. The sigmoidal feature of the field-dependent magnetization diminishes at 10.0 K close to T_N values (Figure S2 in the Supporting Information).

Because of the inherent difficulty in treating the orbitally unquenched Fe^{2+} ion,[1b,15] we just used the 1D Fisher model[16] scaled to $S = 2$ to estimate the intrachain coupling in **1Fe**. The best fitting of the magnetic data above 20 K (Figure S3 in the Supporting Information) produced $J = 2.39(1)$ cm^{-1} and $g = 2.341(4)$ with an agreement factor of $R = 2.05 \times 10^{-5}$ [$R = \sum(\chi_o - \chi_c)^2/\sum\chi_o^2$]. The J value is comparable to those in $[\mathrm{Fe(N_3)_2(pyrazine)}]_n$[15] with double-EO-azido bridges. For **2Co**, it is well-known that the Co^{2+} ion is most frequently Ising-like with $S_{\mathrm{eff}} = 1/2$ at low temperatures;[1] thus, the 1D Ising chain model[17] was applied to estimate the intrachain ferromagnetic coupling. Susceptibility data (Figure S4 in the Supporting Information) under a 2 kOe field and between 14 and 30 K were used to fit the expression $\chi = (1/3)\chi_{\parallel} + (2/3)\chi_{\perp}$ for powder data.[18] During the fitting procedure, it was found that $g_{\perp}$ was almost zero, indicating the strong Ising-like anisotropy of the system, like other Co^{2+} chain complexes;[18c] thus, equation $\chi = (1/3)\chi_{\parallel}$ was finally used, and the best-fitted results are $J = 13.89(4)$ cm^{-1} and $g_{\parallel} = 9.52(2)$ with $R = 1.56 \times 10^{-5}$. The ferromagnetic coupling between EO-azido-bridged Co^{2+} ions has been documented.[2c,19] It is obvious that, in the two compounds, the intrachain ferromagnetic exchange pathway is mainly via the two EO-azido bridges with M−N−M angles close to 97°. The global antiferromagnetic ordering of the two compounds arose from the interchain interactions, being estimated by $zJ' = -g\beta H_C/2S$,[5] and is ca. −0.6 cm^{-1}, using the H_C's at 2 K and the derived g values. Dipole−dipole as well as exchange effects via hydrogen bonds might be possible, and the interchain interactions should be mediated by interchain hydrogen bonds. Although some results[20] have been reported, the role of hydrogen bonds in mediating magnetism is still not clear.

In conclusion, we have synthesized two new magnetic chains in which the magnetic metal ions are linked by a 3-fold bridge of two EO azido and one *syn*−*syn* formato ligands, and this is the first time that magnetic coordination polymers including a mixed azido/formato bridge are reported. The magnetic chains are isolated by countercations of $[(\mathrm{CH_3})_2\mathrm{NH_2}]^+$. Both materials are metamagnets because of the strong intrachain ferromagnetic coupling versus weak interchain antiferromagnetic coupling. It is expected that the interchain interaction will be further weakened if more bulky diamagnetic cations are employed, and endeavors are in progress along this line.

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Supporting Information Available: X-ray crystallographic files in CIF format for **1Fe** and **2Co** and a PDF file containing Table S1 and Figures S1−S4. This material is available free of charge via the Internet at http://pubs.acs.org.

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