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An Antiferromagnetic Mn(III) Chain Bridged by Hydrogencyanamide: [Mn^{III}(5-Brsalen)($\mu_{1,3}$-NCNH)]$_n$

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The design and synthesis of transition metal coordination polymers bridged by small conjugated ligands, such as cyano, azido, oxalato, and nitrido, are currently under intense investigation in view of their structure diversity and in the context of molecule-based magnets.[1] As a potential nitrogen-based ligand, cyanamide ($NCNH_2$) and its basic forms ($NCNH^-$ or NCN^{2-}) have been used to prepare a number of alkali-metal,[2] alkaline-earth-metal,[3] and rare-earth-metal[4] salts by different synthetic routes, but their transition metal coordination chemistry and the ability to mediate the magnetic coupling, which are important though, still remain inactively explored. Among those reported structures of cyanamide transition metal coordination complexes,[5,6] most have molecular cluster structures, and only three $NCNH^-$-bridged coordination complexes, to our knowledge, have been reported so far.[6] Constructing magnetic coordination polymers with cyanamide is still a great challenge. Since $NCNH^-$ is isoelectronic with the azide anion, polymers bridged by $NCNH^-$ should also exist with regard to those well characterized polymer structures bridged by azide. On the other hand, dicyanamide (dca, $N(CN)^{2-}$) has been well used as a functional ligand to synthesize coordination polymers with interesting magnetic properties as well as various topologies due to its versatile coordination modes.[7] Moreover, among those different coordination modes of bridging dca, the $\mu_{1,3}$-M—N≡C—N—M pathway was found to provide the strongest coupling which leads to the long-range magnetic ordering. This observation further inspires us to explore the cyanamide ligand as a bridging ligand to obtain a new series of coordination polymers with interesting magnetic properties. Here we report an unprecedented hydrogencyanamide-bridged 1-D Mn(III) chain, [Mn^{III}(5-Brsalen)($\mu_{1,3}$-NCNH)]$_n$, **1**. The magnetic study of **1** shows a weak ferromagnetic ordering at low temperature due to spin canting and an unusual spin reorientation induced by an applied field. To the best of our knowledge, complex **1** is the first hydrogencyamamide-bridged coordination polymer.

The simple reaction of $NCNH_2$ with $MnClO_4\cdot 6H_2O$, 5-Brsalen, and NaOH in a 1:1:1:2 molar ratio in methanol solution yielded small deep-red crystals of complex **1**.

Complex **1** features a NCNH-bridged Mn(III) chain.[8] As shown in Figure 1a, the Mn(III) ion adopts a distorted octahedral geometry coordinated by the N_2O_2 donor atoms of one 5-Brsalen ligand in the equatorial mode and the N donor atoms of two $NCNH^-$ ions in the axial positions. Each $NCNH^-$ ligand functions as a trans-$\mu_{1,3}$ bridge to link monomeric [Mn^{III}(5-Brsalen)]$^+$ units into a 1-D zigzag chain (Figure 1b), in comparison to $\mu_{1,3}$-N_3-bridged chains.[9] In the equatorial plane, Mn(1), O(1), O(2), N(1), and N(2) are

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(8) Crystallographic data for **1** follow: monoclinic, space group $P2_1/c$, deep red, $a = 13.3699(4)$ Å, $b = 11.7277(4)$ Å, $c = 11.5495(1)$ Å, $\beta = 105.978(2)°$, $V = 1740.98(9)$ Å^3, $Z = 4$, $D_{calcd} = 1.984$ Mg/m^3, GOF = 0.979, R1 = 0.0326, wR2 = 0.0670 ($I > 2\sigma$), R1 = 0.0632, wR2 = 0.0733 (all data).

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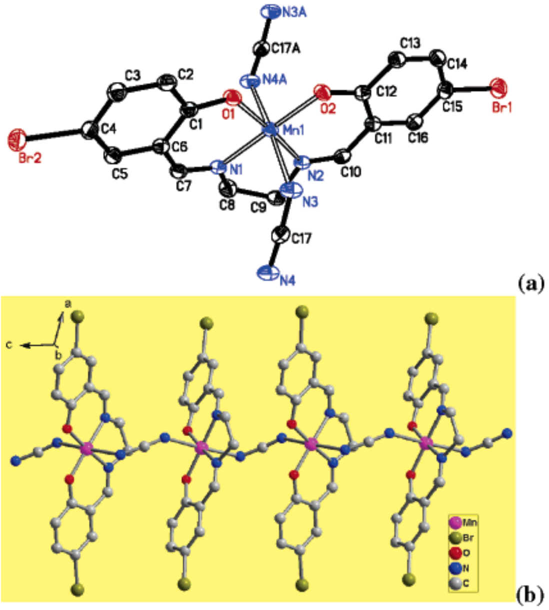

Figure 1. (a) Molecular structure of compound **1** (30% probability ellipsoids). (b) View of the zigzag chain.

nearly coplanar (rms deviation = 0.012(9) Å). The bond lengths of Mn(1)−O(1), Mn(1)−O(2), Mn(1)−N(1), and Mn(1)−N(2) are 1.881(2), 1.880(1), 1.976(2), and 1.991(2) Å, respectively, which are close to those in other Mn(III)−salen complexes.[9b] As expected, the bond lengths in the axial position of Mn(1)−N(3) and Mn(1)−N(4A) (2.245(2) and 2.407(3) Å, respectively) are elongated due to a Jahn-Taller distortion at the high-spin d^4 metal center,[9] and also indicate an asymmetric coordination of “NCNH” bridge. For comparison, in the previously reported dinuclear structure of $[Cu_2(C_9H_{21}N_3)_2(\mu\text{-NCNH})_2]](ClO_4)\cdot 2H_2O$ ($C_9H_{21}N_3$ = *N*,*N*′,*N*′′-trimethyl-1,4,7-triazacyclononane) which also possesses an end-to-end “NCNH” bridge, the NCNH bridges have close Cu−N distances ranging from 1.962(5) to 2.017(6) Å.[6b]

In complex **1**, the C(17)−N(3)H and C(17)−N(4) bond distances at 1.294(4) and 1.171(4) Å, respectively, as well as the N(4)−C(17)−N(3)H angle of 174.3(3)° emphasize the importance of resonance structure (a) $N{\equiv}C{-}NH^-$ much more than resonance structure (b) $N^-{=}C{=}NH$ in the bonding description of the $NCNH^-$ bridge.[10] The intrachain distance between the two Mn^{III} centers bridged by $NCNH^-$ ion is about 5.878 Å, which is longer than that in the complex $[Mn(salen)N_3]$.[9b] Surprisingly, the nearest interchain Mn−Mn separation is as small as 5.386 Å owing to the rich hydrogen bonding interactions (Figure S1).

The temperature dependence of the magnetic susceptibility of **1** was measured from 2 to 300 K in an applied magnetic field of 2 kOe (Figure 2a). On cooling, the χ_m value increases slowly to a maximum at ca. 8.0 K, and then, after a small downturn, it exhibits a relatively abrupt increase on further cooling at about 4.0 K, which may indicate the presence of an antiferromagnetic (AF) coupling and a weak ferromagnetic phase transition due to spin canting at low temperature. The data above 50 K obey the Curie−Weiss law with C = 3.015(5) cm^3 mol^{-1} K and $\theta = -16.1(1)$ K. The Curie constant is close to 3.0 cm^3 mol^{-1} K expected for one isolated spin-only Mn(III) ion, while the negative θ value confirms a dominant AF coupling between Mn(III) ions. Although this is at very low temperatures where some anisotropy may be significant, manganese(III) is expected to be Heisenberg-like in its magnetic properties.[9a] The best fit of the magnetic data above 5 K in terms of the Heisenberg 1-D chain using the Fisher model[11] with $H = -2JS_{Mn}S_{Mn}$ and intrachain coupling J gives the following parameters: $J = -0.99(3)$ cm^{-1}, $zJ' = -1.0(2)$ cm^{-1} ($z = 4$), and $g = 2.004(2)$ with $R = 7.6 \times 10^{-4}$ $\{R = \sum[(\chi_m T)_{obs} - (\chi_m T)_{calcd}]^2/\sum(\chi_m T)_{obs}{}^2\}$. Fitting the same set of data using the model given by Weng and modified by Hiller[12] gives the following best fit parameters: $J = -0.85(2)$ cm^{-1}, $zJ' = -1.3(1)$ cm^{-1} ($z = 4$), and $g = 2.0$ (fixed) with $R = 7.6 \times 10^{-4}$. These values prove an obvious AF coupling between not only intrachain Mn(III) ions but also interchain Mn(III) centers. As shown in the inset of Figure 2a, χ_m versus T curves measured in a field of 200−50 kOe show that the weak ferromagnetic phase transition is greatly influenced by the increase of the applied field; at 30 kOe, the characteristic of spin-canting nearly disappears. Interestingly, at a higher field, 50 kOe, the shape of the χ_m versus T plot is obviously different from those at low fields, indicating another magnetic transition possibly from a spin-canted AF phase to another AF state (Figure S2). Furthermore, the maximum around 7.0−8.0 K suggests an AF ordering in **1**. This unusual filed-induced spin

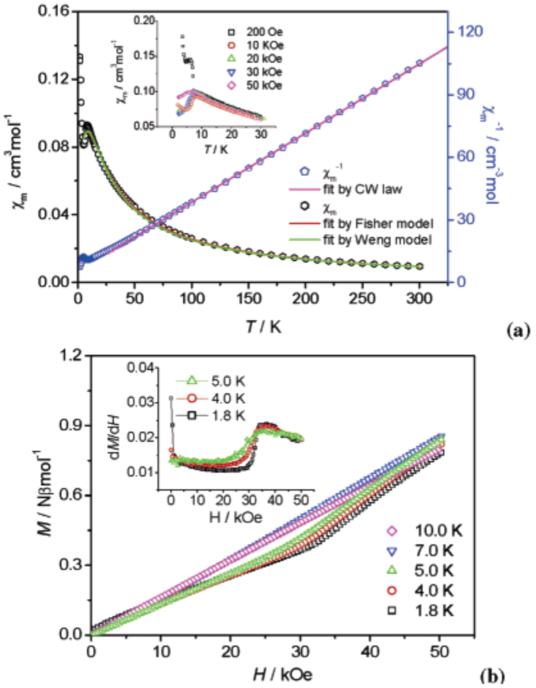

Figure 2. (a) χ_m and $\chi_m{}^{-1}$ vs T plots in an applied field of 2 kOe with a theoretical fit for **1**. Inset: χ_m vs T plots at different fields. (b) Field dependence of magnetization at different temperatures. Inset: field dependence of d*M*/d*H*.

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reorientation was further confirmed by the plots of *M* versus *H* measured at different temperatures (Figure 2b). We found that the curves of *M* versus *H* below ca. 5.0 K all exhibit an inflection point as the applied field increases. The critical field, at ca. 36 kOe, was determined by the d*M*/d*H* versus *H* curve. Moreover, the magnetization only reaches a value of ca. 0.84 Nβ mol^{-1} at 50 kOe, obviously below the theoretical saturation value of 4 Nβ mol^{-1} (for Mn(III) $g = 2$, $S = 2$). The divergence of the zero-field (ZFC) and field-cooled (FC) *M*(*T*) data (Figure S3) below $T_C = 2.5$ K displays a long-range ferromagnetic ordering at low field, while the peak at ca. 7.5 K further confirms the presence of an AF ordering in **1**. The ac magnetic susceptibility data (Figure S4) also ensure the appearance of magnetic ordering in **1**. The critical temperature $T_c = 2.8$ K is determined by the peaks of both χ_m' versus *T* and χ_m'' versus *T* plots, whereas another peak at ca. 7.5 K in the χ_m' versus *T* curve gives the critical temperature of AF ordering, $T_N = 7.5$ K. Furthermore, a hysteresis loop was detected in the ordered phase at 1.77 K (Figure S5), characteristic of a weak ferromagnet, with a coercive field of ca. 36 Oe and remnant magnetization of ca. 0.007 Nβ mol^{-1}.

In conclusion, a novel Mn(III) chain bridged by hydrogencyanamide was structurally and magnetically characterized for the first time in this paper. Although the magnetic interaction through cyanamide in complex **1** is not as strong as that through the azide bridge,[9] this work provides a unique example to construct magnetic coordination polymers through a new type of small conjugated ligands. Recently, we have obtained several other 1-D chain compounds bridged by NCNH$^-$, and the study of their magnetic properties is in progress.

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Supporting Information Available: Synthesis, IR, and more structural diagrams and magnetic data (PDF). Crystal data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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