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$\mu_{1,1}$-Azide-Bridged Ferromagnetic Mn^{III} Dimer with Slow Relaxation of Magnetization

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A new end-on azide-bridged dimeric Mn^{III} complex has been synthesized by using the tridentate *N*-isonicotinamidosalicylaidimine ligand. Magnetic studies show that the complex has a high-spin ground state of $S = 4$ and is ac out-of-phase frequency-dependent.

Because of the rich coordination modes and an efficient pathway of magnetic exchange, the azido ligand has attracted considerable interest in the past decade.[1] Complexes with novel magnetic properties have been prepared by using this anion, and their magnetostructural correlations have been extensively studied.[2,3] To date, the azido ligand has been found to bridge metal ions in the modes of $\mu_{1,1}$-(end-on, EO),[4] $\mu_{1,3}$-(end-to-end, EE),[5] $\mu_{1,1,3}$,[6] $\mu_{1,1,1}$,[7] $\mu_{1,1,1,1}$,[8] $\mu_{1,1,3,3}$,[9] or unusual $\mu_{1,1,1,3,3,3}$ fashions.[10] Ferromagnetic interactions are usually transmitted by the EO bridging mode of the azido ligand as are antiferromagnetic interactions by the EE bridging mode.[11]

Azido-bridged Mn$^{II/III}$ compounds have evoked much attention mainly for the understanding of the interaction between magnetic centers and for the development of new molecule-based magnets.[1,2,11] As far as azido-bridged Mn^{III} complexes are concerned, quite rare examples, [Mn(salpn)N$_3$] [H$_2$salpn = *N*,*N*′-bis(salicylidene)-1,3-diaminopropane],[12] [Mn(salen)N$_3$] [H$_2$salen = *N*,*N*′-bis(salicylidene)-1,2-diaminoethane],[13] and [Mn(acac)$_2$N$_3$] (acac$^-$ = acetylacetonate anion),[14] have been reported, which display $\mu_{1,3}$-azide-bridged one-dimensional structures and antiferromagnetic behavior. To the best of our knowledge, no $\mu_{1,1}$-azido-bridged dinuclear Mn^{III} complex has been reported to date. Polynuclear mixed-valence Mn$^{III/II}$ complexes with $\mu_{1,1}$-azide bridges have been reported recently; however, the coexistence of the multibridging pathways precludes clear studies on the magnetic coupling via N$_3^-$ bridges.[15] To clarify the magnetic coupling nature via the EO azide pathway, the synthesis of such compounds is expected.

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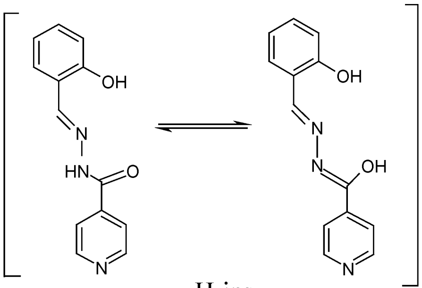
Chart 1



H$_2$ins

The synthesis is, however, not an easy task. Because of the Jahn−Teller effect, the four coordination atoms of a tetradentate Schiff base ligand usually occupy the equatorial plane of the Mn^{III} ion with two axial positions for the nitrogen atoms of the azides, yielding one-dimensional chains rather than dinuclear structures as mentioned above.[12−14] To avoid this, we have chosen a tridentate Schiff base ligand, *N*-isonicotinamidosalicylaidimine (H$_2$ins; Chart 1),[16] and have successfully synthesized the first EO azide-bridged Mn^{III} dimeric complex [Mn(ins)($\mu_{1,1}$-N$_3$)(CH$_3$OH)]$_2$ (**1**).[17]

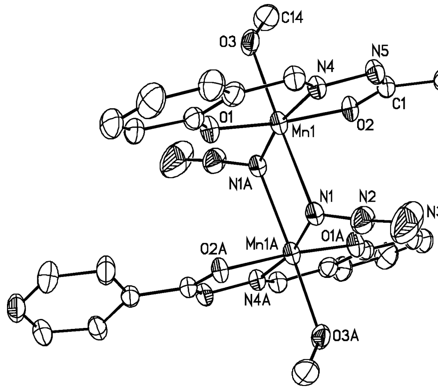


Figure 1. Structure of **1** with atomic numbering at the 30% probability level.

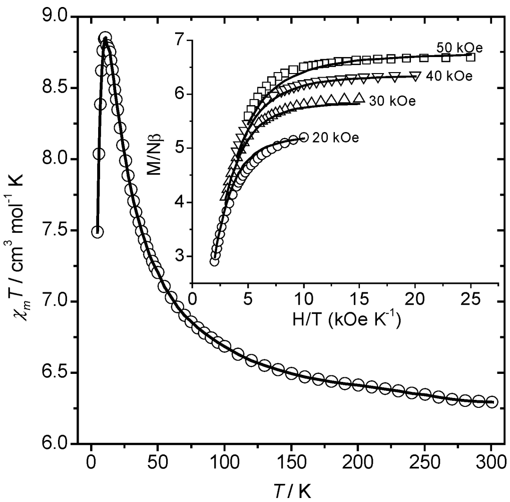


Figure 2. χ_mT vs T plot (5000 G) for complex **1**. The solid line represents the best fit to the experimental data with the parameters discussed in the text. Inset: Magnetization vs H/T plot in the range 2−10 K and 20−50 kOe. The solid lines represent the best-fit results using the parameters g = 1.92 and D_{Mn2} = −0.784 cm^{-1}.

X-ray crystallography[18] shows that the structure of complex **1** (Figure 1) consists of $\mu_{1,1}$-azido-bridged dinuclear molecules in which two inverse center-related Mn^{III} ions are in an axially elongated octahedral geometry. Each metal atom is coordinated in the equatorial coordination plane by N_2O_2 donor atoms from the tridentate ligand ins^{2-} and one azido anion (Mn1−O1 = 1.859(2) Å, Mn1−O2 = 1.909(2) Å, Mn1−N4 = 1.985(3) Å, and Mn1−N1A = 1.968(3) Å). Two axial positions are occupied by an oxygen atom of methanol and a nitrogen atom of another azido anion with longer distances (Mn1−O3 = 2.208(2) Å and Mn1−N1 = 2.381(3) Å). Because of the Jahn−Teller effect of Mn^{III}, $\mu_{1,1}$-azido ligands bridge two [Mn^{III}(ins)(CH$_3$OH)]$^+$ parts in an equatorial−axial fashion with one short bond length and one long Mn−N$_{azido}$ bond length of 1.968(3) and 2.381(3) Å, respectively. The bridging bond angle of Mn1A−N1−Mn1 is 100.30(11)°, and the out-of-plane deviation angle of the azido group is 33.7° (represented as τ in the literature[19]). The Mn···Mn intramolecular separation is 3.350 Å. The axially coordinated methanol molecules are hydrogen-bonded to the pyridyl group of an adjacent dimeric unit [O3···N6A = 2.699 Å (A: $-x + 1, -y, -z$); O3−H10···N6A = 177.04°; Supporting Information] to form a one-dimensional chain. Other weak interactions such as the C−H···O hydrogen bond (C14···O2A = 3.492 Å; C14−H13···O2A = 138.64°), C−H···N hydrogen bond [C5···N3B (B: $-x + 2, -y + 1, -z$) = 3.494 Å; C5−H3···N3], and CH/π bond (2.759 Å, between hydrogen atoms of the methyl group and phenyl ring) link these chains to form a three-dimensional network.

Magnetic measurements were performed from 300 to 5.0 K in an applied field of 1000 Oe. The χ_mT vs T plot is shown in Figure 2. At 300 K, the χ_mT values per Mn$_2$ are 6.27 emu K mol^{-1} for **1**. These values are slightly higher than that expected for two isolated spin systems $S_{Mn1} = S_{Mn2} = 2$ (6.0 emu K mol^{-1} with g = 2.0). With a decrease in the temperature, the χ_mT value increases more and more sharply to reach a maximum value of 8.85 emu K mol^{-1} at 11 K and then decreases to 7.48 emu K mol^{-1} at 5 K because of the presence of zero-field splitting and/or interdimer anti-

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(18) Crystal data: **1** ($C_{28}H_{26}N_{12}O_6Mn_2$), M_w = 736.46, T = 293 K, triclinic, space group $P\bar{1}$, a = 7.872(2) Å, b = 10.017(2) Å, c = 10.443(2) Å, α = 95.50(3)°, β = 105.46(3)°, γ = 93.93(3)°, U = 786.2(3) Å^3, Z = 1, ρ_{calcd} = 1.555 g cm^{-3}, μ = 0.866 mm^{-1}, λ(Mo Kα) = 0.710 70 Å, 2748 unique reflections, 2340 observed reflections [$I > 2\sigma(I)$], R1 = 0.0463, wR2 = 0.1294 (all data), and GOF = 1.051 based on 222 parameters.

ferromagnetic interaction that are dominant at low temperatures. These results indicate that the overall behavior of **1** corresponds to a ferromagnetic interaction mediated by the $\mu_{1,1}$-azido bridges.

The magnetic susceptibilities have been fitted based on the full spin Hamiltonian:

$$H = S_1 \cdot J \cdot S_2 + \sum_{i=1}^{2} (S_i \cdot \mathbf{D}_i \cdot S_i + \mu_B B \cdot \mathbf{g}_i \cdot S_i)$$

The terms correspond to anisotropic exchange coupling, single-ion zero-field splitting, and electronic Zeeman splitting, respectively.[20] The second term is related to the usual $DS_z^2 + E(S_x^2 - S_y^2)$ term. The best-fit parameters are $J = 3.47(2)$ cm^{-1}, $g = 2.01$, $D = -9.15(2)$ cm^{-1}, and $E = 0.10(2)$ cm^{-1} with an agreement factor of $R = \sum(\chi_{\text{obsd}}T - \chi_{\text{cald}}T)^2/\sum(\chi_{\text{obsd}}T)^2 = 4.2 \times 10^{-4}$. The D value (single-ion zero-field splitting) is too large for a Mn$^{\text{III}}$ ion because, in the full-diagonalization method, we do not consider intermolecular interactions (J'). D is, thus, overestimated. The calculation of E was constrained to a magnitude $E \leq D/3$. The negative D for Mn$^{\text{III}}$ in complex **1** also indicates that the elongated Mn$^{\text{III}}$ coordination geometry usually possesses negative D.[21]

Ferromagnetic interactions have been widely observed in $\mu_{1,1}$-azido-bridged Cu$^{\text{II}}$, Mn$^{\text{II}}$, and Ni$^{\text{II}}$ dimers, and the theory about magnetic behaviors of these dinuclear complexes has been carefully studied on the basis of the spin-polarization model and density functional theory calculation.[22] An elongated Mn$^{\text{III}}$ ion possesses a $t_{2g}^3e_g^1$ ($d_{xy}^1d_{xz}^1d_{yz}^1$, $d_{z^2}^1$) electronic configuration with a $^5B_1$ ground state.[23] The weak axial overlap (long Mn−N$_{\text{axial}}$ bond distances) would suggest a weak interaction. The ferromagnetic coupling for the present complex is probably due to the orbital orthogonality of d_{z^2} and the d_π orbitals ($d_{xy}d_{xz}d_{yz}$).[24]

Magnetization data measured at 2−10 K and in the applied field of 20−50 kOe show that the isofield lines do not superimpose, indicating the presence of appreciable zero-field splitting. Assuming an $S = 4$ ground state, the data were fit using the anisofit 2.0 program,[25] giving the parameters of $g = 1.92$ and $D_{\text{Mn2}} = -0.784$ cm^{-1} (inset of Figure 2).[26] Thus, the spin-reversal energy barrier ΔE between $M_S = 4$ and -4 spin states can be calculated to be $\Delta E/k = 17.9$ K ($\Delta E = 12.5$ cm^{-1}) via $\Delta E/k = S^2 \cdot |D_{\text{Mn2}}|/k$. The temperature dependence of the ac magnetic susceptibility at zero dc and a 3-Oe ac field for complex **1**, as displayed in Figure 3, shows that the out-of-phase ac magnetic susceptibility has nonzero values below 4.0 K and is frequency-dependent. This suggests the presence of slow relaxation of magnetization in complex **1**,[27,28] consistent with the dc magnetic measurements. It is worth noting that some Mn$^{\text{III}}$ dimeric complexes have been recently reported to exhibit magnetic properties similar to those of complex **1**.[28]

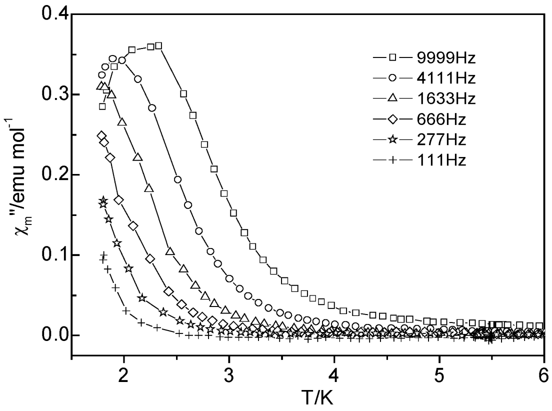

Figure 3. Out-of-phase component of the ac susceptibility at different frequencies for **1**.

In summary, we have successfully prepared a $\mu_{1,1}$-azido-bridged Mn$^{\text{III}}$ dimer in a facile way. As far as we are aware, the title complex is the first reported $\mu_{1,1}$-azido-bridged dinuclear Mn$^{\text{III}}$ complex. Ferromagnetic Mn$^{\text{III}}$−Mn$^{\text{III}}$ coupling and a negative axial zero-field-splitting parameter (D_{Mn2}) for the dimer result in slow relaxation of the magnetization. This work shows that the $\mu_{1,1}$-azido-bridged Mn$^{\text{III}}$ complexes should form an interesting system of molecule-based magnets. Future work involves the synthesis of more $\mu_{1,1}$-azido-bridged Mn$^{\text{III}}$ complexes to gain a clear magnetostructural relationship and to improve the magnetic properties.

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Supporting Information Available: X-ray crystallographic file (CIF), a plot showing the interdimeric contacts, and the temperature dependence of zero-static ac magnetic susceptibility χ'_mT at different frequencies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Magnetic data were fitted using a homemade FORTRAN 99 computer program, which employs the Hamiltonian indicated in the text. All of the terms are included in the Hamiltonian matrix. Matrix diagonalization using EISPACK subroutines yields the eigenvalues and eigenvectors, from which the susceptibility and magnetization equations are determined. The program uses nonlinear least-squares routine DSTEPIT (from QCPE, Bloomington, IN) for fitting purposes.

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