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An Unusual 1D Manganese Azido Complex with Novel EO/EO/EO/EE Coordination Mode: Synthesis, Structure, and Magnetic Properties

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A novel one-dimensional manganese(II) azido complex, $[Mn_2(N_3)_4(phen)_2]_n$ (**1**), in which the azido bridging ligands take on an unusual new type of combination with the metal center as the sign of $[–EO–EO–EO–EE–]_n$, has been hydrothermally synthesized, and its magnetic properties have been studied.

The azide anion is one of the most commonly employed pseudohalide bridging ligands in the design of polynuclear transition-metal complexes with characteristic and tunable physical properties.[1] It has been widely stated that the exchange is, with some exceptions, generally ferromagnetic in nature for the end-on ($\mu_{1,1}$ or EO) mode and antiferromagnetic for the end-to-end ($\mu_{1,3}$ or EE) mode.[2,3] At the same time, structural parameters (bond angles and lengths, etc.) greatly affect the nature and magnitude of the magnetic exchange interactions in these systems.[4] Furthermore, different bridging modes of the azido ions may simultaneously exist in the same species, leading to novel topologies and magnetic behaviors.[5,6] In these kinds of compounds, so-called "magnetic systems alternating in sign", two or more exchange coupling parameters (J) are necessary to fit the experimental results, in contrast to the "uniform magnetic systems" in which all azido bridges have both the same coordination mode and the same structural parameters.[7] In these systems, different combinations of EO and EE modes have resulted in some unusual alternating chains with $[-EO-EO-EO-EO-EE-]_n$, $[-EO-EE-]_n$, and $[-EO-EE-EE-]_n$ sequences showing interesting magnetic properties.[6a,b,7a,8−10] To the best of our knowledge, the sequence of $[-EO-EO-EO-EE-]_n$ has not yet been reported. We successfully

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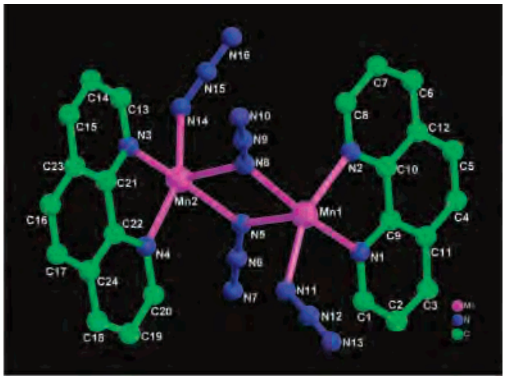

Figure 1. Unique crystallographic unit of complex **1** with atoms labeled.

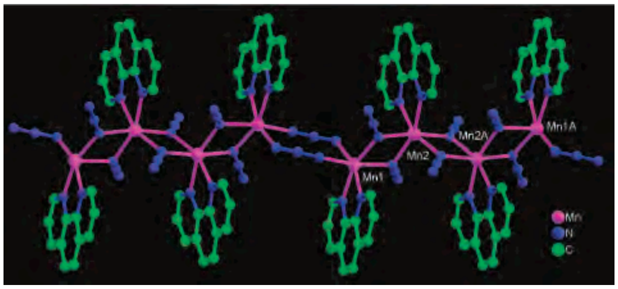

Figure 2. 1D chain of complex **1**.

isolated, for the first time, a one-dimensional (1D) manganese(II) azido complex, $[Mn_2(N_3)_4(phen)_2]_n$ (**1**), with this new $[-EO-EO-EO-EE-]_n$ sequence.

Complex **1** was synthesized from $Mn(OAc)_2{\cdot}4H_2O$, NaN_3, and phenanthroline under hydrothermal conditions.[11] X-ray analysis[12] reveals that the unique crystallographic unit of **1** contains two Mn^{II} ions, four azide anions, and two phen molecules, in which each Mn^{II} ion is coordinated in distorted octahedral geometry (Figure 1). Mn1 is coordinated by two N atoms from phen, two N atoms from two azide anions of the EE mode, and two N atoms from two azide anions of the EO mode. Mn2 is coordinated by two N atoms from phen and four N atoms from four azide anions of the EO mode. Selected bond lengths and angles are given in Table S1 in the Supporting Information. As shown in Figure 2, the overall aspect of **1** is a 1D chain, which is constructed by tetranuclear units. In this basic unit, one metal center is bonded by double EO azides, while adjacent units are joined by double EE azides.

From a magnetic point of view, complex **1** represents a novel kind of 1D Mn^{II} system with alternating EE and EO azide bridging ligands. The alternation may be represented as $[-EO(1)-EO(2)-EO(1)-EE\text{-}]_n$, indicating by 1 and 2 two different distortions in the same kind of bridge. 1D manganese(II) azido systems present a great variety of structures. In a very recent paper,[13] a study of all of these structures related to their magnetic behaviors has been reported. We can, thus, summarize the different kinds of structures as $[-EE-]_n$ (all bridges EE); $[-EO-]_n$ (all bridges EO); $[-EO-EO-EO-EO-EE-]_n$; $[-EO-EE-]_n$ (being EE single or double); $[-EO-EE-EE-]_n$. Thus, the pattern shown in **1** is new and not reported so far: $[-EO-EO-EO-EE-]_n$. This pattern is schematized in Figure 3. In this scheme, the three *J* values (magnetic parameters) have been indicated. Plots of $\chi_M T$ vs *T* and reduced magnetization vs *H* at 2 K (inset) for complex **1** are shown in Figure 4. Taking into consideration the 1D structure, magnetic data are given for one Mn^{II} ion. $\chi_M T$ starts at 4.50 $cm^3\ mol^{-1}$ K at 300 K, which is the typical value for one isolated Mn^{II} ion (g = 2.03). This value is almost constant to 100 K, decreasing rapidly to 0.5 $cm^3\ mol^{-1}$ K at 2 K. This feature is indicative of global antiferromagnetic coupling among the Mn^{II} ions. The plot of $M/N\beta$ vs *H* at 2 K corroborates this fact: the magnetization at 5 T achieves only 2.0 $N\beta$ instead of 5 $N\beta$, which corresponds to a noncoupled Mn^{II} ion. Complex **1** is,

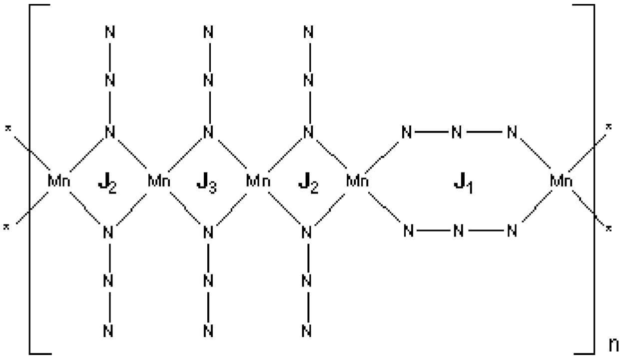

Figure 3. Schematic representation of the alternation pattern in complex **1**, showing the *J* pathways.

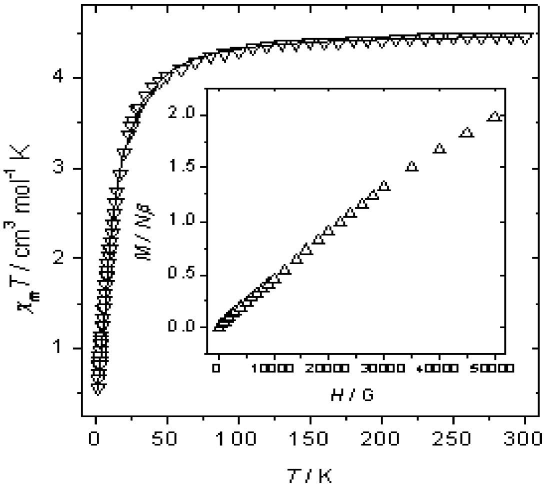

Figure 4. Plots of $\chi_M T$ vs *T* and $M/N\beta$ (inset) vs *H* for complex **1**. The solid line represents the best-fit calculation.

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(11) Complex **1** and some unknown black powder were hydrothermally synthesized under autogenous pressure. A mixture of $Mn(OAc)_2{\cdot}4H_2O$, NaN_3, phen, and H_2O in a ratio of 1:1:1:2000, in which a small amount of nicotinic acid or pyrazine-2-carboxylic acid and $Gd(NO_3)_2$ was added for improving the purity and yield, was sealed in a Teflon-lined autoclave, heated to 140 °C for 2 days, and cooled to room temperature at 10 °C h^{-1}. The crystals were obtained in ca. 30% yield based on Mn. Elemental analysis is satisfactory. ***Caution!*** *Azide complexes are potentially explosive. Only a small amount of the materials should be prepared and handled with care.*

(12) Crystal data for **1**: triclinic, $P\bar{1}$, a = 10.286(2) Å, b = 11.324(3) Å, c = 13.701(3) Å, α = 94.593(4)°, β = 107.180(4)°, γ = 116.760(3)°, V = 1318.3(5) Å^3, Z = 2, λ(Mo Kα) = 0.710 73 Å, 7340 reflections collected, 5217 unique reflections (R_{int} = 0.0249), R1 = 0.0506, wR2 = 0.1263 [$I > 2\sigma(I)$]. CCDC no. 617038.

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Table 1. Main Structural Data of Complex **1** (α and θ in Degrees), Exchange Coupling Constants (J_i; Figure 3) Obtained in This Work Compared to the Experimental Data Found in the Literature ($J_{\mathrm{lit.}}$) for Similar Geometrical Parameters

unit *i*	α	θ	J_i/cm^{-1}	$J_{\mathrm{lit.}}$/cm^{-1}
1			−5.4	−7/−15
2	101.5	32.8	+2.1	+1.8[a]
	103.5	13.5		
3	102.8	0.3	−0.1	+2.0[a]

[a] Values estimated by a mathematical interpolation using the structural and magnetic experimental data found in the literature.

thus, a 1D extended system with two kinds of connections between the metal ions, present in a ratio 3:1: (i) a double-bridge EO azide and (ii) a double-bridge EE azide. A more detailed analysis shows that the EO azido ligands are not equivalent through the chain (Table 1). There is a more regular connection where the two Mn−N(azido)−Mn angles (α) in Mn_2N_2 unity are equivalent. However, there are two equivalent asymmetrical units with two different α values. Despite that the average for these values is very close to that found in symmetrical unit, we have decided to use the topology displayed in Figure 3 with the spin Hamiltonian shown in eq 1. Because of the large value of the local spin

$$H = -\sum_{i=0}^{\infty}[J_1 S_{4i+1}S_{4i+2} + J_2 S_{4i+2}S_{4i+3} + J_3 S_{4i+3}S_{4i+4} + J_2 S_{4i+4}S_{4i+5}] \quad (1)$$

moment for Mn$^{\mathrm{II}}$ ions, $S = {}^5/_2$, we can consider them as classical spin moments, i.e., as vectors. An exact law that describes the magnetic behavior of classical regular 1D systems was obtained by Fisher.[14] Later, Abu-Youssef et al. and one of us found similar exact laws for classical alternating chains.[6b,13] Following this methodology and Figure 3, we can express the wave-vector-dependent susceptibility in terms of Langevin's functions:

$$S(q) = 1/NkT[4 + \sum_{r=0}^{\infty} 2(u_1^{r+1}\, u_2^{2r}\, u_3^{r} + 2u_1^{r}\, u_2^{2r+1}\, u_3^{r} + u_1^{r}\, u_2^{2r}\, u_3^{r+1} + 2u_1^{r+1}\, u_2^{2r+1}\, u_3^{r} + 2u_1^{r}\, u_2^{2r+1}\, u_3^{r+1} + 2u_1^{r+1}\, u_2^{2r+1}\, u_3^{r+1} + u_1^{r}\, u_2^{2r+2}\, u_3^{r+1} + u_1^{r+1}\, u_2^{2r+2}\, u_3^{r} + u_1^{r+1}\, u_2^{2r+2}\, u_3^{r+1})] \quad (2)$$

where *r* is an integer number that allows us to consider the different pair correlation functions generated for our topology. Langevin's function depends on the exchange coupling constants as follows:

$$u_i = \coth[J_i S(S+1)/T] - T/J_i S(S+1) \quad (3)$$

The integration of this series (eq 2) allows us to deduce the expression for the bulk susceptibility per site:

$$\chi_{\mathrm{M}}T = \frac{Ng^2 S(S+1)}{12k}\,\frac{D}{1 - u_1 u_2^2 u_3} \quad (4)$$

where

$$D = 4 + 2u_1 + 4u_2 + 2u_3 + 4u_1u_2 + 4u_2u_3 + 2u_1u_2^2 + 2u_2^2u_3 + 4u_1u_2u_3 + 4u_1u_2^2u_3$$

The best fit was obtained with the exchange parameters $J_1 = -5.4 \pm 1.3$ cm^{-1}, $J_2 = 2.1 \pm 0.5$ cm^{-1}, and $J_3 = -0.1 \pm 0.1$ cm^{-1}; $g = 2.03 \pm 0.005$ with an agreement factor, *F*, defined as

$$F = \sum[(\chi_{\mathrm{M}}T)_{\mathrm{obsd}} - (\chi_{\mathrm{M}}T)_{\mathrm{calcd}}]^2 \Big/ \sum[(\chi_{\mathrm{M}}T)_{\mathrm{obsd}}]^2$$

equal to 8.8×10^{-5}. Owing to the standard deviation, J_3 can be taken as zero. Another set of *J* values have been tried; however, the results did not improve the previous fit. These *J* values are comparable to those reported for similar Mn$^{\mathrm{II}}$ systems. Indeed, J_1 is antiferromagnetic, such as all EE conformation modes.[13] J_2 is ferromagnetic, in agreement with the EO coordination mode. The value close to zero (or very slightly negative) for J_3 seems more peculiar. The average Mn−N−Mn angles (see structural section and Table 1) for the moieties corresponding to J_2 and J_3 are almost the same. The only difference lies in the inversion center in the central part (J_3), where the azido ligand (N_3^-) is placed in the plane of the Mn_2N_2 core ($\theta \cong 0°$), which usually does not occur. In the two parts corresponding to J_2, the azido bridging ligands are not coplanar with the Mn_2N_2 core ($\theta = 32.8°$ and 13.5°; see Table 1). With the Mn−N−Mn angle being almost the same (average), the non-coplanarity of the azido bridges enhances the ferromagnetic component, such as has been shown by Ruiz et al.[4a]

To date, it is not possible to correlate the alternated structure with the blocking ligands used in the synthesis. We have tried to do a first approach, which is shown in Table S2 in the Supporting Information. It is very complicated to draw any conclusion. It is worth mentioning that all more alternated systems, such as −EO−EO−EO−EO−EE−, −EO−EO−EO−EE−, and −EO−EE−EE−, only appear when using monodentate ligands. Maybe this is totally serendipitous, but it would be a great challenge for the experimentalist to synthesize a new system with the alternation −EO−EO−EE−, which is lacking so far.

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Supporting Information Available: Tables of selected bond lengths and angles of complex **1** and different types of alternating manganese(II) azido chains and their blocking ligands and corresponding references and X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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