# A Novel Azido and Pyrazine-Dioxide Bridged Three-Dimensional Manganese(II) Network with Antiferromagnetic Ordering ($T_N = 62$ K) and a Spin Flop State

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Much attention has been paid to the molecule-based magnetic materials in the past decades.[1] The azide ligand is a suitable candidate for the design of magnetic coordination polymers because of its good superexchange pathway.[2] Its end-to-end (EE) and end-on (EO) coordination modes favor antiferromagnetic and ferromagnetic interactions, respectively. Furthermore, the magnetic properties can be tuned by modifying the bond parameters of the bridging region. The high-dimensional networks are of particular interest, as it is believed that the bulk magnetic properties can be enhanced by increasing the dimensionality. One of the synthetic strategies to high-dimensional azides is to increase the number of azide ligands by adding a countercation, such as in $Cs_n[Mn(N_3)_3]_n$,[3] $[N(C_2H_5)_4]_n[Mn_2(N_3)_5(H_2O)]_n$,[3] $Cs_{2n}[Co_3(N_3)_8]_n$,[4] $Cs_2[Ni(N_3)_4]\cdot H_2O$,[4] and $[N(CH_3)_4][Mn(N_3)_3]$.[5] Another is the introduction of a second bridging ligand to extend the architectures such as in $[Mn_2(N_3)_4(bipym)]_n$[6] and $[MnL(N_3)_2]_n$ (L = 4,4′-bipy,[7] pyrazine,[8] 1,2-bis(4-pyridyl)ethane[9]). Using the latter approach, we succeeded in assembling a three-dimensional (3D) network, $Mn(N_3)_2(pzdo)$ (**1**), through azide and pyrazine−dioxide (pzdo) ligands. Its structure and magnetic properties are presented herein.

The reaction of $MnCl_2$, $NaN_3$, and pyrazine−dioxide in aqueous solution affords red prismatic crystals of $Mn(N_3)_2(pzdo)$.[10] X-ray diffraction analysis revealed that it consists of a 3D network in which $Mn^{2+}$ ion is located on an inversion center and octahedrally coordinated to four azido and two pzdo ligands in a trans arrangement.[11] The axial Mn−N3a distance is 2.2505(15) Å, slightly longer than the equatorial Mn−N1 2.1714(14) Å and Mn1−O1 2.1884(11) Å. Azide ligands connect $Mn^{2+}$ ions in an EE mode, giving a two-dimensional (2D) quadratic layer in the *bc* plane, as shown in Figure 1a, where the intralayer Mn···Mn separation is 6.0052(9) Å. The pzdo ligand, adopting a trans bridging mode, further extends the 2D sheet into a 3D network, as seen in Figure 1b. The 2D quadratic layer structural topology was known for thiocyanato(SCN)−Mn $[Mn(SCN)_2(CH_3OH)_2]_n$[12] and dicyanamide(dca)−Mn $[Mn(dca)_2(C_2H_5OH)_2]\cdot(CH_3)_2CO$[13] and other azido−Mn compounds, $[Mn(minc)_2(N_3)_2]_n$ (minc = methylisonicotinate)[14] and $[Mn(4\text{-acetylpyridine})_2(N_3)_2]_n$[15] in which the layers are well isolated by pyridinyl ligands with interplane Mn···Mn distances of 11.8−12.42 Å. While the interlayer Mn···Mn separation through bridging pzdo is 8.3392(4) Å in compound **1**, the nearest interlayer

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(10) Compound **1** was prepared by mixing $NaN_3$ (2 mmol, 0.165 g) and pzdo (1 mmol, 0.112 g) in 20 mL of aqueous solution, followed by the slow addition of 10 mL of aqueous solution of $MnCl_2\cdot 6H_2O$ (1 mmol, 0.234 g) with stirring at room temperature. The resulting solution was filtered and the filtrate was allowed to stand at room temperature. After 1 month, red block single crystals were collected, washed with small amounts of water and ethanol, and dried in air (yield 64%). Calcd. for $C_4H_4MnN_8O_2$: C, 19.12; H, 1.59; N, 44.62. Found: C, 19.18; H, 1.71; N, 44.74%. IR (KBr pallet): 3435 w, 3394 w, 3363 w, 3127 m, 3081 w, 3060 w, 2485 w, 2096 vs, 2051 vs, 2004 m, 1477 s, 1450 vs, 1306 w, 1248 m, 1235 s, 1188 w, 1081 w, 1058 w, 937 w, 853 m, 806 s, 638 w, 608 w, 541 w, 414 w $cm^{-1}$.

(11) Crystal data. Compound **1**: $C_4H_4MnN_8O_2$, $Mr = 251.09$, monoclinic, $P2(1)/c$, $a = 6.4216(2)$ Å, $b = 10.0990(5)$ Å, $c = 6.5008(3)$ Å, $\beta = 99.622(3)°$, $U = 415.66(3)$ Å$^3$, $Z = 2$, $Dc = 2.006$ Mg/m$^3$, $\mu$ (Mo K$\alpha$) = 1.583 mm$^{-1}$, $F(000) = 250$, GoF = 0.994, $T = 293(2)$ K. A total of 7703 reflections were collected and 991 are unique ($R_{int} = 0.0352$). The final R1 and wR2 are 0.0262 and 0.0697, respectively, for 79 parameters and 854 reflections [$I > 2\sigma(I)$]. A suitable single crystal was selected for X-ray diffraction analysis. The data collection was performed on a Nonius Kappa CCD diffractometer with graphite monochromated Mo K$\alpha$ radiation (0.71073 Å) at 293 K. The structure was solved by the direct method and refined by the full-matrix least-squares technique based on $F^2$ using the SHELX97 program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculation positions.

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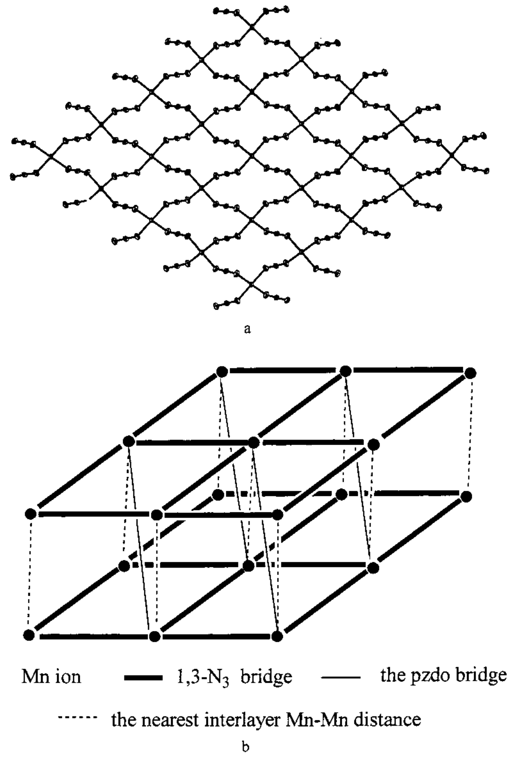

**Figure 1.** (a) A 2D sheet formed by $\mu$-1,3-azido bridges. (b) Schematic view of a three-dimensional network of **1**.

Mn···Mn separation is indeed much smaller, say only 6.422 Å, owing to the angular connection mode for the pzdo ligands, unlike the linear mode of pyrazine or 4,4′-bipy. The bridging azido is almost linear with the N1−N2−N3 angle of 178.63(17)°. The bond angles of Mn−N1−N2 and Mn1b−N3−N2 are 136.58(12)° and 119.76(12)°, respectively, smaller than those observed in 3D $[N(CH_3)_4][Mn(N_3)_3]$ (165° and 135°, respectively), 3D $[Mn(4,4'\text{-bipy})(N_3)_2]_n$ (152.9° and 128.5°, respectively), and 2D $[Mn(4\text{-acetylpyridine})_2(N_3)_2]_n$ (129.4°−152.9°). The torsion angle Mn−N−N−N−Mn, defined as the dihedral angle between the planes formed by the atoms Mn1−N1−N2−N3 and Mn1D−N3−N2−N1, is 143.05°. Therefore, the intralayer Mn···Mn separation, 6.0 Å, is also smaller than 6.4 Å in 3D $[N(CH_3)_4][Mn(N_3)_3]$. Overall, the 3D arrangement in **1** may be roughly described as a cubic-like network with Mn···Mn separations 6.0, 6.0, and 6.4 Å in three directions.

ESR measurements for polycrystalline samples at room temperature show an isotropic signal at $g = 2.00$. The signal becomes sharp and intense at 77 K and does not change in shape significantly. This fact indicates that the octahedral environment of the $Mn^{2+}$ ion does not alter with temperature.

The variable-temperature magnetic susceptibility for a collection of small crystals was measured in the temperature range of 1.8−300 K under different applied fields (Figure 2). The magnetic susceptibility, $\chi_M$, increases as the temperature is lowered, reaching a maximum of 0.024 cm$^3$ mol$^{-1}$ at ca. 68.5 K and then sharply goes down to the value of 0.004 cm$^3$ mol$^{-1}$ at 1.8 K. This is neither the normal expected value (0.016 cm$^3$ mol$^{-1}$) of about $^2/_3$ the maximum value for a powder sample of a 3D antiferromagnet nor zero, which may arise from the irregular orientation of the small crystals. The $\chi_M T$ value at room temperature is 3.75 cm$^3$ mol$^{-1}$ K, smaller than the value (4.38 cm$^3$ mol$^{-1}$ K) expected for an uncoupled $Mn^{2+}$ ion. It decreases smoothly with decreasing temperature and finally approaches zero. The magnetic data above 110 K can be fitted well to the Curie−Weiss law with $C = 5.67$ cm$^3$ mol$^{-1}$ K and $\theta = -149.4$ K, indicating a considerably strong antiferromagnetic (AF) coupling. The Neel temperature, $T_N$, of complex **1** was determined as the sharp peak of $d(\chi_M T)/dT$ at 62 K shown in the inset of Figure 2[16] and further evidenced by the in phase of zero field ac magnetic susceptibility $\chi'(T)$, which has a maximum at ca. 63 K under $H_{ac} = 5$ Oe and frequencies of 111, 199, 355, 633, and 1111 Hz. No frequency dependence was observed.

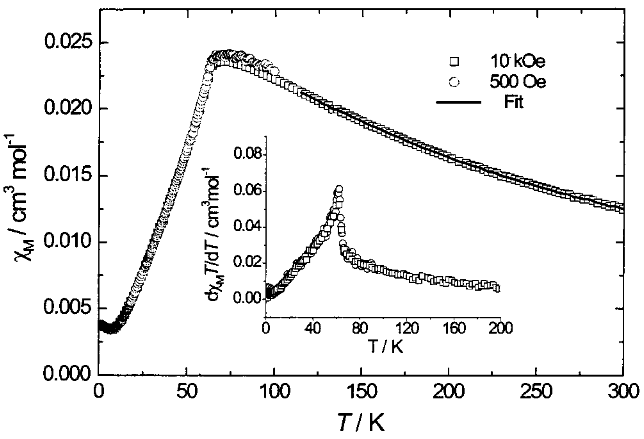

**Figure 2.** Plot of $\chi_M$ versus $T$ at 10 kOe (□) and 500 Oe (○) for **1**. The solid line corresponds to the best fit of the data. Inset: $d(\chi_M T)/dT$ versus $T$.

The fitting using a model[17] for a quadratic layer did not give a satisfactory result. That is, interaction mediated via the pyrazine−dioxide could not be negligibly small. Therefore, on the basis of the structural analysis, the high-temperature magnetic susceptibility of this compound may be explained by the model developed by Rushbrook and Wood for a Heisenberg antiferromagnet on a simple cubic lattice with the exchange Hamiltonian $H = -2J\Sigma_{\langle i,j\rangle}\mathbf{S}_i\cdot\mathbf{S}_j$,[18] namely,

$$\chi = \frac{35Ng^2\beta^2}{12kT}\left(1 + \sum_{n=1}^{6} C_n x^n\right) \qquad (1)$$

with $x = J/kT$ and $C_1 = 35$, $C_2 = 221.67$, $C_3 = 608.22$, $C_4 = 26\,049.66$, $C_5 = 210\,986$, and $C_6 = 8\,014\,980$. The best fitting of the magnetic data above 110 K using eq 1 gives $J = -1.16$ cm$^{-1}$ and $g = 2.03$, in good agreement with the result from the ESR measurements. The $J$ value is also comparable with $-1.74$ cm$^{-1}$ for another 3D compound, $[N(CH_3)_4][Mn(N_3)_3]$.[5]

The field dependence of the magnetization at different temperatures below $T_N$ shows a pronounced sigmodial shape, especially at lower temperature (Figure 3). The behavior is due to a spin−flop transition, which occurs if the Ising-like anisotropy is small compared to the weakest antiferromagnetic interaction, and this is the case for the present $Mn^{2+}$ compound **1**. The magnetiza-

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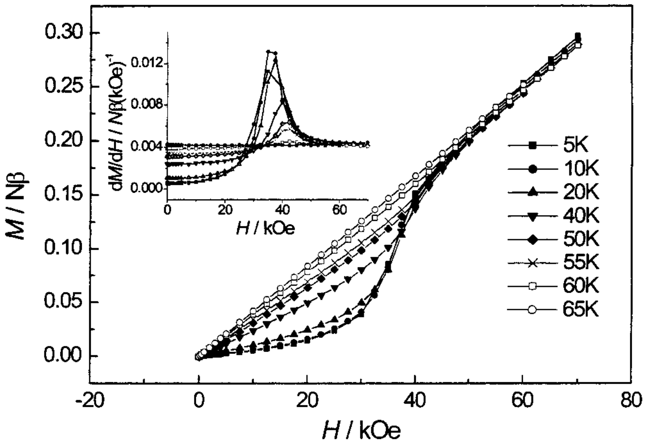

**Figure 3.** Magnetization versus applied field at different temperatures. Inset: d*M*/d*H* vs *H*.

tion below $T_N$ increases very slowly with increasing field due to considerably strong antiferromagnetic 3D interactions among $Mn^{2+}$ ions and then increases quickly for a transition from an antiferromagnet to a spin−flop state at a transition field around 35−42.5 kOe, dependent on the measured temperature (inset of Figure 3).[19] When the temperature is higher than $T_N$, the curve of magnetization vs field is close to a line, indicative of a paramagnetic state. The magnetization is only 0.29 N$\beta$ at 70 kOe, far from the saturation value of the $Mn^{2+}$ ion, which suggests again a strong 3D antiferromagnetic ordering. The spin−flop transition itself demonstrates that the anisotropy interaction, probably produced by a stronger intralayer (in an *ab* plane) interaction through azido in comparison with the interlayer interaction through pzdo, should be quite weak. This might be the reason for the good fitting between the experimental susceptibility data and a 3D cubic AFM model.

One of the reported 2D analogues, $Mn(N_3)_2$(pyz), exhibited ferro- and antiferromagnetic interactions via $\mu$-1,1-$N_3$, and $\mu$-pyz bridges, respectively,[8] and showed a lower magnetic ordering temperature ($T_N$ = 2 K). In this work, substituting pyz with pzdo not only provides a three-dimensional network **1** but also yields a higher temperature antiferromagnet ($T_N$ = 62K) with a spin−flop transition. Further investigation on a single-crystal sample is underway.

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**Supporting Information Available:** Figure showing the local connections in compound **1** and selected bond distances and angles, packing diagram of **1** along the [001] direction, curves of $\chi_M T$ (○) and $1/\chi_M$ (□) versus $T$, ac susceptibility of **1** measured at zero applied dc field with $H_{ac}$ = 5 Oe, frequency $f$ = 111−1111 Hz (PDF). An X-ray crystallographic file (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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