Synthesis and Crystal Structure of a New 3D Scaffold-Like Compound $[Mn(4,4'\text{-bipy})(N_3)_2]_n$

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A new 3D scaffold-like compound $[Mn(4,4'\text{-bipy})(N_3)_2]_n$ has been synthesized and its structure determined by single-crystal X-ray analysis. The molecular structure consists of a three-dimensional network in which Mn^{2+} are linked by EE bridged azido ligands and 4,4'-bipy ligands. Magnetic measurement indicates that the overall magnetic behavior is weakly antiferromagnetic.

The development of rational synthetic routes to novel high-dimensional coordination compounds continues to be a challenge for inorganic chemists.[1] 4,4'-bipyridine (4,4'-bipy) is a well-known rigid bridging ligand for propagating coordination polymers.[2] Undoubtedly azido ion is also a suitable candidate for the design of the architecture of high-dimensional coordination compounds. In fact, several 'end-to-end' (EE) or/and 'end-on' (EO) μ-azido bridged and 4,4'-bipy bridged nD (n=1-3) complexes have been reported.[3-4]

In the view of remarkable ability of both azido and 4,4'-bipy bridging units to generate high-dimensional coordination compounds and to mediate interaction between paramagnetic metal ions, we tried to prepare a compound with these two types of bridges. Herein we report a new three-dimensional (3D) compounds $[Mn(4,4'\text{-bipy})(N_3)_2]_n$ with a scaffold-like structure. To our knowledge, the titled compound is the first example of scaffold-type complex with both azido and 4,4'-bipy bridges.

The titled compound obtained by the following method: A solution of 4,4'-bipyridine (38.44 mg, 0.2 mmol) in methanol (10 ml) was added dropwise to a stirred aqueous solution (10 ml) of $Mn(OAc)_2$ (49 mg, 0.2 mmol); then NaN_3 (26 mg 0.4 mmol) dissolved in water (10 ml) was added slowly. The clear yellow solution was left to stand undisturbed at room temperature. Three days later, X-ray qualified light yellow single crystals were obtained, which were filtered, washed with water, methanol, ether, and dried in vacuum. yield: 78%.[5-8]

The X-ray structure analysis shows that the molecular structure consists of a three-dimensional network in which Mn^{2+} are linked by EE bridged azido ligands and 4,4'-bipy ligands. The Mn coordination environment can be considered as a distorted octahedral. Mn(II) is coordinated with two nitrogen atoms from two bridging 4,4'-bipy groups [Mn(1)-N(11) = 2.269(19) Å, Mn(1)-N(21) = 2.303(19) Å] and four bridging N_3^- groups [Mn(1)-N(1) = Mn(1)-N(1g) =2.221(11) Å, Mn(1)-N(3p) = Mn(1)-N(3t) = 2.192(11) Å] as shown in Fig. 1. The other four nitrogen atoms from the four bridging azido ligands are connected with four adjacent Mn(II) ions in other planes, respectively. The other two nitrogen atoms in two 4,4'-bipy ligands are coordinated to two adjacent manganese(II) ions also in different planes. In this way, a scaffold-like network is generated in the unit cell, as shown in Figure 2. Mn(II) ions are in the knots of the network. The bridged azides are almost linear (the N_1-N_2-N_3 angle is 177.3(6)°), and for the azido bridges the Mn(1)-N1-N2 angle is 128.5(6)° and N3-N2-Mn(1a) angle is 152.9(6)°, in a good agreement with the results usually obtained for this kind of bridging mode.[3d] N(1), N(3p), N(1g), N(3t) from four azido bridges form a plane, and Mn(1) is in the center of the plane (Plane MnN_4). The two pyridine rings of two 4,4'-bipyridine bridging to Mn(1) are both almost perpendicular to the plane MnN_4. The dihedral angle are 89.52° and 90.10° respectively. The N(11)-Mn(1)-N(21) angle is 180.0(16)°. The two pyridine rings of a 4,4'-bipyridine are not in a plane. Their dihedral angle is 32.18°. In this way the distorted 4,4'-bipyridine ligand can bridge Mn(II) ions in different planes to form a three-dimensional network. The metal-metal separation across the bridging 4,4'-bipy is 11.648 Å for Mn(1)··· Mn(1e), and that across azido bridge is 5.946 Å for Mn(1)··· Mn(1a). They are in a good agreement with the results of normal azido and 4,4'-bipy bridging groups.[9,10] This three dimensional scaffold-like network is unique.

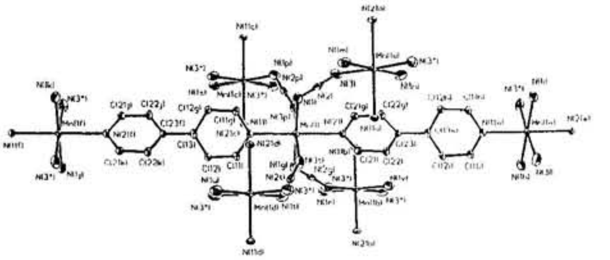

Figure 1. The ORTEP drawing of $[Mn(4,4'\text{-bipy})(N_3)_2]_n$. Selected interatomic bond distances (Å) and angles (°): Mn(1)–N(1) 2.221(11), Mn(1)–N(11) 2.268(19), Mn(1)–N(21) 2.303(19), Mn(1)–N(1g) 2.221(11), Mn(1)–N(1p) 2.191(11), Mn(1)–N(3t) 2.191(11), N(3)–Mn(1) 2.191(11), N(1)–Mn(1)–N(11) 89.8(8), N(1)–Mn(1)–N(21) 90.2(8), N(11)–Mn(1)–N(21) 180.0(16), N(1)–Mn(1)–N(1g) 179.7(3), N(11)–Mn(1)–N(1g) 89.8(8), N(21)–Mn(1)–N(1g) 90.2(8), N(1)–Mn(1)–N(3p) 88.2(5), N(11)–Mn(1)–N(3p) 90.9(8), N(21)–Mn(1)–N(3p) 89.1(8), N(1A)–Mn(1)–N(3p) 91.8(2), N(1)–Mn(1)–N(3t) 91.8(2), N(11)–Mn(1)–N(3t) 90.9(8), N(21)–Mn(1)–N(3t) 89.1(8), N(1g)–Mn(1)–N(3t) 88.1(8), N(3p)–Mn(1)–N(3t) 178.2(8).

The magnetic behavior of the compound is represented in Figure 3, in the forms of $\chi_m T$ vs T. The observed $\chi_m T$ value is 4.27 cm^3 K mol^{-1} at 295.8 K, which is slightly lower than the spin-only value of 4.34 cm^3 K mol^{-1} for Mn(II) (S = 5/2) and g_{Mn} = 2. A gradual decrease in $\chi_m T$ is observed as the temperature is

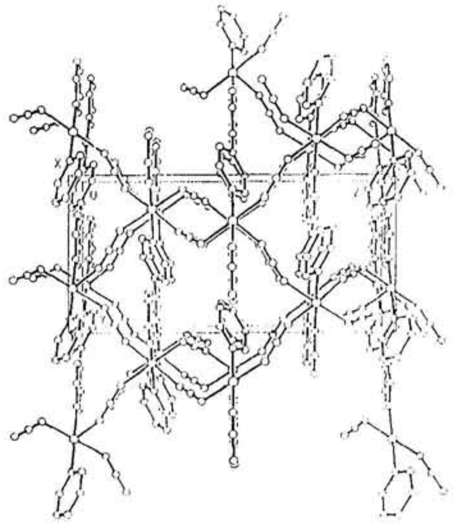

Figure 2. The view of thc crystal cell of the compound.

decreased($\chi_m T$ = 0.146 cm^3 K mol^{-1} at 4 K), indicating the presence of an antiferromagnetic interaction within the molecule.

Magneto-structural data of complex and two different 4,4'-bipy and N_3^- bridges allow us to foresee three kinds of magnetic exchange coupling within 3D network. Because no a suitable theoretical model is available in the literature[11,12] for such a complex system, detailed magnetic analyses were not done for the present compound, but Figure 3 clearly indicates that the overall magnetic behavior is weakly antiferromagnetic. Further studies on magnetic properties and similar systems are going on in our laboratory.

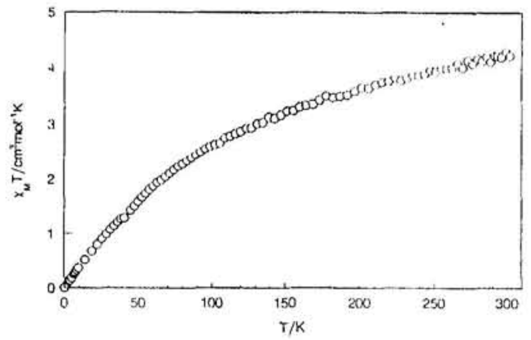

Figure 3. Plots of the products $\chi_m T$ vs temperature for [Mn(4,4'-bipy)$(N_3)_2$]$_n$.

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References and Notes

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5 Anal. Found: C, 40.83; H, 2.84; N, 38.30%.Calcd. for $MnC_{10}H_8N_8$: C, 40.69; H, 2.73; N, 37.96. *m. p.* 260 °C (decom.). *IR* (cm^{-1}): ν_{N3^-} 2125; $\nu_{4,4'\text{-bipy}}$ 1610, 1420, 820.

6 Crystal data: $MnC_{10}H_8N_8$, M = 295.17, tetragonal, $P4_12_12$, a = 8.236(1) Å, c = 16.946(1) Å, V = 1149(1) Å^3, z = 4, D_m = 1.710(1), D_x = 1.705 gcm^{-3}, R = 0.037, *w*R = 0.045 and S = 1.37. It was mounted on a computer-controlled Enraf-Nonius CAD4 diffractometer equipped with a graphite-monochromatized Mo-Kα radiation (λ = 0.71073Å). Cell parameters were determined by a least-squares calculations based on the setting angles and 25 reflections with 2θ angles ranging from 9.24 to 12.11° at 299(1) K. The intensities of the ±hkl reflections were measured up to $\theta_{max} = 23°$; the ω-2θ scan technique was employed, the ω-scan width equal to (0.65 + 0.35 tanθ)°, and the scan speed 0.92–5.49 ° min^{-1}. A total of 795 independent reflections was measured giving 758 observed reflections ($I \geqslant 3\sigma(I)$) used in the refinement. Three standard reflections monitored every 60 min showed no intensity variation during the data collection. No absorption correction was made during processing. The structure was solved by direct method (SHELX86 and SHELX93)[7,8] using SDP-PLUS program and refined by the full-matrix least-squares method with use of the SHELXL-93 package of program. The final refinement was by full-matrix least-squares with the fuction minimzed being $\Sigma w(|F_o| - |F_c|)^2$ where $w^{-1} = \sigma^2(F) + 99.00000F^2$. Convergence was reached at. The highest peak on the final difference-Fourier map had the value of 0.95 eÅ.

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