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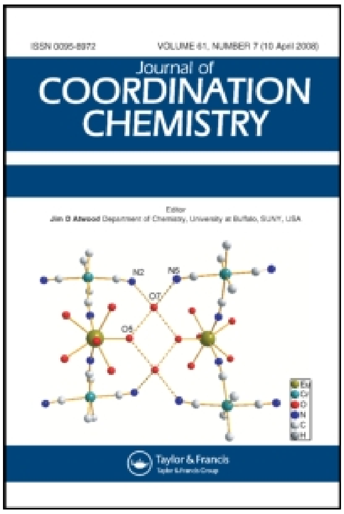

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A New Azide-Bridged Three-Dimensional Supramolecular Manganese(II) Compound: Synthesis, Crystal Structure and Magnetic Properties

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A NEW AZIDE-BRIDGED THREE-DIMENSIONAL SUPRAMOLECULAR MANGANESE(II) COMPOUND: SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES

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A three-dimensional supramolecular compound $[Mn(N_3)_2(H_2O)_3(hmt)]_n$, where hmt stands for hexamethylenetetramine, was synthesized and characterized by IR, crystal structure and magnetic susceptibility. The compound $[Mn(N_3)_2(H_2O)_3(hmt)]_n$, crystallizes in the orthorhombic system, space group P_n2_1a, with $a = 6.5201(9)$, $b = 9.322(2)$, $c = 22.192(3)$ Å, $\beta = 90^\circ$ and $Z = 2$. The Mn atom is coordinated in an octahedral arrangement by three nitrogen atoms from three azido ions, and three oxygen atoms from three water molecules, respectively. The azide ligand bridges Mn atoms in μ-1,3 fashion, forming a zigzag chain. Hmt connected with the zigzag chain by hydrogen bonds, to form a three-dimensional supramolecular structure. The magnetic susceptibility data show that there is an antiferromagnetic exchange interaction in the title compound. The data were modeled using an infinite chain model leading to $J = -4.8\,\mathrm{cm}^{-1}$.

Keywords: Crystal structure; Three-dimensional supramolecular manganese (II) compound; Azido ion bridge; Hexamethylenetetramine; Magnetic property

INTRODUCTION

There has been considerable interest in the extended structure of supramolecular complexes assembled by coordination bonds and hydrogen bonds [1], due to their potential application in catalysis [2], host-guest chemistry [3], and the evolution of optical, magnetic and electrical properties [4]. The assembly of these complexes strongly depends on the selection of both the metallic centers and ligands [5,6]. Hexamethylenetetramine (hmt), as a potential tetradentate ligand or hydrogen bond acceptor, has been used to produce multi-dimensional polynuclear species and supramolecular compounds with metal ions [7]. On the other hand, the azido ligand N_3^-

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can bond two metal ions symmetrically either μ-1,1, through a terminal nitrogen which typically couples spins ferromagnetically [8,9] or μ-1,3 through both terminal nitrogen which couples spins antiferromagnetically [10]. Several dinuclear [9,11], tetranuclear [12], one-dimensional (1D) [10,13], two-dimensional (2D) [8,14,15] and three-dimensional (3D) [16] polymeric complexes have been synthesized and characterized using azide N_3^- as a bridging ligand. Thus, a suitable combination of hmt, azido ligand and metal ions may lead to preparation of high-dimensional species. Here we report a novel three-dimensional supramolecular compound $[Mn(N_3)_2(H_2O)_3(hmt)]_n$.

EXPERIMENTAL

Materials and Physical Measurements

Hexamethylenetetramine (hmt) and sodium azide were used as purchased. Elemental analyses (C, H, N) were determined on a Perkin–Elmer 2400 microanalysis instrument. An IR absorption spectrum (KBr pellet) was recorded on a Nicolet FTIR 170X spectrophotometer. Variable–temperature magnetic susceptibilities were determined on a SQUID Quantum Design MPMS-2 magnetometer.

Preparation of $[Mn(N_3)_2(H_2O)_3(hmt)]_n$

An aqueous solution (3.5 mL) of sodium azide (0.260 g, 4 mmol) was slowly added to an aqueous solution (6 mL) of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.724 g, 2 mmol) and hmt (0.140 g, 1 mmol) with stirring for *ca.* 10 min. The obtained solution was allowed to stand in the dark for about 3 weeks at room temperature to give brown crystals: yield 16%. Anal. Calcd. for $C_{12}H_{36}Mn_2N_{20}O_6$ (%): C, 21.62; H, 5.40; N, 42.04. Found: C, 21.65; H, 5.74; N, 41.96. IR spectrum: 3392 cm^{-1} (s), 2933 (s), 2358 (w), 2125 (s), 2073 (vs), 1668 (w), 1465 (m), 1377 (m), 1233 (s), 1013 (sh), 807 (m), 691 (s) 669 (s), 640 (m), 556 (m), 507 (m).

X-ray Structure Determination of $[Mn(N_3)_2(H_2O)_3(hmt)]_n$[1]

A brownish black crystal with dimensions of 0.48 × 0.44 × 0.28 mm was mounted on a Siemens P_4 diffractometer for data collection by using graphite-monochromatic MoK_α radiation ($\lambda = 0.71073$ Å) at 291(2) K, and 4147 reflections were collected, of which 2868 were independent and 2237 were observed with $F_0 > 4\sigma(F_0)$. Data were corrected for empirical absorption. The structure was solved by direct methods, followed by difference Fourier synthesis. The structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms.

All calculations were performed on an IBM PC computer with Siemens SHELXL-97 program. The final R value is 0.0244 and refinement with the complete data set yielded $wR = 0.0594$. The scattering factors were taken from Ref. [17]. The crystallographic data were summarized in Table I.

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[1] CCDC 155458.

TABLE I Summary of crystal data, data collection and structure refinement for the complex $[Mn(N_3)_2(H_2O)_3(hmt)]_n$

Formula	$C_6H_{18}MnN_{10}O_3$
M_r	333.245
Temperature	291(2) K
Wavelength	0.71071 Å
Crystal system	Orthorhombic
Space group	$Pn2_1a$
Unit cell dimensions	$A = 6.5201(9)$ Å $\alpha = 90°$
	$B = 9.322(2)$ Å $\beta = 90°$
	$C = 22.192(3)$ Å $\gamma = 90°$
Volume	1348.8(4) $Å^3$
Z	4
Density (calculated)	1.641 Mg/m^3
Absorption coefficient	1.006 mm^{-1}
$F(000)$	692
Crystal size	0.48 × 0.44 × 0.28 mm
θ range	1.84–27.98°
Index ranges (h, k, l)	$-7/8$, $-11/12$, $-26/29$
Reflections collected	4147
Independent reflections	2868 (R_{int})
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2868/10/206
Goodness-of-fit on F^2	0.942
Final R, wR indices ($I > 2\sigma(I)$)	0.0244, 0.0559
R, wR indices (all data)	0.0360, 0.0594
Extinction coefficient	0.0220 (10)
Largest diff. peak and hole	0.242 and -0.215 e $Å^{-3}$

RESULTS AND DISCUSSION

Crystal Structure

As shown in Fig. 1, Mn(II) has octahedral geometry, of which the equatorial plane is composed of N8,N10a from two azido ligands and oxygen atoms O1,O2 from two water molecules, and the apical positions are occupied by nitrogen atom N5 from an azido ligand and oxygen atom O3 from water. The main bond parameters that involve the manganese coordination polyhedron are as follows: Mn–N5 2.2206(14) Å, Mn–N8 2.201(6) Å, Mn–N10a 2.181(6) Å, Mn–O1 2.214(5) Å, N8–Mn–N10a (symmetry operation: $a - x + 1$, $y - 1/2$, $-z + 1$) 92.32(9), N8–Mn–O2 177.2(2)°, N5–Mn–O3 178.06(15)°, N9–N8–Mn 136.9(6)°. The distance between Mn–Mnb (symmetry operation: $b - x + 1$, $y + 1/2$, $-z + 1$) atoms is 6.286 Å. Two azido ligands in the equatorial plane bridge two manganese atoms in μ-1,3 fashion forming a zigzag chain along the axis. One of the most notable features of the structure is the formation of hydrogen bonds, which leads to the production of a three-dimensional network. In the $[Mn(N_3)_2(H_2O)_3(hmt)]_n$ complex, as shown in Fig. 2, O3–H30B – N5* [2.967(19) Å], O1–H10A – N7* [2.825(8) Å] and O2–H20A – N7* [2.919(8) Å] hydrogen bonds exist between the zigzag chains, which leads to fomation of a three-dimensional network. Hmt molecules are clathrated in the cavities of the network and connect with the Mn complex *via* hydrogen bonds: O3–H30A – N1 [2.8174(18) Å], O1–H10B – N3* [2.807 (7) Å] and O2–H20B – N2* [2.828(7) Å]. The shortest and the largest Mn(II)–Mn(II) distance between the closest neighbors in the same layer *via* hydrogen bonds are 7.612, and 15.656 Å. The neighboring interlayer Mn(II)–Mn(II) separation is 6.520 Å.

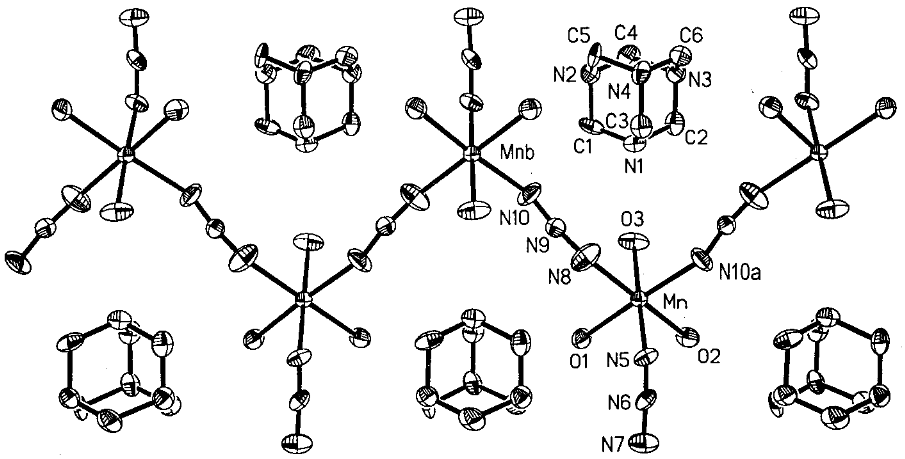

FIGURE 1 The molecular structure of the complex $[Mn(N_3)_2(H_2O)_3(hmt)]_n$ (ellipsoids at the 35% probability level). Relevant bonds parameters: Mn–N(10a) 2.181(6), Mn–O(3) 2.1970(13), Mn–N(8) 2.201(6), Mn–O(2) 2.208(5), Mn–O(1) 2.214(5), Mn–N(5) 2.2206(14) Å; N(10a)–Mn–O(3) 88.9(2), N(10a)–Mn–N(8) 92.32(9), O(3)–Mn–N(8) 89.1(2), N(8)–Mn–O(2) 177.2(2), N(10a)–Mn–O(1) 175.5(2), O(3)–Mn–O(1) 90.5(2), O(3)–Mn–N(5) 178.06(15), N(8)–Mn–N(5) 90.3 (2), N(9)–N(8)–Mn 136.9(6)°.

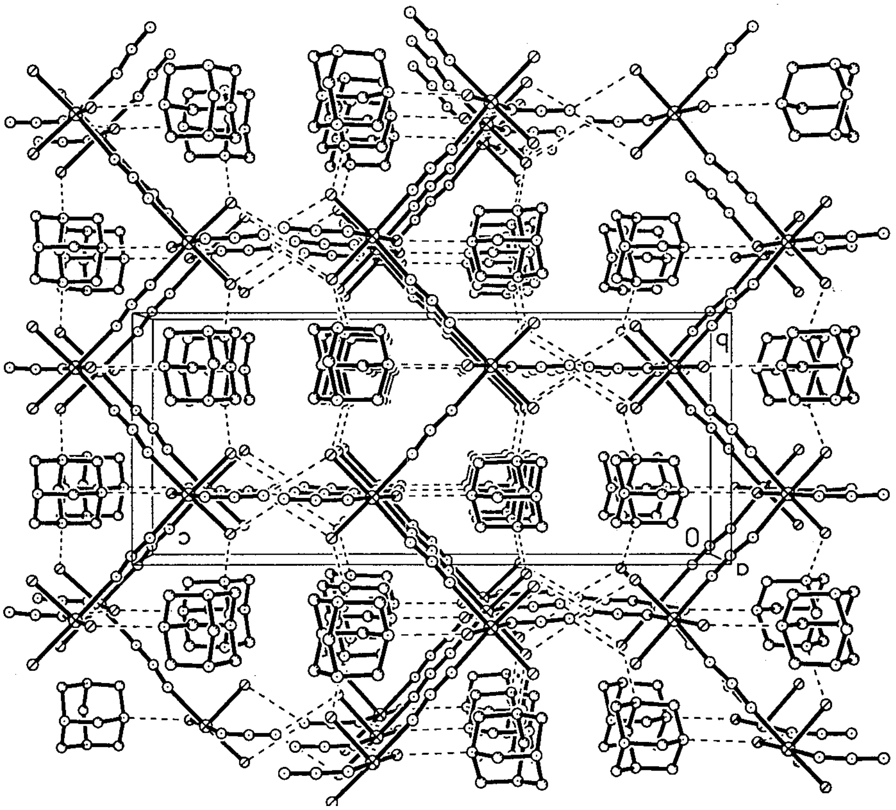

FIGURE 2 The crystal packing diagram of the complex $[Mn(N_3)_2(H_2O)_3(hmt)]_n$.

IR Spectrum

The strong broad band at 3392.9 cm^{-1} and the weak band at 1668.5 cm^{-1} belong to the ν(OH) stretching mode and δ(HOH) bending mode of coordinated water. The strong bands at 2125 and 2073 cm^{-1} are $\nu_{as}(N_3^-)$ stretching mode of N_3^- [18].

Magnetic Property

Variable–temperature magnetic susceptibility measurements were performed on a powder sample in the range 299–5.21 K with a SQUID Quantum Design MPMS-2 magnetometer. Global antiferromagnetic behavior is evident from the magnetic measurements as shown in Fig. 3. The χ_m values increases as the temperature decreases (Fig. 3) to reach a sharp maximum at about 27 K and then decreases on cooling 5.21 K. The $\chi_m T$ value at room temperature is 3.77 $\text{cm}^3\,\text{mol}^{-1}$ K (Fig. 3), which is smaller than the value expected for spin-only of Mn(II) ions. With decreasing temperature, $\chi_m T$ drops gradually. This behavior is characteristic of an antiferromagnetic interaction in the whole temperature range. The magnetic susceptibility data of the title compound were successfully analyzed in the terms of the equation (Eq. 1) derived by the infinite–chain model ($H = -J\Sigma S_{Ai} \cdot S_{Ai+1}$) [19]. The least-square analysis for the compound yields $J = -4.80\,\text{cm}^{-1}$ and $g = 2.0$ (fixed). The goodness-of-fit R was defined as $R = [\phi/(n-k)]^{1/2}$, where n and k are the number of data points and parameters respectively, $\phi = \Sigma[(\chi_m)_i^{\text{obs}} - (\chi_m)_i^{\text{calc}}]^2$ is equal to 3.45×10^{-3}. This result supports the presence of an intrachain antiferomagnetic interaction *via* bridging azido ligands.

$$\chi_m = \{Ng^2\mu_B S_A(S_A+1)/3k_B T\}\{(1+u)/(1-u)\} \tag{1}$$

where

$$u = \coth K - 1/K \quad \text{and} \quad K = JS_A(S_A+1)/k_B T.$$

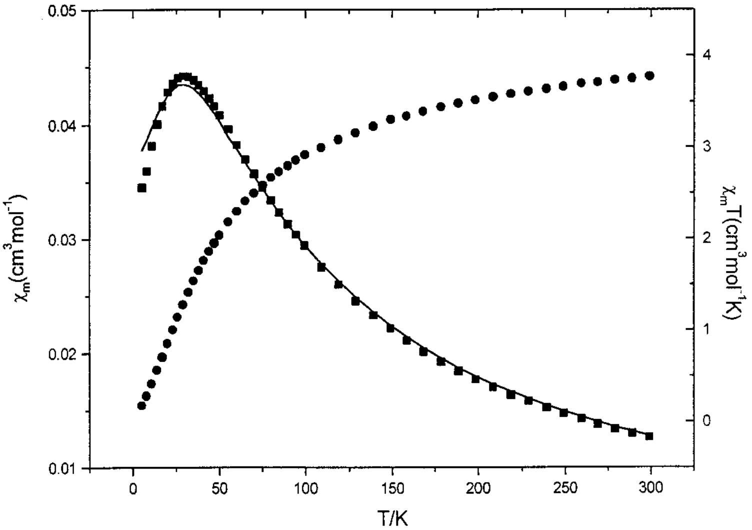

FIGURE 3 Temperature dependence of χ_m and $\chi_m T$ *vs.* T for $[\text{Mn}(\text{N}_3)_2(\text{H}_2\text{O})_3(\text{hmt})]_n$. The solid line (—) shows the best theoretical fit.

The conclusion can be drawn from the 3D supramolecular structure. The hydrogen bonds are important in construction of higher dimensional coordination polymers. Hmt molecules were enveloped in the void cavities which stabilized crystal packing. There is an antiferromagnetic interaction in the title compound, and behavior is typical for azide N_3^- bridges in μ-1,3 modes [15].

Acknowledgement

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Supplementary Material

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 155485.

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