

Hydrogen- and Covalent-Bond-Linked 3D Manganese Array

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Introduction

There has been considerable interest in the study of magnetically coupled metal complexes with extended structures on account of their promising application in the field of molecular magnetism.^{1–3} In order to build a spatially well-spanned framework, certain features of the bridging ligands which connect paramagnetic metal centers and mediate superexchange interactions between them can be utilized since they can play an important role in the molecular arrangement in a crystal. For example, the conformational flexibility, the versatile binding mode, and the ability to form hydrogen bonds are cases in point. In this context, the bpe ligand [bpe = 1,2-bis(4-pyridyl)ethane], which has broad relevance to the construction of solid-state architecture and crystal engineering, is very useful for growing crystals through adoption of its flexible conformation.^{4,5} Also, the tp group [tp = terephthalate], with versatile binding modes, has been utilized in preparing extended structures,^{6,7} and the introduction of moderately strong, specific and directional hydrogen bonds into molecular structure has increased the molecular dimensionality.^{8–11} Thus, the appropriate combination of bpe, tp, and the hydrogen bond, which has not been reported before, would open new routes to magnetically coupled multidimensional systems. Consequently, a rational approach to achieve higher dimensional network structures of paramagnetic metal centers has been attempted by using bpe and tp as building motifs and the hydrogen bond as sewing cotton. Here we report on a novel 3D complex, [Mn(bpe)(H₂O)₄]_{0.5n}(tp)_{0.5n}-(bpe)_n (**1**), whose solid-state structure spreads out via hydrogen bonds of aqua ligands with tp counterdianions and packing bpe ligands.

Experimental Section

Synthesis. To a stirred solution of manganese(II) acetate (0.50 mmol) in water, an equimolar amount of 1,2-bis(4-pyridyl)ethane in methanol was added. The resulting mixture was treated with an aqueous

Table 1. Crystallographic Data for **1**

empirical formula	C ₂₂ H ₂₄ N ₃ O ₄ Mn _{0.5}
fw	421.91
cryst syst	triclinic
space group	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.5450(13)
<i>b</i> (Å)	10.5971(9)
<i>c</i> (Å)	10.7499(10)
α (deg)	67.543(7)
β (deg)	77.570(9)
γ (deg)	82.882(9)
<i>V</i> (Å ³)	1083.0(2)
<i>Z</i>	2
<i>D</i> _{calcd} (g cm ⁻³)	1.294
abs coeff, μ (mm ⁻¹)	0.363
<i>R</i> 1 ^a	0.0499
<i>wR</i> 2 ^b	0.1311

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_c|$. ^b $wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}$, where $w = 1 / [\sum^2(F_o^2) + (0.0715P)^2 + 1.0257P]$, $P = (F_o^2 + 2F_c^2) / 3$.

Table 2. Selected Bond Distances (Å) and Angles (deg) for **1**

Mn1–O1	2.149(2)	Mn1–O2	2.170(2)
Mn1–N1	2.312(2)	N2···O1	2.777
N3···O2	2.839	O4···O1	2.628
O3···O2	2.672	Mn···Mn	13.993
O1–Mn–O2	88.44(9)	O2–Mn1–N1	87.82(9)
O1–Mn1–N1	88.70(9)	C1–N1–Mn1	120.3(2)
C5–N1–Mn1	123.4(2)		

solution of dipotassium terephthalate (0.50 mmol) with 10 min of stirring. Slow evaporation of the filtrate gave white crystalline **1** in 33% yield based on Mn. Elemental Anal. Calcd for **1**, C₂₂H₂₄N₃O₄Mn_{0.5}: C, 62.63; H, 5.73; N, 9.96. Found: C, 62.84; H, 5.86; N, 9.99. Selected IR data (cm⁻¹, KBr pellet): 3042 (s, broad, additional two spikes seen at 2929 and 2871), 1607 (s, bpe pyridyl skeletal), 1561 (s, tp ν_a (CO₂⁻)), 1422 (m), 1367 (s, tp ν_s (CO₂⁻)), 1223 (w), 1085 (w), 1070 (w), 1015 (w), 1003 (m), 831 (s), 811 (m), 749 (m), 548 (s), 510 (m).

Physical Measurements. Elemental analyses for C, H, and N were performed at the Elemental Analysis Service Center of the Korea Basic Science Institute. Infrared spectra were obtained from KBr pellets with an EQUINOX 55 spectrometer. Magnetic susceptibilities were carried out under 0.2 T using a Quantum Design MPMS-7 SQUID susceptometer. Diamagnetic corrections of **1** were estimated from Pascal's tables.

Crystallographic Data Collection and Structure Determination of 1. Data were collected at 293 K using an Enraf-Nonius CAD4TSB diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) in the $\omega/2\theta$ scan mode. The unit cell parameters were calculated by least-squares refinement of 25 well-centered reflections in the range $17.58^\circ < 2\theta < 29.966^\circ$. All data were corrected for Lorentz polarization effects. ψ -scan absorption correction with a transmission minimum and maximum of 95.82% and 99.94%, respectively, was applied. A total of 3509 reflections were measured in the $2.08^\circ < \theta < 24.97^\circ$, and 3090 reflections were assumed to be observed applying the condition $F_o > 4\sigma(F_o)$. Crystallographic data and details of data collection are listed in Table 1.

The structure was solved with the SIR92 program¹² and refined by least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the SHELXL93 program.¹³ All hydrogen atoms except for hydrogens bound to water molecules were calculated at

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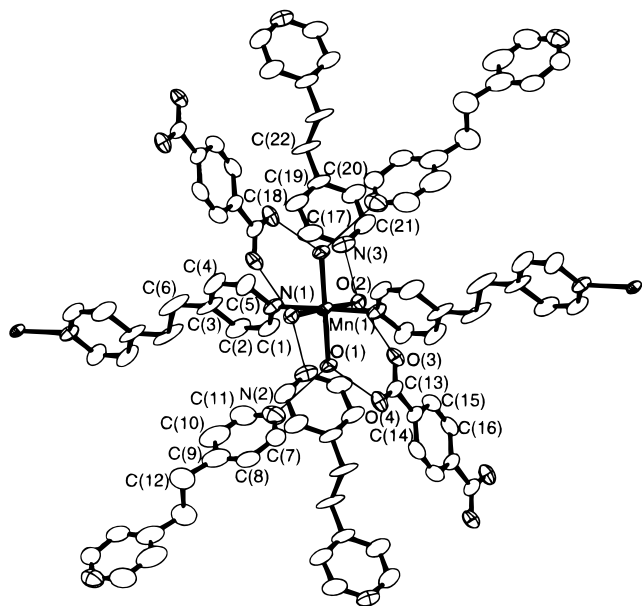


Figure 1. ORTEP representation of the repeating unit with the atom-numbering scheme and all of the symmetry-related fragments around the Mn atom (50% thermal ellipsoids).

idealized positions. The goodness of fit for all observed reflections was 1.068. Maximum shift/esd = 0.001 and maximum and minimum peaks in the final difference synthesis were 0.768 and $-0.255 \text{ e}\text{\AA}^{-3}$, respectively.

Results and Discussion

The molecular structure consisting of the repeating unit with atom-numbering scheme and all the symmetry-related fragments around the Mn atom is depicted in Figure 1. Selected bond distances and angles are reported in Table 2. The Mn atom of the asymmetric unit lies on the crystallographic inversion center. The geometry around the Mn(II) ion is octahedral with a large tetragonal elongation. The four oxygen atoms of the coordinated water molecules define the equatorial positions, whereas two nitrogen atoms of bridging bpe (=N1-bpe) ligands occupy the axial ones. The axial Mn–N bond distance of 2.312(2) Å is significantly longer than the equatorial Mn–O bonds of 2.149(2) and 2.170(2) Å. Each axial N1-bpe ligand, of which two pyridyl rings are nearly planar and parallel with an interplanar distance of ca. 0.5 Å, bridges Mn(II) ions, forming a 1D chain with an intrachain intermanganese distance of 13.993 Å. Other pyridyl rings of packing bpe (=N2-bpe, N3-bpe) molecules are also planar and parallel but show different interplanar distances of ca. 0.9 and 1.4 Å, reflecting the conformational flexibility. All of the bpe adopt the anticoinformation, and among them the N3-bpe has the longest separation between pyridyl ring planes.

The infrared spectrum of **1** reflects the binding patterns of the aqua and tp moieties.¹⁴ The most characteristic feature is the extremely broad O–H absorption occurring in the region 3500–2500 cm^{-1} . This band is attributed to the strong hydrogen bonds associated with the coordinated water molecules as verified by the crystal structure analysis. In addition, the Δ value of 194 cm^{-1} defined as the difference between $\nu_a(\text{CO}_2^-)$ and $\nu_s(\text{CO}_2^-)$ indicates that the structure of carboxylate groups of tp in **1** is either bridging or ionic.¹⁴

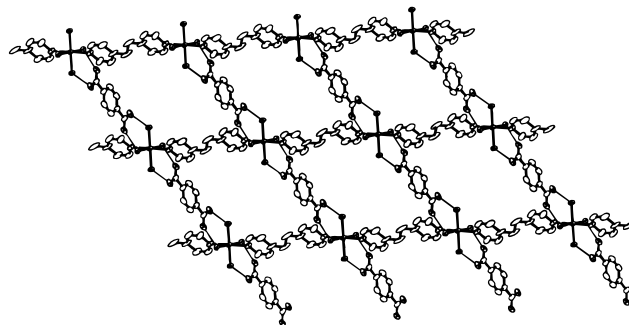


Figure 2. View of sheet A. The packing bpe molecules are omitted for clarity.

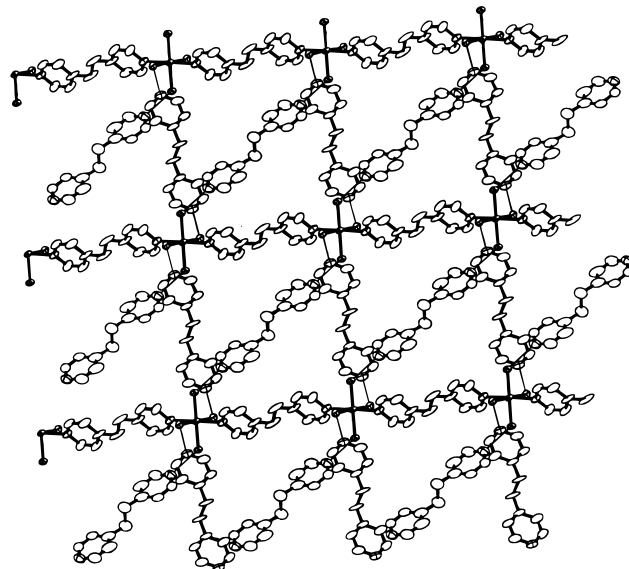


Figure 3. View of sheet B. The tp counteranions are omitted for clarity.

The hydrogen bonds between the coordinated water molecules and packing bpe molecules and tp counteranions contribute to the enhancement of molecular dimensionality. The four coordinated water molecules are hydrogen-bonded to four packing bpe molecules ($\text{N}2\text{--O}1 = 2.777 \text{ \AA}$; $\text{N}3\text{--O}2 = 2.839 \text{ \AA}$), and two tp counteranions ($\text{O}4\text{--O}1 = 2.628 \text{ \AA}$; $\text{O}3\text{--O}2 = 2.672 \text{ \AA}$) all of which are again hydrogen-bonded to other coordinated water molecules belonging to four adjacent 1D chains, resulting in an overall 3D manganese array. The 3D structure can be viewed as two intersecting sheets A and B with a dihedral angle of 73.5°. The sheet A as illustrated in Figure 2 consists of 1D chains linked by hydrogen bonds with tp dianions, giving a dihedral angle of 82.5° between the N1-bpe pyridyl ring and the tp phenyl ring and an intermanganese distance of 15.196 Å within the hydrogen-bonded tp 1D chain. Shown in Figure 3 is the sheet B resulting from interconnecting 1D chains with bpe packing molecules via hydrogen bonds. The intermanganese distances linked via packing N2- and N3-bpe molecules are 17.745 and 16.600 Å, respectively.

The magnetic susceptibilities (χ_m) were measured in the temperature range 1.8–300 K. The χ_m and $\chi_m T$ vs T plots for **1** are shown in Figure 4. When the temperature is lowered, the χ_m value reaches a sharp maximum at around 4 K, indicative of overall antiferromagnetic coupling between magnetic centers. At room temperature, the $\chi_m T$ value is equal to 3.67 $\text{cm}^3 \text{ K mol}^{-1}$, already smaller than what is expected for uncoupled Mn(II) ions. The $\chi_m T$ value decreases smoothly upon cooling to about 40 K and then decreases rapidly to reach the value of 0.41 $\text{cm}^3 \text{ K mol}^{-1}$ at 1.8 K. Best fitting of the variable-

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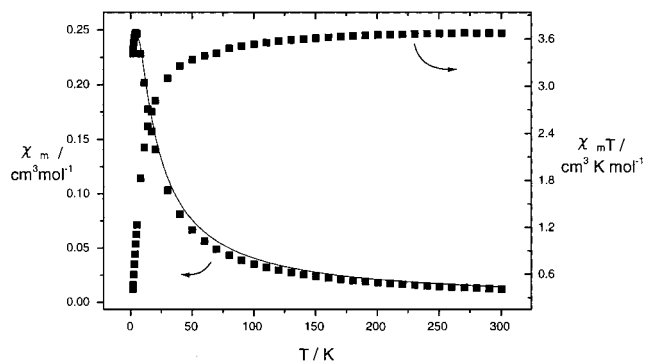


Figure 4. Temperature dependence of χ_m and $\chi_m T$ vs T for $[\text{Mn}(\text{bpe})\text{-(H}_2\text{O)}_4]_{0.5n}(\text{tp})_{0.5n}(\text{bpe})_n$ (**1**). The solid line shows the best theoretical fit.

temperature magnetic data for **1** to the equation (eq 1) derived by the infinite-chain model ($H = -J\sum S_{A_i} \cdot S_{A_{i+1}}$)¹⁵ yields $g = 2.0$ (fixed), $J = -0.84 \text{ cm}^{-1}$. The measure of the goodness of fit R , defined as $R = [\Phi/(n - k)]^{1/2}$ where n is the number of data points, k is the number of parameters, and $\Phi = \sum[(\chi_m)_i^{\text{obs}}$

$-(\chi_m)_i^{\text{calc}}]^2$, is equal to 6.18×10^{-3} . This result supports the presence of a weak intrachain antiferromagnetic interaction via the coordinatively bridging bpe ligand.

$$\chi_m = \{Ng^2\beta^2 S_A(S_A + 1)/3kT\} \{(1+u)/(1-u)\} \quad (1)$$

with

$$u = \coth[JS_A(S_A + 1)/kT] - [kT/JS_A(S_A + 1)]$$

The reported 3D structure clearly shows the availability of hydrogen bonds to develop higher dimensional systems. In addition, the bpe ligand used here favors crystal packing due to flexible conformation and may expand the diversity of molecular structure by replacement of the dianion with a variety of anionic bridging ligands.

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Supporting Information Available: Tables giving details of the crystallographic data collection, atomic coordinates, isotropic thermal parameters, anisotropic thermal parameters, and bond distances and angles for **1** (6 pages). Ordering information is given on any current masthead page.

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