

КРАТКИЕ СООБЩЕНИЯ

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CRYSTAL STRUCTURE OF A NEW MONONUCLEAR COMPLEX OF Mn(II) WITH A bbbi LIGAND
(bbbi = 1,4-BIS(BENZIMIDAZOL-1-YL)-2-BUTENE)

G.-H. Cui, T.-F. Liu, C.-H. He, C.-H. Jiao

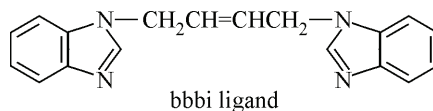
College of Chemical Engineering, Hebei United University, Tangshan, Hebei Province, P. R. China 063009,
e-mail: tscghua@126.com

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A new mononuclear complex $\text{Mn}(\text{bbbi})_2(\text{H}_2\text{O})_4(\text{ClO}_4)_2 \cdot (\text{bbbi})_2 \cdot (\text{H}_2\text{O})_2$ **1** (bbbi = 1,4-bis(benzimidazol-1-yl)-2-butene) is synthesized under hydrothermal conditions and characterized by IR spectroscopy, elemental analysis, and single crystal X-ray structural analysis. Crystal data for **1**: triclinic, $P\bar{1}$, $a = 8.8478(7)$ Å, $b = 15.0550(11)$ Å, $c = 16.4310(12)$ Å, $\alpha = 108.657(7)^\circ$, $\beta = 104.044(7)^\circ$, $\gamma = 99.317(7)^\circ$, $V = 1942.2(3)$ Å³, $Z = 1$, final $R = 0.0621$. Each manganese atom is octahedrally coordinated by four aqua ligands and two nitrogen atoms of two distinct bbbi ligands. The molecule is stabilized by hydrogen bonding and $\pi \cdots \pi$ interactions.

Key words: bis(benzimidazole), hydrogen bond, manganese(II), mononuclear complex.

Introduction. The synthesis and investigation of new coordination polymers have recently been of great interest in the fields of crystal engineering and coordination chemistry owing to their intriguing structures and potential applications as functional materials in molecular magnetism, catalysis, gas sorption, fluorescent sensing, and optoelectronic devices [1, 2]. A significant number of efforts have been contributed to the building of these complexes with 0D, 1D, 2D, or 3D framework structures by the selection of a variety of dicarboxylate and N-donor ligands over the past decade. Flexible bis(benzimidazole) ligands as an important family of flexible N-donor ligands have attracted great interest [3—5]. The flexible nature of the alkyl $(-\text{CH}_2-)_n$ spacer allows those ligands to bend and rotate freely so as to conform to the coordination geometries of central metal ions. We are interested in the reactions of such types of ligands with various metal salts to investigate the influence of the metal ions, counter ions, and the variation of ligand spacers on the framework structures. Here we report the preparation and crystal structures of a new mononuclear manganese(II) complex based on the flexible bbbi ligand (bbbi = 1,4-bis(benzimidazol-1-yl)-2-butene) whose complexes are rarely reported [6].



Experimental. Reagents and apparatus. All commercially available starting materials were of analytical grade and used as received. The bbbi ligand was prepared according to the literature method [6]. Elemental analyses were taken on a Perkin-Elmer 240C analyzer. IR spectra (KBr pellet) were obtained on a FT—IR 170 SX (Nicolet) spectrometer. The single crystal X-ray diffraction measurement was carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at 293(2) K. Intensities of reflections were measured using graphite-monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) with ω scan mode in

Table 1

Crystal data and structure refinement summary for 1

Empirical formula	$C_{72}H_{76}MnCl_2N_{16}O_{14}$
CCDC number	805203
M	1515.33
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions a, b, c , Å; α, β, γ , deg.	8.8478(7), 15.0550(11), 16.4310(12); 108.657(7), 104.044(7), 99.317(7)
Volume, Å ³	1942.2(3)
Z	1
d_{calc} , g/cm ³	1.296
μ , mm ⁻¹	3.235
$F(000)$	1008
Crystal size, mm	0.22×0.20×0.19
θ range, deg.	2.96—25.02
Crystal color and shape	Pale block
Range of h, k, l	−9/10, −17/17, −19/19
Reflections collected/unique	13778 / 6849
Max. and min. transmission	0.923 and 0.899
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6849 / 0 / 465
Goodness-of-fit on F^2	0.942
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0621$, $wR2 = 0.1116$
R indices (all data)	$R1 = 0.1634$, $wR2 = 0.1207$
Residual peak and hole, e/Å ³	0.686 and −0.377

the range of $2.96^\circ < \theta < 25.02^\circ$. Unit cell dimensions were obtained with least-squares refinements, and semi-empirical absorption corrections were applied using the SADABS program [7]. The structure was solved by a direct method [8] and non-hydrogen atoms were obtained in successive difference Fourier syntheses. The final refinements were performed by full-matrix least-squares methods on F^2 by the SHELXL-97 program package [9]. Water H atoms were located in a difference Fourier map; other hydrogen atoms were included in calculated positions and refined with fixed thermal parameters riding on their parent atoms. The summary of the crystallographic data and structure analysis is given in Table 1. CCDC-805203 contains the supplementary crystallographic data for complex 1. These data can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

Preparation of $Mn(\text{bbbi})_2(\text{H}_2\text{O})_4(\text{ClO}_4)_2 \cdot (\text{bbbi})_2 \cdot (\text{H}_2\text{O})_2$ (1). A mixture of manganese(II) perchlorate hexahydrate (0.1 mmol, 36.2 mg), bbbi ligand (0.1 mmol, 29.0 mg), dipicolinic acid (0.1 mmol, 16.7 mg), NaOH (0.20 mmol, 8.0 mg), and H₂O (10 ml) was placed in a teflon-lined stainless vessel and heated to 160 °C for 5 days under autogenous pressure, and then cooled to room temperature at a rate of 10 °C/h. The pale crystal of 1 was obtained in 31.5 % yield based on Mn. Anal. calcd. for $MnC_{72}H_{76}Cl_2N_{16}O_{14}$ (%): C, 57.07; H, 5.06; N, 14.79. Found (%): C, 56.57; H, 5.03; N, 14.65. IR (KBr pellet, cm⁻¹): 3431(s), 2388(w), 1629(m), 1503(s), 1456(m), 1366(m), 1099(s), 990(m), 744(m), 623(m).

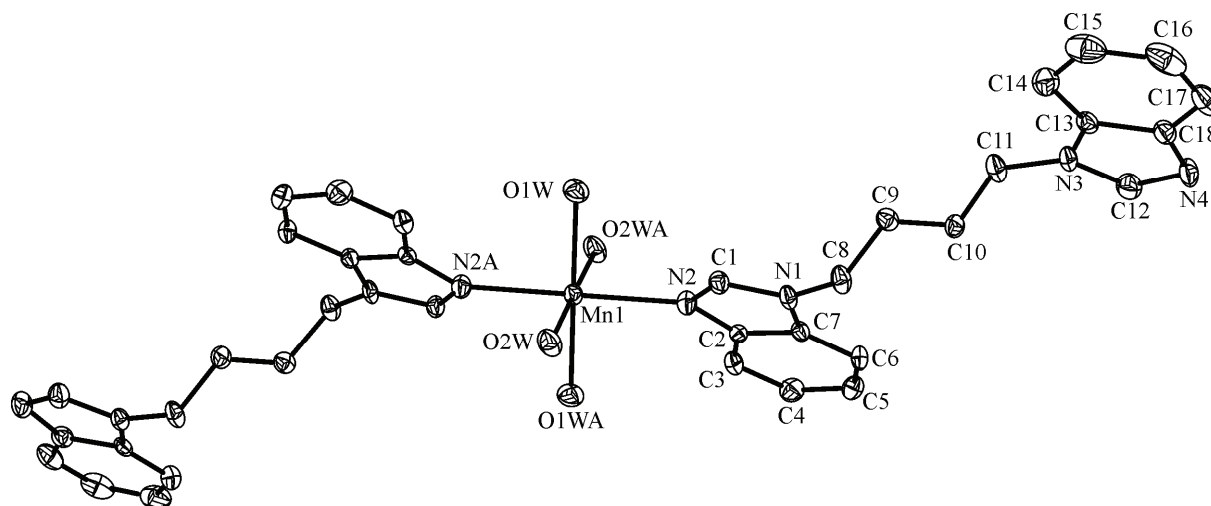


Fig. 1. Coordination mode of the $[\text{Mn}(\text{bbbi})_2(\text{H}_2\text{O})_4]^{2+}$ cation in mononuclear complex **1** (symmetry code: $A = -x+1, -y, -z$; hydrogen atoms were omitted for clarity)

ATTENTION! Although we experienced no problems with the compounds reported in this work, perchlorate salts are potentially explosive and should be handled with great caution and in small quantities.

Results and discussion. Synthesis and general methods. Reactions of $\text{Mn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with bbbi and dipicolinic acid in the 1:1:1 molar ratio at $\text{pH} = 7\text{--}8$ gave rise to a mononuclear complex $\text{Mn}(\text{bbbi})_2(\text{H}_2\text{O})_4(\text{ClO}_4)_2 \cdot (\text{bbbi})_2 \cdot (\text{H}_2\text{O})_2$ under hydrothermal condition, which is stable in air. The broad band at 3431 cm^{-1} in the spectra of complex can be attributed to stretching vibrations (νOH) of water molecules. The strong absorption bands at 1099 cm^{-1} and 623 cm^{-1} clearly indicated the presence of ionic perchlorate. The characteristic bands at 2388 cm^{-1} , 1629 cm^{-1} , 1503 cm^{-1} , 1456 cm^{-1} , 1099 cm^{-1} , 1366 cm^{-1} can be regarded as the bending vibrations of C—H or the ring stretching frequency of the bbbi molecules [10a].

Description of the crystal structure. The coordination mode of $[\text{Mn}(\text{bbbi})_2(\text{H}_2\text{O})_4]^{2+}$ ion in mononuclear complex **1** (Fig. 1) and the selected bond lengths and angles are listed in Table 2. The asymmetric unit of **1** consists of one crystallographically independent $\text{Mn}(\text{bbbi})(\text{H}_2\text{O})_2^{2+}$ cation, two uncoordinated perchlorate anions; two and a half of free bbbi and two water molecules are not ligands but are entrapped in the crystal lattice. The Mn ion, the mid-point of the $\text{C}26\text{—C}26^i$ and $\text{C}35\text{—C}35^{ii}$ ($i = -x+1, -y+1, -z+1$, $ii = -x+2, -y+1, -z+1$) bond is situated at an inversion center. Each Mn(II) ion is six-coordinated by four aqua molecules and two nitrogen atoms from two distinct bbbi to form a slightly distorted octahedron. Meanwhile, the *cis* angles around the central Mn(II) atom vary from $87.57(10)^\circ$ to $92.43(10)^\circ$, indicating a slight distortion. The average bond length of Mn—OH₂ is

Table 2

Selected bond lengths (Å) and angles (deg.) for complex **1**

Mn(1)—O(2W)	2.173(3)	O(1WA)—Mn(1)—N(2A)	87.57(10)	O(2W)—Mn(1)—N(2)	89.85(12)
Mn(1)—N(2)	2.273(3)	O(2WA)—Mn(1)—O(1WA)	90.91(11)	O(1WA)—Mn(1)—N(2)	92.43(10)
Mn(1)—O(1W)	2.221(2)	O(2W)—Mn(1)—O(1WA)	89.09(11)	O(1W)—Mn(1)—N(2)	87.57(10)
		O(2WA)—Mn(1)—N(2)	90.15(12)	O(1W)—Mn(1)—N(2A)	92.43(10)
				O(2W)—Mn(1)—N(2A)	90.15(12)

Symmetry code: $A = -x+1, -y, -z$.

Hydrogen bonding geometry (Å, deg.) of complex **1**

D—H...A	D—H	H...A	D...A	D—H...A	D—H	H...A	D...A
O(2W)—H(2A)...N(4) ⁱ	0.87	2.02	2.877(6)	O(2W)—H(2B)...O(1W)	0.86	2.28	3.132(4)
O(3W)—H(3B)...O(2W) ⁱⁱ	0.86	1.84	2.669(4)	O(1W)—H(1B)...N(8)	0.86	2.21	3.026(6)
O(3W)—H(3C)...N(4) ⁱⁱⁱ	0.83	2.11	2.894(6)	O(1W)—H(1C)...N(6)	0.83	2.86	2.762(4)
O(1W)—H(1C)...O(2W) ^{iv}	0.83	2.25	3.083(6)	C(27)—H(27A)...O(2)	0.93	2.58	3.439(10)

Symmetry codes: (i) $x, -1+y, z$; (ii) $1-x, 1-y, -z$; (iii) $-1+x, y, z$; (iv) $-x+1, -y, -z$.

2.197(2) Å and the corresponding Mn—N bond length is 2.273(3) Å. The shortest intermolecular Mn...Mn separation is 8.848 Å. Within free bbbi, the benzimidazole planes are planar as expected. The dihedral angle between two benzimidazole planes from the same free bbbi is 0° showing that the two benzimidazole rings are parallel to each other. The angle between the benzimidazole planes of coordinated bbbi is 1.9(3)°. The Cl—O distances are all between 1.264(4) Å and 1.459(6) Å, O—Cl—O bond angles vary from 101.5(4)° to 114.0(4)°, all being in the normal range of perchlorate ions reported [10].

The uncoordinated and coordinated water molecules as well as the benzimidazole groups lead to complicated 3D strong hydrogen bonding interactions in the structure of **1** (Table 3). The whole water molecule forms hydrogen bonds with the N atoms acting as H acceptors of the bbbi ligand or to one another, the O...O distances vary from 2.669(4) Å to 3.132(4) Å; the O...N distances are in the range of 2.762(4) Å to 3.026(6) Å. Meanwhile, weak C—H...O hydrogen bonds form between the aromatic C—H group of free bbbi benzimidazole rings and uncoordinated perchlorate oxygen atoms [C(27)—H(27A)...O(2)]; the related hydrogen bonding bond distance and angle are as follows: C(27)...O(2) = 3.439(10) Å and C—H...O = 154°, being in the normal range of such interactions. Furthermore, there are intermolecular $\pi\cdots\pi$ packing interactions between the imidazole rings and the adjacent benzene rings of coordinated bbbi ligands; the centroid-centroid distance is 3.754(3) Å, and the dihedral angle is 19.95°. The molecule of **1** is stabilized by those supramolecular interactions.

In summary, a new mononuclear Mn(II) complex based on the bbbi ligand has been hydrothermally prepared and structurally characterized by single crystal X-ray diffraction analysis. Each Mn(II) ion in the complex is six-coordinated in a slightly distorted octahedron geometry. The molecule of **1** is stabilized by hydrogen bonding and $\pi\cdots\pi$ interactions.

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