

Structure, Characterization and *ab Initio* Calculations of $[\text{Mn}(\text{4,4'}\text{-bipy})_2(\text{H}_2\text{O})_4][\text{HOOC}\text{C}_6\text{H}_4\text{SSC}_6\text{H}_4\text{COO}]_2$

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The title compound was obtained by reaction of $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$, $\text{NH}_3 \cdot \text{H}_2\text{O}$, 4,4'-bipyridine, and 2,2'-dithio-bis(benzoic acid) ($\text{H}_2\text{-DTBB}$) in aqueous solution. It was characterized by single crystal X-ray crystallography, elemental analysis and IR spectroscopy. The compound is composed of one $[\text{Mn}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}$ cation and two H-TDBB^{1-} anions, where Mn^{2+} adopts an octahedral geometry and is coordinated by four water oxygen atoms and two N atoms of 4,4'-bipyridine ligands. The $[\text{Mn}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}$ cations are linked into one-dimensional chains by $\text{O-H} \cdots \text{N}$ hydrogen bonds. These cationic chains are further organized into a two-dimensional network with the H-TDBB^{1-} anions through hydrogen bonds.

Key words: Crystal Structure, *ab Initio* Calculation, Hydrogen Bonds, Supramolecule

Introduction

Rational design and synthesis of metal coordination polymers have been attracting chemists' interest and constitute an important area in crystal engineering [1–3]. The structure and properties of coordination polymers can be controlled by choosing appropriate bridging ligands and metal ions with rigid 4,4'-bipyridine ligands used most frequently [2]. 4,4'-Bipyridine or a combination with other ligands can be used for the construction of intriguing supramolecular architectures by means of covalent coordination and hydrogen bonds to give one-dimensional structures [4–6] including linear, zigzag and helical chains, and higher-dimensional coordination polymers [7–16] including diverse grids and larger networks.

In the above mentioned references, 4,4'-bipyridine usually acts as a non-chelating bidentate ligand in metal coordination polymers because the two 4,4'-bipyridine nitrogen atoms have the same coordination ability. In contrast, 4,4'-bipyridine acting as monodentate ligand in metal coordination polymers has been reported in only few cases [17–21].

Herein we present a compound $[\text{Mn}(\text{bipy})_2(\text{H}_2\text{O})_4][\text{HOOC}\text{C}_6\text{H}_4\text{SSC}_6\text{H}_4\text{COO}]_2$, in which 4,4'-bipyridine is acting as a bridging bidentate ligand coordinated to Mn(II). It forms a two-dimensional array through hydrogen bonds.

Experimental Section

General

All chemicals were of reagent grade as received from commercial sources and used without further purification. C, H, N elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer. The infrared spectrum was recorded on KBr pellets with a Nicolet 170SXFT-IR spectrometer in the range of 400–4000 cm^{-1} . Because the Mn atom occupies a crystallographic centre of inversion (see below) we carried out quantum chemical calculations on half the unit of the title compound with HF methods at the Lan2dz level using the GAUSSIAN 03 program [22]. All quantum chemical calculations have been done on a Pentium IV processor which was also used for the crystal structure determination calculations.

Synthesis

2,2'-Dithio-bis(benzoic acid) (0.167 mmol, 0.051 g) was dissolved in aqueous ammonia (13 $\text{mol} \cdot \text{L}^{-1}$, 0.5 mL) and diluted with water (20 mL). $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.167 mmol, 0.033 g) was added slowly and the mixture was added to an ethanol solution (5 mL) of 4,4'-bipyridine (0.167 mmol, 0.026 g) dropwise. The resulting solution was heated for 15 min at 100 °C, filtered, and kept for crystallization. After four days, yellow-brown crystals suitable for single crystal X-ray diffraction were obtained.

Elemental analysis: calcd. C 54.90, H 4.03, N 5.34; found C 54.39, H 3.78, N 4.93. – IR: $\nu = 3395.38(\text{m})$, 1667.74(s),

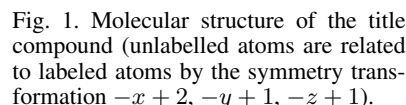


Table 2. Selected bond lengths (Å) and angles (deg) of the title compound^a.

Mn(1)–O(5)	2.152(2)	Mn(1)–O(5) ^{#1}	2.152(2)
Mn(1)–O(6) ^{#1}	2.205(2)	Mn(1)–O(6)	2.205(2)
Mn(1)–N(1)	2.252(2)	Mn(1)–N(1) ^{#1}	2.252(2)
S(1)–C(8)	1.796(2)	S(1)–S(2)	2.060(1)
S(2)–C(2)	1.789(2)	O(1)–C(13)	1.314(3)
O(2)–C(13)	1.211(3)	O(3)–C(14)	1.239(3)
O(4)–C(14)	1.266(2)	C(1)–C(6)	1.392(3)
C(1)–C(2)	1.410(3)	C(1)–C(13)	1.483(3)
C(2)–C(3)	1.391(3)	C(3)–C(4)	1.383(3)
C(4)–C(5)	1.378(3)	C(5)–C(6)	1.371(4)
C(7)–C(12)	1.391(3)	C(7)–C(8)	1.406(3)
C(7)–C(14)	1.511(3)	C(8)–C(9)	1.388(3)
C(9)–C(10)	1.377(3)	C(10)–C(11)	1.372(3)
C(11)–C(12)	1.369(3)		
O(5)–Mn(1)–O(5) ^{#1}	180.0	O(5)–Mn(1)–O(6) ^{#1}	91.9(1)
O(5) ^{#1} –Mn(1)–O(6) ^{#1}	88.1(1)	O(6) ^{#1} –Mn(1)–O(6)	180.0(1)
O(6) ^{#1} –Mn(1)–N(1)	91.5(1)	O(5)–Mn(1)–N(1)	90.0(1)
O(6)–Mn(1)–N(1)	88.5(1)	O(5) ^{#1} –Mn(1)–N(1)	89.95(6)
N(1)–Mn(1)–N(1) ^{#1}	180.0	O(6)–Mn(1)–N(1) ^{#1}	91.5(1)

CCDC (654248) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crys-

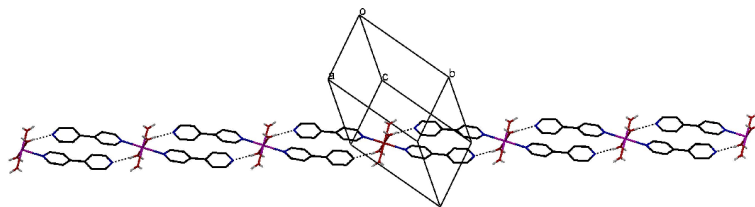


Fig. 2. Necklace structure of the one-dimensional chain of the cations $\{[\text{Mn}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}\}_n$.

tallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

Crystal and molecular structure

The title complex consists of $[\text{Mn}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}$ cations and isolated H-TDBB^{1-} anions (Fig. 1). In the $[\text{Mn}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}$ cation, Mn^{2+} lies on a crystallographic centre of inversion and is in a slightly distorted octahedral geometry coordinated by four water oxygen atoms in the equatorial plane and two nitrogen atoms of different 4,4-bipyridine ligands in the axial positions. Mn^{2+} and the four aqua oxygen atoms have Mn–O distances 2.152(1) and 2.205(1) Å. The Mn(1)–N bond length and the N(1)–Mn(1)–N(1)#1 angle are 2.252(1) Å and 180.0° , respectively, with an angle of 88.5° to the equatorial plane. These results are similar to those for $[\text{Mn}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_4](\text{Hsb})_2$ [17] and $[\text{Mn}(4,4'\text{-bipy})_2(\text{H}_2\text{O})_4](\text{sb})(4\text{H}_2\text{O})$ [17]. The two pyridyl rings of 4,4'-bipyridine are slightly staggered with a dihedral angle of 11.8° . The H-TDBB^{1-} anion acts as a counterion with a dihedral angle of 73.6° between its two phenyl rings. $[\text{Mn}(\text{bipy})_2(\text{H}_2\text{O})_4]^{2+}$ cations are linked through $\text{O}(\text{water})\cdots\text{N}$ hydrogen bonds into a necklace structure (Fig. 2). In addition, H-TDBB^{1-} anions also form an infinite one-dimensional chain by $\text{O}(\text{carboxyl})\cdots\text{H}\cdots\text{N}$ hydrogen bonds. These chains are finally organized into a two-dimensional network by $\text{O}(\text{water})\cdots\text{H}\cdots\text{N}$ hydrogen bonds.

Theoretical calculations

Stability

The total energy of the title compound (the combination of the chains of cations and anions) is -1600.99024143 a. u., while the energy of the HOMO is -0.23844 a. u. and the energy of the lowest LUMO is -0.02680 a. u. The HOMO–LUMO gap is 0.21164 a. u. The large absolute value of the energy

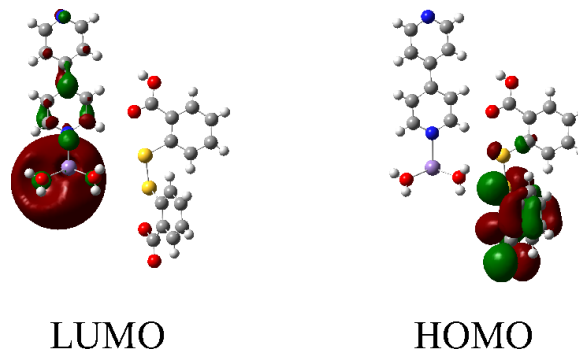


Fig. 3. Representations of the HOMO/LUMO's of the title compound.

gap indicates that the title compound has high stability.

Frontier molecular orbital composition

In order to study the structure and bonding characteristics, frontier molecular orbital populations have been analyzed. The atomic orbital composition in the frontier molecular orbitals were expressed as the atomic orbital coefficient square sum in the type of atomic orbitals and corrected by normalizing the specific molecular orbital [24]. The stereographs of selected frontier molecular orbitals of the title compound are shown in Fig. 3.

The orbital composition investigation indicates: First, the components of the HOMO come mainly from orbitals of four carboxyl oxygen atoms (61.7%), the two sulfur atoms (14.5%) and twelve carbon atoms of the H-TDBB^{1-} anion (23.3%). The results suggest that the carboxyl oxygen atoms are the active sites and can react with metal centers or hydrogen-bond donors [25]. Second, the components of the LUMO come mainly from Mn(II) (65.7%), coordinated nitrogen atoms (4.71%) and ten carbon atoms (23.8%) of the 4,4'-bipyridine ligand. These results are reflected by Fig. 3. In addition, these results show that Mn(II) has a stronger electron-accepting ability with coordi-

nated N atoms and water oxygen atoms having little contribution to the five occupied frontier molecular orbitals. The strength of the Mn–N and Mn–O bonds appears to be relative weak in agreement with their longer bond lengths (Table 2).

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