

## 2,2-联吡啶-3,3-二羧酸桥联的具有 2D 网络结构的 Mn 配位聚合物的合成、晶体结构

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## Synthesis, Crystal Structure of A Novel 2D Network Manganese(II) Polymer Bridged by 2,2-bipyridine-3,3-dicarboxylate

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**Abstract:** A Manganese(II) polymer  $\{[\text{Mn}(\text{bpdc})(\text{bipy})(\text{H}_2\text{O})] \cdot 4.5\text{H}_2\text{O}\}_n$  has been synthesized (bpdc=2,2-bipyridine-3,3-dicarboxylate, bipy=4,4-bipyridine) and characterized by IR, UV, elemental analysis and X-ray crystal structure determination. It crystallizes in Monoclinic system, space group  $P2_1/n$  with  $a=1.010\ 13(8)$  nm,  $b=1.164\ 66(9)$  nm,  $c=2.147\ 40(16)$  nm,  $\beta=98.22\ 20(10)^\circ$ ,  $V=2.500\ 4(3)$  nm<sup>3</sup>,  $Z=4$ ,  $D_c=1.467$  g·cm<sup>-3</sup>,  $F(000)=1\ 144$ ,  $R_1=0.049\ 0$ ,  $wR_2=0.141\ 2$ . The crystal structure shows that the Mn<sup>2+</sup> ions have octahedral coordination geometry with two coordination situations. The Mn<sup>2+</sup> (1) ion is coordinated with two N atoms of two bipy, and chelated by four O atoms from four carboxylate groups of two bpdc ligands. The neighbor Mn<sup>2+</sup> (2) ion is coordinated with two oxygen atoms from two water, two N atoms of two 4,4-bipy and two O atoms from two carboxylate groups of two bpdc ligands. Mn(1) and Mn(2) ions are bridged by bpdc and bipy ligands, forming a novel 2D network. CCDC: 651043.

**Key words:** Mn(II) polymer; 2,2-bipyridine-3,3-dicarboxylate; crystal structure

Considerable interest has been focused on the transition metal coordination polymers of one-, two- and three-dimensional infinite framework in recent years because of their abundant topologic structure and potential applications<sup>[1-3]</sup>. The self-assembly of suitable

ligands and metal centers have been proved to be an efficient route for the formation of such compounds<sup>[4,5]</sup>.

2,2-bipyridine-3,3-dicarboxylate is regarded as a good self-assembly block of metal ions with multi-pyridine and multi-carboxylate spacers, and has

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received increasing attention<sup>[6–10]</sup>. Owing to their strong chelating bipyridyl moiety and carboxyl groups, it often acts as bis (monodentate), tridentate or bis(bidentate) bridging spacers, and facilitates to the self-assemble of polymer<sup>[11,12]</sup>. Herein, we also report the self-assembly preparation, crystal structure of the title compound  $[\text{Mn}(\text{bpdc})(\text{bipy})(\text{H}_2\text{O})] \cdot 4.5\text{H}_2\text{O}$ , which is bridged by the 2,2-bipyridine-3,3-dicarboxylate forming a novel 2D network.

## 1 Experimental

### 1.1 Material and instruments

2,2-bipyridine-3,3-dicarboxymethoxy (bpdc) was prepared according to the literature method<sup>[13]</sup>. All other chemicals were obtained from commercial sources and used without further purification.

IR spectra were recorded on a Shimadzu FTIR-8700 spectrophotometer with pressed KBr pellets. Elemental analyses (C, H and N) were carried out on a Perkin-Elmer 240C analyzer. UV spectra were obtained on a UV-2501PC.

### 1.2 Synthesis of the title complex

An aqueous solution (5 mL) of  $\text{MnSO}_4$  (0.101 4 g, 0.6 mmol) was added dropwise to an ethanol solution (10 mL) of bpdc (0.672 0 g, 0.3 mmol). The mixture was heated in 60 °C water bath for about 5 h, and then an ethanol solution (5 mL) of 4,4-bipyridine (0.999 6 g,

0.64 mmol) was added into it. The pH of solution was set to about 6 with dilute aqueous solution of NaOH. After 24 h reflux, the mixture was filtered. The yellow block crystal suitable for X-ray single crystal structure analysis was obtained from the solution after several days. Yield: 45%. Anal. Calc. for  $\text{C}_{22}\text{H}_{25}\text{MnN}_4\text{O}_{9.5}$  (%): C 47.83; H 4.56; N 10.14. Found (%): C 47.83; H 4.58; N 10.13. IR (KBr,  $\text{cm}^{-1}$ ): 3 442.3(s), 3 261.4(m), 2 181.3(m), 1 948.0(m), 1 581.5(s), 1 529.4(s), 1 402.2(s), 1 367.4(s), 1 220.9(s), 1 066.6(m), 852.5(m), 775.3(m), 628.8(w), 499.5(w).

### 1.3 X-ray crystal structure determination

All measurements were made on a Bruker SMART APEX II CCD diffractometer with graphite-monochromatized Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\ \text{nm}$ ). The data were collected using  $\varphi$ - $\omega$  scans at 293(2) K, and corrected for Lorentz-polarization effects. A total of 14 983 reflections were collected in the range of  $2.59^\circ \leq \theta \leq 25.50^\circ$ , of which 4 613 ( $R_{\text{int}}=0.025\ 3$ ) were independent and 3 675 were observed [ $I>2\sigma(I)$ ]. The structures were solved by direct methods and refined by full-matrix least squares on  $F^2$  with SHELXTL program. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were added theoretically. Crystal data and experimental details for the title complex are contained in Table 1.

CCDC: 651043.

Table 1 Crystal data of the title complex

|                                       |   |   |  |
|---------------------------------------|---|---|--|
| Empirical formula                     | $\text{C}_{22}\text{H}_{25}\text{MnN}_4\text{O}_{9.50}$ | Absorption coefficient / $\text{mm}^{-1}$                       | 0.588  |
| Formula weight                        | 552.40  | $F(000)$  | 1 144  |
| Temperature / K                       | 291(2)  | Crystal size / mm   | 0.31×0.20×0.17   |
| Crystal system                        | Monoclinic  | $\theta / (^\circ)$   | 2.59~25.50   |
| Space group                           | $P2_1/n$  | Limiting indices  | $-12 \leq h \leq 12, -14 \leq k \leq 14, -26 \leq l \leq 25$ |
| $a / \text{nm}$                       | 1.010 13(8)   | Reflections collected / unique                                  | 14 983 / 4 613 ( $R_{\text{int}}=0.025\ 3$ )                 |
| $b / \text{nm}$                       | 1.164 66(9)   | Data / restraints / parameters                                  | 4 613 / 289 / 336  |
| $c / \text{nm}$                       | 2.147 40(16)  | Goodness-of-fit on $F^2$  | 1.060  |
| $\beta / (^\circ)$                    | 98.222 0(10)  | Final $R$ indices [ $I>2\sigma(I)$ ]                            | $R_1=0.049\ 0, wR_2=0.14\ 12$                                |
| $D_c / (\text{g}\cdot\text{cm}^{-3})$ | 1.467   | Largest diff. peak and hole / ( $\text{e}\cdot\text{nm}^{-3}$ ) | 851, -785  |
| $Z$                                   | 4   |   |  |

## 2 Result and discussion

### 2.1 Spectrum characteristic

The IR and UV spectra of the compound were

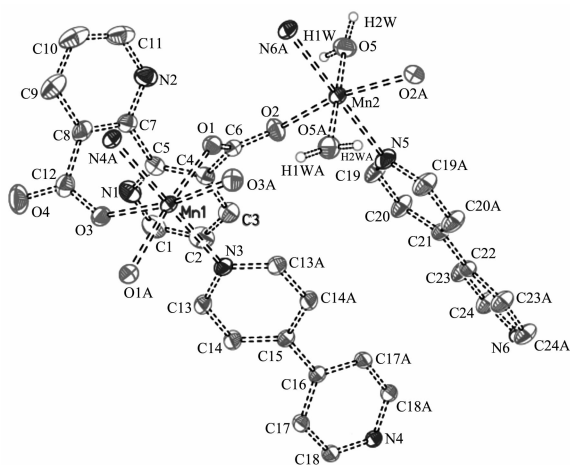
interpreted by comparison with those of free 2,2-bipyridine-3,3-dicarboxylate acid and 4,4-bipyridine. The strong and broad band at  $3\ 442.3\ \text{cm}^{-1}$  is ascribed to the stretching vibration of uncoordinated water

molecule in the compound. Compared with the carboxylic stretches ( $1\,716.5$ ,  $1\,434.9\text{ cm}^{-1}$ ) of the free 2,2-bipyridine-3,3-dicarboxylic acid, the absorption peak of its coordinated carboxyl  $\nu_{\text{as}}(\text{COO}^-)$  and  $\nu_{\text{s}}(\text{COO}^-)$  shift to  $1\,581.5$  and  $1\,367.4\text{ cm}^{-1}$ , respectively. The  $\Delta\nu$  [ $\nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$ ]= $214.1\text{ cm}^{-1}$  between the two bands of the coordinated carboxyl is bigger than  $200\text{ cm}^{-1}$ , which indicates that in the complex the coordinated carboxyl is monodentated<sup>[14]</sup>. In addition to the above, the characteristic absorption bands of 4,4-bipyridine shift from  $1\,592.0$ ,  $1\,407.0$ ,  $807.0$  and  $609.0\text{ cm}^{-1}$  to  $1\,529.4$ ,  $1\,402.2$ ,  $775.3$  and  $628.8\text{ cm}^{-1}$ , respectively. This indicates that the 4,4-bipyridine is coordinated with the central Mn(II) ion.

The strong and broad band from  $200\text{ nm}$  to  $300\text{ nm}$  of free 2,2-bipyridine-3,3-dicarboxylic acid and 4,4-bipyridine in ethanol solution shift to a narrow sharp peak at  $292.2\text{ nm}$  of the title compound in ethanol solution in the UV spectra. It also indicates that the Mn(II) ions are coordinated with ligands. These are consistent with the results of crystal structure analysis.

## 2.2 Crystal structure of the title complex

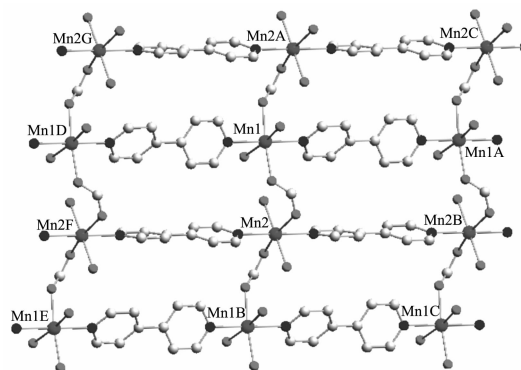
The molecular structure and coordination polyhedron are illustrated through the Fig.1, 2 and 3, respectively. The selected bond lengths and bond angles are given in Table 2, and details of hydrogen bonds are shown in Table 3. To make the describe more clearly, the free water molecules and Hydrogen atoms of



Lattice water molecules and hydrogen atoms except H1W, H2W, H1WA, H2WA are omitted for clarity, Symmetry code:  $-x+1/2, y, -z+1/2$

Fig.1 A Simplified asymmetric unit of the title compound

the title compound are omitted in figures.



Hydrogen atoms and lattice water molecules are omitted for clarity, Symmetry code: 1A:  $x, 1+y, z$ ; 1D:  $x, y-1, z$ ; 1C:  $x-1, y+1, z$ ; 1E:  $x-1, y-1, z$ ; 2C:  $x+1, y+1, z$ ; 2G:  $x+1, y-1, z$

Fig.2 Perspective view of the simplified 2D network of the title compound

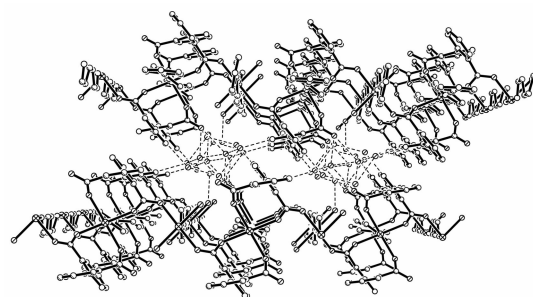


Fig.3 Packing diagram of the title compound

The crystal structure revealed that the title compound crystallizes in the monoclinic space group  $P2_1/n$  with the asymmetric unit consisting of 1  $\text{Mn}^{2+}$ , 1 bpdc, 1 bipy and  $5.5\text{H}_2\text{O}$ . As shown in Fig.1, the  $\text{Mn}^{2+}$  ions are octahedral coordination geometry with two coordination situations. Each bpdc ligand shows a chelating bridging tridentate coordination mode from two carboxylate groups with the pyridyl nitrogen atoms uncoordinated. To the best of our knowledge, the unusual coordination mode of bpdc in the title compound is few reported. The coordination atoms around  $\text{Mn}^{2+}(1)$  ion are two N atoms (N3, N4A) from two 4,4-bipy, four chelating carboxyl O atoms (O1, O3, O1A, O3A) from four carboxylate groups of two bpdc ligands. The bond angles of O(1)-Mn(1)-O(3A), O(1A)-Mn(1)-O(3A), O(1)-Mn(1)-O(3), O(1A)-Mn(1)-O(3) are  $82.30(8)^\circ$ ,  $98.24(8)^\circ$ ,  $98.24(8)^\circ$ ,  $82.30(8)^\circ$ , respectively. The total of these bond angles is  $361.08$ . The bond angle of N(3)-Mn(1)-N(4A) is  $180^\circ$ , which shows that

**Table 2** Selected bond lengths (nm) and bond angles (°)

|                  |              |                   |            |                  |            |
|------------------|--------------|-------------------|------------|------------------|------------|
| Mn(1)-O(1)       | 0.215 86(19) | Mn(1)-O(3)        | 0.224 2(2) | Mn(2)-O(2)       | 0.214 1(2) |
| Mn(2)-O(5)       | 0.218 7(2)   | Mn(1)-N(3)        | 0.229 5(3) | Mn(1)-N(4A)      | 0.225 6(3) |
| Mn(2)-N(5)       | 0.229 7(3)   | Mn(2)-N(6A)       | 0.225 5(3) |                  |            |
| O(1A)-Mn(1)-O(3) | 82.30(8)     | O(1)-Mn(1)-O(1A)  | 173.66(10) | O(1)-Mn(1)-O(3)  | 98.24(8)   |
| O(1)-Mn(1)-N(4A) | 93.17(5)     | O(3)-Mn(1)-N(4A)  | 85.18(5)   | O(3)-Mn(1)-O(3A) | 170.35(11) |
| O(1A)-Mn(1)-N(3) | 86.83(5)     | O(1)-Mn(1)-O(3A)  | 82.30(8)   | O(3)-Mn(1)-N(3)  | 94.82(5)   |
| O(3A)-Mn(1)-N(3) | 94.82(5)     | O(1A)-Mn(1)-N(4A) | 93.17(5)   | O(1)-Mn(1)-N(3)  | 86.83(5)   |
| N(4A)-Mn(1)-N(3) | 180.0        | O(2)-Mn(2)-O(2A)  | 166.30(12) | O(2)-Mn(2)-O(5)  | 83.08(9)   |
| O(2A)-Mn(2)-O(5) | 97.01(9)     | O(2)-Mn(2)-O(5A)  | 97.01(9)   | O(5)-Mn(2)-O(5A) | 179.23(12) |
| O(2)-Mn(2)-N(6A) | 96.85(6)     | O(5)-Mn(2)-N(6A)  | 89.61(6)   | O(2)-Mn(2)-N(5)  | 83.15(6)   |
| O(2A)-Mn(2)-N(5) | 83.15(6)     | O(5)-Mn(2)-N(5)   | 90.39(6)   | N(6A)-Mn(2)-N(5) | 180.0      |

Symmetry code: A:  $x+1/2$ ,  $y$ ,  $-z+1/5$ .**Table 3** Hydrogen bonds

| D-H...A             | D-H / nm | d(H-A) / nm | d(D...A) / nm | ∠DHA / (°) |
|---------------------|----------|-------------|---------------|------------|
| O(9)-H(10W)···N(1B) | 0.085    | 0.020 2     | 0.028 65(5)   | 171.5      |
| O(9)-H(9W)···O(8)   | 0.085    | 0.019 5     | 0.027 99(9)   | 179.5      |
| O(8)-H(8W)···O(6B)  | 0.085    | 0.025 1     | 0.032 62(18)  | 147.7      |
| O(8)-H(7W)···O(7B)  | 0.085    | 0.020 5     | 0.027 11(10)  | 133.6      |
| O(7)-H(5W)···N(2C)  | 0.086    | 0.021 6     | 0.029 01(6)   | 145.0      |
| O(6)-H(4W)···O(6D)  | 0.085    | 0.022 3     | 0.030 83(16)  | 179.2      |
| O(6)-H(3W)···O(7)   | 0.088    | 0.023 8     | 0.029 41(14)  | 122.1      |
| O(6)-H(3W)···O(5C)  | 0.088    | 0.021 0     | 0.026 98(8)   | 124.9      |
| O(5)-H(2W)···O(3E)  | 0.084    | 0.018 9     | 0.027 28(3)   | 176.4      |
| O(5)-H(1W)···O(6E)  | 0.082    | 0.020 6     | 0.026 98(8)   | 134.7      |

Symmetry transformation: B:  $x$ ,  $y$ ,  $z+1$ ; C:  $x+1$ ,  $y$ ,  $z$ ; D:  $-x+1$ ,  $-y+1$ ,  $-z$ ; E:  $x-1$ ,  $y$ ,  $z$ .

the atoms N(3), N(4A) are at the axial position, and the four atoms O (1), O (1A), O (3A) and O (3A) are at the quadrilateral positions. While the  $\text{Mn}^{2+}(2)$  ions are coordinated with two O atoms (O5, O5A) of two-coordinated water, two N (N5, N6A) atoms of two 4,4-bipy and two O atoms (O2, O2A) from two carboxylate groups of different bpdc ligands. The bond angles of O (2)-Mn(2)-O(5), O(2A)-Mn(2)-O(5), O(2A)-Mn(2)-O(5A), O(5A)-Mn(2)-O(2) are 83.08(9)°, 97.01(9)°, 83.08(9)°, 97.01(9)°, respectively. The total of these bond angles is 360.18. The atoms N5, N6A are also at the axial position. Therefore, the octahedral coordination geometry of central ions  $\text{Mn}^{2+}$  is slightly distorted. The mean Mn-O distance and Mn-N distance of the title compound are 0.218 21 nm, 0.227 57 nm respectively, which are slightly different from the Mn-O distance (0.218 35 nm) and Mn-N (0.224 1 nm) distance obser-

ved in  $[\text{Mn}(\text{C}_{12}\text{H}_6\text{N}_2\text{O}_4)(\text{H}_2\text{O})_2]_n$ <sup>[9]</sup>. The dihedral angle between two bpdc pyridine rings is 61.6°, indicating a severe distortion, bigger than the dihedral angle of  $[\text{Co}(\text{bpdc})(\text{H}_2\text{O})_2]$  and  $[\text{Ni}(\text{bpdc})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ <sup>[10]</sup>. Contrasting to the bpdc ligand, the dihedral angle of pyridine rings of bipy are 32.9 and 12.2, indicating a slight non-coplanarity.

As shown in Fig.2, the  $\text{Mn}^{2+}(1)$  ions and  $\text{Mn}^{2+}(2)$  ions are bridged by two Oxygen atoms (O1, O2) of a carboxylate group of bpdc ligands. Along a axes, the distance of  $\text{Mn}^{2+}(1)$  and  $\text{Mn}^{2+}(2)$  is 0.517 9 nm and the Mn2-Mn1-Mn2A angle is 154.47°. Linked through bpdc ligands, it formed an infinite zigzag chain. Along b axes, the neighbor  $\text{Mn}^{2+}$  ions are linked by 4,4-bipy with the distance of 1.1647nm, and the angle between  $\text{Mn}^{2+}$  is 180. Thus, bridged by 4,4-bipy and bpdc ligands, the title compound formed a 2D network.

It is worthy to note that there are abundant solvent water molecules absorbed in the interspaces of neighbor 2D network through the hydrogen bonds (in Fig.3). The hydrogen bond length and bond angles are from 0.189 nm to 0.251 nm and  $133.6^\circ$  to  $179.5^\circ$ , respectively. Those hydrogen bonds stabilized the crystal and formed a 3D network finally.

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