

以 2,2'-联吡啶-4,4'-二甲酸和 2-甲基吡嗪[3,2-f:2',3'-h]喹喔啉 为配体的三维锰(II)配位聚合物的合成、晶体结构和荧光性质

陈 钦¹ 胡耀元¹ 倪 良^{*1} 姚 加² 王 蕾¹ 蒋银花¹ 张文莉¹

(¹ 江苏大学化学与化工学院, 镇江 212013)

(² 浙江大学化学系, 杭州 310027)

摘要: 采用水热法合成了一个锰的配合物 $[\text{Mn}(\text{bpydc})(\text{Medpq})]_n$ (**1**) (H_2bpydc =2,2'-联吡啶-4,4'-二甲酸, Medpq =2-甲基吡嗪[3,2-f:2',3'-h]喹喔啉), 并利用元素分析、红外光谱、紫外可见光谱、热分析和 X-射线单晶衍射对其结构进行了表征。单晶结构分析表明配合物 **1** 属于单斜晶系, Cc 空间群, 晶胞参数 $a=2.031\ 6(4)\ \text{nm}$, $b=1.564\ 5(3)\ \text{nm}$, $c=0.719\ 26(14)\ \text{nm}$, $\beta=103.97(3)^\circ$, $V=2.218\ 5(8)\ \text{nm}^3$, $Z=4$ 。配合物 **1** 是一个锰(II)离子经由 bpydc^{2-} 连接形成的三维网络结构。配合物 **1** 的固体荧光光谱表明它具有很强的荧光性。应用 Gaussian 03W 程序, 在 HF/LANL2DZ 水平上对标题化合物的自然键轨道(NBO)进行了分析, 结果表明 Mn(II)与配位原子间的价键类型都属于共价键范畴。

关键词: 锰(II)配合物; 晶体结构; 2,2'-联吡啶-4,4'-二甲酸; 荧光性质; 自然键轨道

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Synthesis, Crystal Structures and Fluorescent Property of a 3D Manganese(II) Coordination Polymer with 2, 2'-Bipyridine-4, 4'-dicarboxylic Acid and 2-Methyldipyrido [3, 2-f: 2', 3'-h]quinoxaline

CHEN Qin¹ NI Liang^{*1} HU Yao-Yuan¹ YAO Jia² WANG Lei¹ JIANG Yin-Hua¹ ZHANG Wen-Li¹

(¹School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang, Jiangsu 212013, China)

(²Department of Chemistry, Zhejiang University, Hangzhou 310027, China)

Abstract: A coordination polymer $[\text{Mn}(\text{bpydc})(\text{Medpq})]_n$ (**1**) (H_2bpydc =2,2'-bipyridine-4,4'-dicarboxylic acid, Medpq =2-methyldipyrido [3,2-f:2',3'-h]quinoxaline) has been hydrothermally synthesized and structurally characterized by elemental analysis, FT-IR spectrum, UV-Vis spectrum, TG and single-crystal X-ray diffraction. Complex **1** crystallizes in monoclinic system, space group Cc with $a=2.031\ 6(4)\ \text{nm}$, $b=1.564\ 5(3)\ \text{nm}$, $c=0.719\ 26(14)\ \text{nm}$, $\beta=103.97(3)^\circ$, $V=2.218\ 5(8)\ \text{nm}^3$, $Z=4$. The crystal structure of the complex is a 3D network of hexacoordinate Mn^{2+} ions, in which Mn^{2+} ions are bridged by bpydc^{2-} ligands and decorated by Medpq ligands. Furthermore, the complex **1** indicates intense fluorescence in the solid state at room temperature. Natural bond orbital (NBO) analysis is performed by using the NBO method built in Gaussian 03 Program. The calculation results show a covalent interaction between the coordinated atoms and Mn^{2+} ions. CCDC: 875842.

Key words: manganese(II) coordination polymer; crystal structure; 2,2'-bipyridine-4,4'-dicarboxylic acid; fluorescent property; natural bond orbital

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*通讯联系人。E-mail: niliang@ujs.edu.cn

0 Introduction

Crystal engineering of supramolecular metal-organic frameworks are of great interest due to their intriguing structural motifs and potential applications in nonlinear optics, magnetism, molecular adsorption, catalysis and molecular sensing^[1-6]. As one kind of important elements of N-containing heterocyclic systems in coordination chemistry, phenanthroline (phen) and its derivatives were reported that they have been widely used in the construction of metal-organic coordination polymers^[7-12]. As a derivative of 1,10-phenanthroline, 2-methyldipyrido[3, 2-f:2', 3'-h]quinoxaline (Medpq) possessing an extended system is a planar rigid bidentate chelating reagent, which can not only act as a terminal ligand but also potentially providing supramolecular interactions^[13].

Nitrogen-containing pyridine carboxylic acids as one kind of great bridging ligands can bind transition metal ions to build coordination polymers. 2,2'-bipyridine-4,4'-dicarboxylic acid (H_2bpydc) is an excellent N-heterocyclic dicarboxylic ligand, which can provide N and O donor atoms to construct novel structures^[14]. As a flexible ligand, H_2bpydc can rotate around the C-C bond, and contains multi-pyridine and multi-carboxylate groups. It can offer a variety of coordination geometries, such as bis(monodentate), tridentate, bis(syn,syn-bridging bidentate), bis(syn,anti-bridging bidentate), and bis (chelating-bridging bidentate)^[15-17]. So it may be regarded as a good self-assembly block to facilitate the construction of coordination polymer and has received increasing attention^[18-22].

In our work, a new metal-organic coordination polymer $[Mn(bpydc)(Medpq)]_n$ has been hydrothermally synthesized and structurally characterized with 2,2'-bipyridine-4,4'-dicarboxylic acid and 2-methyldipyrido[3,2-f:2', 3'-h]quinoxaline. In addition, theoretical calculations and fluorescence have also been discussed.

1 Experimental

1.1 Materials and physical measurements

The neutral chelating ligand Medpq was

synthesized according to the literature method^[23-24]. $MnCl_2 \cdot 4H_2O$, 2,2'-bipyridine-4,4'-dicarboxylic acid and NaOH were purchased commercially and used without further purification. Elemental analysis was carried out with a Perkin-Elmer 240C analyzer. Transmission mode FT-IR spectrum was obtained between $4\ 000\ cm^{-1}$ and $400\ cm^{-1}$ using a Nicolet Nexus 470 infrared spectrometer. UV-Vis absorption spectrum was recorded on a Hitachi UV-2450 spectrophotometer at room temperature. Thermogravimetric analysis (TG) of the crystal was performed on a Germany Netzsch STA449C with heating rate of $10\ ^\circ C \cdot min^{-1}$ under flowing nitrogen. Fluorescence measurement was carried out at room temperature with a Cary Eclipse spectrometer.

1.2 Synthesis of $[Mn(bpydc)(Medpq)]_n$

$MnCl_2 \cdot 4H_2O$ (0.10 g, 0.5 mmol), H_2bpydc (0.121 g, 0.5 mmol), Medpq (0.124 g, 0.5 mmol), NaOH (0.016 g, 0.4 mmol) and H_2O (18 mL) were mixed and stirred at room temperature. Then, the mixture was sealed in a 25 mL Teflon-lined autoclave and heated to $165\ ^\circ C$ for seven days. After cooling to room temperature, brown needle crystals of complex **1** were collected by filtration and washed with distilled water. Yield: 58% based on Mn. Calcd. for $C_{27}H_{16}MnN_6O_4$ (%): C, 59.68; H, 2.97; N, 15.46. Found (%): C, 59.67; H, 2.96; N, 15.47. IR (KBr, cm^{-1}): 3 422(m), 3 069(m), 1 669(s), 1 612(s), 1 554(s), 1 389(s), 1 266(m), 1 213(w), 1 074(w), 818(w), 777(m), 740(w), 681(m), 550(m), 411(m).

1.3 Crystal Structure determination

A single crystal of complex **1** with dimensions of $0.20\ mm \times 0.20\ mm \times 0.20\ mm$ was selected and determined by a Bruker Smart Apex II CCD diffractometer equipped with a graphite monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ nm$) by using an φ - ω scan mode at $293\ (2)\ K$. For **1**, a total of 5 118 reflections were collected in range of $3.32^\circ \leq \theta \leq 25.34^\circ$, of which 2 924 were independent (unique) with $R_{int}=0.036\ 5$ and 2 461 were observed with $I>2\sigma(I)$. The structure was solved by direct methods with SHELXS-97 program^[25] and refined by SHELXL-97^[26] using full-matrix least-squares techniques on F^2 . All

non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms of the organic molecules were placed by geometrical considerations and were added to the structure factor calculation. The detailed

crystallographic data and structure refinement parameters for complex **1** are summarized in Table 1.
CCDC: 875842.

Table 1 Crystallographic data and structure refinement for complex **1**

Complex	1	Volume / nm ³	2.218 5(8)
Empirical formula	C ₂₇ H ₁₆ MnN ₆ O ₄	Z	4
Formula weight	543.4	Limiting indices	-16 ≤ h ≤ 24; -18 ≤ k ≤ 18; -8 ≤ l ≤ 8
μ(Mo Kα) / mm ⁻¹	0.647	T / K	293(2)
Crystal size / mm	0.20×0.20×0.20	F(000)	1 108
Crystal system	Monoclinic	θ range for data collection / (°)	3.32 to 25.34
Space group	Cc	D _c / (g·cm ⁻³)	1.627
a / nm	2.031 6(4)	R ₁ , wR ₂ (I > 2σ(I))	0.061 1, 0.136 2
b / nm	1.564 5(3)	R ₁ , wR ₂ (all data)	0.070 4, 0.144 9
c / nm	0.719 26(14)	Goodness-of-fit (GOF) on F ²	1.066
β / (°)	103.97(3)	Reflections collected / unique	5 118/2 924

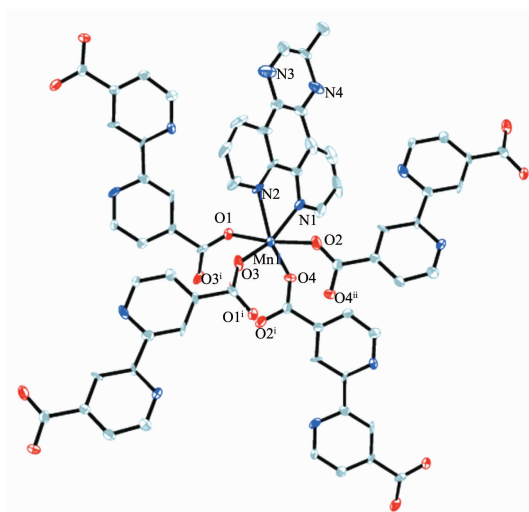
2 Results and discussion

2.1 Description of crystal Structure

Single-crystal X-ray diffraction measurement reveals that complex **1** crystallizes in the monoclinic system with Cc space group and it shows a 3D network structure. The minimum asymmetric unit contains one Mn²⁺ ion, one bpydc²⁻ anion, and one Medpq ligand. As depicted in Fig.1, the central manganese atom is hexacoordinated and displays a

distorted octahedral geometry.

For Mn (1), it is coordinated by two nitrogen atoms (N(1), N(2)) from one Medpq ligand, four oxygen atoms (O(1), O(2), O(3), O(4)) from four bpydc²⁻ ligands. The N(1), N(2), O(3) and O(4) compose the equatorial plane and the axial position is occupied by O (1), O (2). The Mn-O distances in complex **1** are in the range of 0.207 1(8) to 0.218 9(8) nm, the Mn(1)-N(1) distance is 0.230 9(7) nm and Mn(1)-N(2) distance is 0.229 9(9) nm, the N(O)-Mn-O



Hydrogen atoms were omitted for clarity; Symmetry code: ⁱ x, -y+2, z+1/2; ⁱⁱ x-1/2, -y+3/2, z+1/2

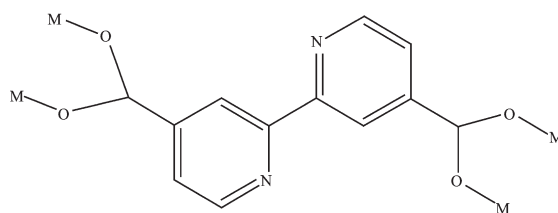
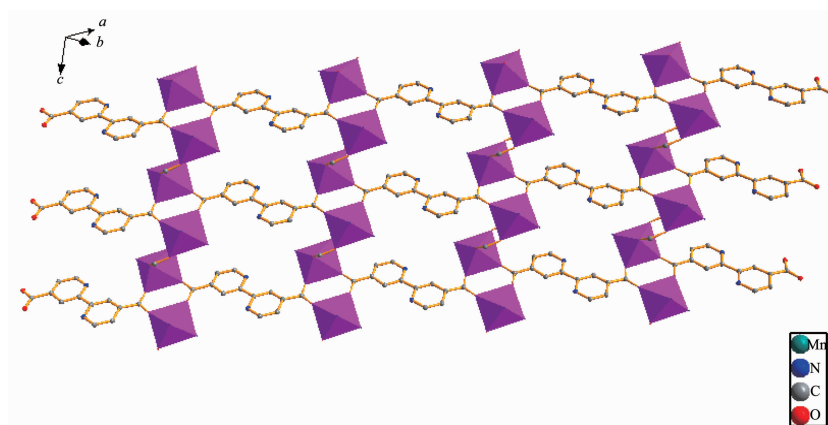
Fig.1 Coordination environment of Mn(II) ion in complex **1** with thermal ellipsoid at the 30% probability level

Table 2 Selected bond lengths (nm) and angles ($^{\circ}$) for complex **1**

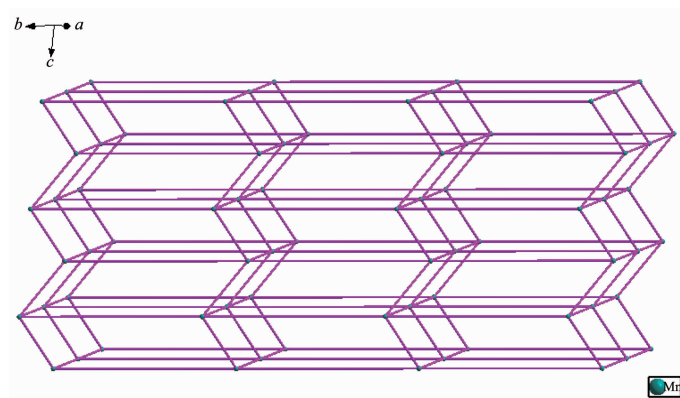
Mn(1)-N(1)	0.230 9(7)	Mn(1)-N(2)	0.229 9(9)	Mn(1)-O(1)	0.218 9(8)
Mn(1)-O(2)	0.217 9(7)	Mn(1)-O(3)	0.207 1(8)	Mn(1)-O(4)	0.210 1(7)
N(1)-Mn(1)-O(1)	91.2(3)	N(1)-Mn(1)-O(2)	82.9(3)	N(1)-Mn(1)-O(3)	158.7(3)
N(1)-Mn(1)-O(4)	90.6(3)	N(2)-Mn(1)-O(1)	83.2(3)	N(2)-Mn(1)-O(2)	90.6(3)
N(2)-Mn(1)-O(3)	87.8(3)	N(2)-Mn(1)-O(4)	161.6(3)	O(1)-Mn(1)-O(2)	172.62(14)
O(1)-Mn(1)-O(3)	89.0(3)	O(1)-Mn(1)-O(4)	95.6(3)	O(2)-Mn(1)-O(3)	94.3(4)
O(2)-Mn(1)-O(4)	89.0(3)	O(3)-Mn(1)-O(4)	110.55(17)		

(N) angles range from $82.9(3)^{\circ}$ to $161.6(3)^{\circ}$. The bond lengths and bond angles are all within the normal ranges^[27]. The selected important bond parameters are given in Table 2.

In complex **1**, Mn (II) ion is coordinated by four bpydc²⁻ ligands to form a 2D wave-like layer structure with bis-bridging bidentate coordination mode (Scheme 1), as shown in Fig.2. The adjacent layers

Scheme 1 Coordination mode of bpydc²⁻ ligand in complex **1**

Hydrogen atoms were omitted for clarity

Fig.2 View of the 2D wave-like layer structure of complex **1**

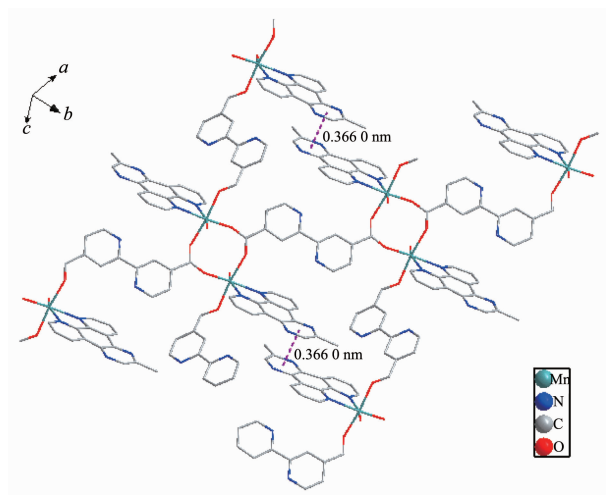
The nodes represent metal Mn(II) center, the lines represent bpydc²⁻ ligand

Fig.3 3D topological structure of complex **1**

are further interconnected via two carboxyl groups to extend into a 3D supramolecular structure. On the basis of the concept of chemical topology, the overall structure can be simplified to a (6,4)-connected 3D network if we define the Mn as a node, bpydc²⁻ligands as lines, and the structure is shown in Fig.3.

The Medpq ligands chelate to Mn(II) ions and

occupy the rhombic cavities along *c* axis direction. Additionally, it can be seen from Fig.4 that there are obvious π - π stacking interactions in complex **1**, which occur between the pyrazine rings of the Medpq ligands in a face-to-face fashion with a distance of 0.366 0 nm. The π - π stacking interactions are beneficial to the stability of the network structure.



Hydrogen atoms were omitted for clarity

Fig.4 π - π stacking interactions in complex **1**

2.2 FT-IR analysis

The FTIR spectrum of complex **1** exhibits two peaks for the carboxylate groups of bpydc²⁻ligands at 1 612 and 1 389 cm⁻¹, which are ascribed to the asymmetric stretching vibration ν_{as} (COO⁻) and the symmetric stretching vibration ν_s (COO⁻), respectively. The difference ($\Delta\nu=223$ cm⁻¹ for **1**) between ν_s (COO⁻) and ν_{as} (COO⁻) is greater than that of an ionic carboxylate unit, showing that all of the carboxylate groups are bis-bridging bidentate coordinated with metals, which is in agreement with the crystal structure^[28]. Meanwhile, the bands of ν (C-N) (1 581 cm⁻¹) and ν (C-H) (1 124, 823 cm⁻¹) of the Medpq ligands shift to lower values around at 1 554, 1 074 and 777 cm⁻¹ for the complex **1** in the spectra, indicating that the coordination of nitrogen atoms to metal ion^[29]. The signal at 550 cm⁻¹ for complex **1** also proves the coordination of metal ions and nitrogen atoms. The band at 411 cm⁻¹ for complex **1** indicates that the metal ions are coordinated with oxygen

atoms^[30]. The IR spectrum of complex **1** is in agreement with the crystal structure.

2.3 Thermal analysis

The thermal stability of complex **1** was investigated by TGA (Fig.5). The TG curve of complex **1** indicates that the first weight loss of 38.8% (Calcd. 44.53%) occurs from room temperature to 510 °C, which is ascribed to the removal of one bpydc²⁻ ligand. Upon further heating, an obvious weight loss of

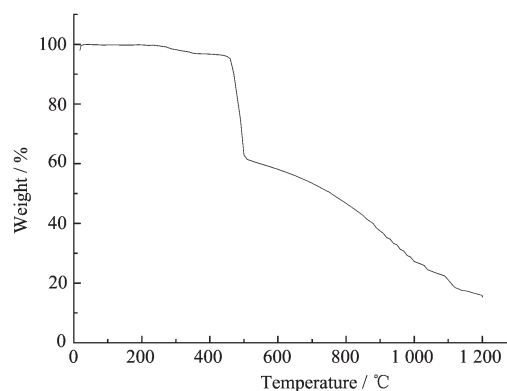


Fig.5 TG curve of complex **1**

45.61% occurs in the range of 510 to 1 200 °C, which closely matches the weight loss of 45.64% for releasing the one Medpq ligand. After the decomposition, the residual weight 15.59% (Calcd. 13.06%) is assigned to MnO.

2.4 UV-Vis spectrum analysis

The optical property of the complex **1** was characterized by UV-Vis spectrum at room temperature in solid state. The UV-Vis spectrum of complex **1** consists of absorption components in the ultraviolet and visible regions. The main experimental bands are at 257, 414 nm for **1**, which can be assigned to ligand-metal charge transfer (LMCT)^[31].

2.5 Fluorescent property

The luminescent property of the complex **1** was investigated in solid state at room temperature. It can be observed that excitation at 346 nm leads to a broad strong fluorescent emission at 468 nm for complex **1** as depicted in Fig.6. In order to understand the nature

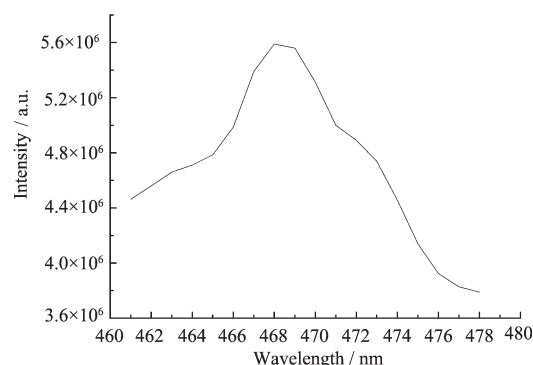


Fig.6 Luminescence spectrum of complex **1** at room temperature

of the emission band, the luminescence property of free Medpq ligand was observed at wavelength of 498 nm (λ_{ex} =420 nm), which could be attributed to the $\pi \rightarrow \pi^*$ and $\pi^* \rightarrow n$ transitions^[32]. Compared to luminescence spectrum of free Medpq ligands, complex **1** shows a small shift, which is probably due to the intraligand transition of the coordinated ligands^[33].

Table 3 Natural atomic charges (e), natural valence electron configurations, Wiberg bond indexes and NBO bond orders (a.u.) for complex **1**

Atom	Net charge	Valence electron configuration	Bond	Wiberg bond index	NBO bond order
Mn1	1.387 52	[core]4s(0.21)3d(5.36)4p(0.02)4d(0.02)5p(0.01)			
N(1)	-0.453 64	[core]2s(1.41)2p(4.03)3p(0.01)	Mn1-N(1)	0.217 9	0.174 1
N(2)	-0.437 45	[core]2s(1.28)2p(4.13)3p(0.02)3d(0.01)	Mn1-N(2)	0.193 4	0.158 0
O(1)	-0.800 92	[core]2s(1.70)2p(5.10)	Mn1-O(1)	0.245 8	0.209 6
O(2)	-0.767 69	[core]2s(1.67)2p(5.08)3d(0.01)	Mn1-O(2)	0.211 3	0.193 7
O(3)	-0.764 01	[core]2s(1.65)2p(5.09)3p(0.01)3d(0.01)	Mn1-O(3)	0.263 4	0.215 8
O(4)	-0.809 51	[core]2s(1.71)2p(5.09)3p(0.01)	Mn1-O(4)	0.315 8	0.245 2

2.6 Theoretical calculations

The Gaussian 03 program^[34] was used in the calculation. The parameters of the molecular structure for the calculation were taken directly from X-ray crystallography complete structure of the complex **1**. Natural bond orbital (NBO) analysis was performed by B3LYP method with the standard 6-31 G (d) basis set for C, H, N, O atoms and the effective core potential basis set Lanl2dz for Mn atom.

The selected natural atomic charges, natural electron configuration, Wiberg bond indexes and NBO bond order (a.u.) for complex **1** are shown in Table 3.

The net charge of Mn atom is equal to 1.387 52 deviating significantly from the formal charge +2, being a result of charge donation from the donor atoms of the ligands. The net charge of coordinated O and N atoms from -0.437 45 to -0.809 51 is resulted from the part electrons transferring from O and N atoms to Mn atom. The electronic configurations of the Mn(II) ion, O and N atoms are $4s^{0.21}3d^{5.36}4p^{0.02}4d^{0.02}5p^{0.01}$, $2s^{1.65} \sim 1.71 2p^{5.08 \sim 5.10} 3p^{0.00 \sim 0.01} 3d^{0.00 \sim 0.01}$ and $2s^{1.28 \sim 1.41} 2p^{4.03 \sim 4.13} 3p^{0.01 \sim 0.02} 3d^{0.00 \sim 0.01}$, respectively. Based on the above results, it can be concluded that the Mn(II) ion coordination with O and N atoms is mainly on 4s and 3d orbits (the

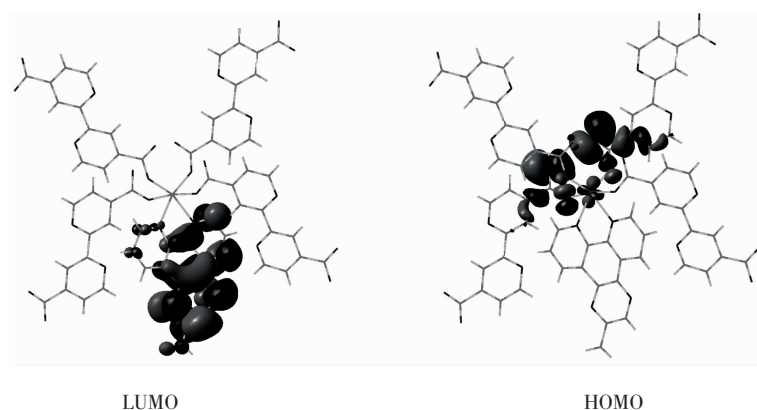


Fig.7 Molecular orbitals of complex 1

electron number of other orbits is so small that can be omitted)^[35], four O atoms and two N atoms bonding with Mn(II) atom are all on 2s and 2p orbits. Therefore, Mn(II) ion obtained some electrons from two nitrogen atoms of Medpq ligand and four oxygen atoms of 2,2'-bipyridine-4,4'-dicarboxylic acid ligand. Thus, according to valence-bond theory, the atomic net charge distribution and the NBO bond orders of complex 1 (Table 3) show the covalent interaction between the coordinated atoms and Mn(II) ion. The differences of the NBO bond orders for Mn-O and Mn-N bonds make their bond lengths be different^[36], which is in good agreement with the X-ray crystal structural data of complex 1.

As can be seen from Fig.7, lowest unoccupied molecular orbital (LUMO) was composed of π orbits of pyridine rings in Medpq, whereas highest occupied molecular orbital (HOMO) consists of d orbits of Mn(II) and π orbits of carboxyl mainly in 2,2'-bipyridine-4,4'-dicarboxylic acid.

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