

含三脚架配体及吡啶甲酸根的锰(II)配合物的合成及结构表征

聂峰梅* 李国兴 王双研 徐 宏 李 敏

(首都师范大学化学系, 北京 100048)

摘要: 本文合成了 2 种含有吡啶甲酸根和三(2-苯并咪唑亚甲基)胺合锰配合物, 并对其进行了红外, 元素分析和 X-射线单晶衍射测定。结果表明, 单核配合物 **1** 和 **2** 分别具有三角双锥和扭曲八面体的几何构型。在配合物 **1** 中, 烟酸根阴离子利用一个羧基氧原子和锰离子配位; 在配合物 **2** 中, 邻吡啶甲酸根阴离子采取 N,O 螯合的配位方式。由于烟酸根和邻吡啶甲酸根的配位方式不同, 导致配合物晶体结构中存在不同类型的氢键。配合物 **1** 形成了由氢键连接的二维网状结构, 而配合物 **2** 只能形成由氢键连接成一维链状结构。

关键词: 三(2-苯并咪唑亚甲基)胺; 锰(II)配合物; 超氧化物歧化酶

中图分类号: O614.71*1

文献标识码: A

文章编号: 1001-4861(2009)12-2113-06

Synthesis and Crystal Structures of Pyridinecarboxylate Manganese(II) Complexes in Tripodal Ligand System

NIE Feng-Mei* LI Guo-Xing WANG Shuang-Yan XU Hong LI Min

(Department of Chemistry, Capital Normal University, Beijing 100048)

Abstract: Two complexes $[\text{Mn}(\text{ntb})(\text{nic})]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**1**) and $[\text{Mn}(\text{ntb})(\text{pic})]\text{ClO}_4 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (**2**) have been prepared and structurally characterized, where ntb is tris(2-benzimidazolylmethyl)amine, nic is anion of nicotinic acid and pic is anion of picolinic acid. X-ray analysis indicates that complexes **1** and **2** are both mononuclear and the Mn(II) center adopts trigonal-bipyramidal and distorted octahedral coordination geometry, respectively. In complex **1**, the nic anion coordinates with Mn(II) ion through one of carboxylate oxygen atoms. In complex **2**, the pic anion coordinates with Mn(II) ion in bidentate N,O-chelating mode. Furthermore, complex **1** reveals 1D, 2D dimensional structures based on intermolecular hydrogen-bonding interactions. Complex **2** has 1D chain through intra-, intermolecular hydrogen-bonding interaction. Crystal data: $[\text{Mn}(\text{ntb})(\text{nic})]\text{ClO}_4 \cdot \text{H}_2\text{O}$ (**1**), $M_r=701.99 \text{ g} \cdot \text{mol}^{-1}$, Triclinic, $P\bar{1}$, $a=1.002\,47(13) \text{ nm}$, $b=1.256\,40(15) \text{ nm}$, $c=1.303\,33(13) \text{ nm}$, $\alpha=83.470(8)^\circ$, $\beta=78.701(9)^\circ$, $\gamma=76.701(10)^\circ$, $V=1.562\,5(3) \text{ nm}^3$, $Z=2$, $R_1=0.070\,5$, $wR_2=0.133\,8$ [$I>2\sigma(I)$]; $[\text{Mn}(\text{ntb})(\text{pic})]\text{ClO}_4 \cdot \text{CH}_3\text{OH} \cdot 2\text{H}_2\text{O}$ (**2**), $M_r=752.04 \text{ g} \cdot \text{mol}^{-1}$, Triclinic, $P\bar{1}$, $a=1.025\,90(13) \text{ nm}$, $b=1.296\,70(16) \text{ nm}$, $c=1.454\,82(17) \text{ nm}$, $\alpha=72.525(7)^\circ$, $\beta=72.041(6)^\circ$, $\gamma=69.880(6)^\circ$, $V=1.687\,3(4) \text{ nm}^3$, $Z=2$, $R_1=0.040\,1$, $wR_2=0.095\,2$ [$I>2\sigma(I)$]. CCDC: 725796, **1**; 725797, **2**.

Key words: tris(2-benzimidazolylmethyl)amine; manganese(II) complex; SOD

Superoxide dismutases (SODs) in microbes, plants and animals play an important role in the protection of cells against oxygen toxicity^[1-4]. These enzymes catalyze the conversion of superoxide (O_2^-) to hydrogen peroxide

and dioxygen via redox active metals. SODs can be classified into three groups (CuZn-SOD, Fe-SOD and Mn-SOD), according to the metals in the active site of enzymes. MnSOD is found in eukaryotic cell,

收稿日期: 2009-06-03。收修改稿日期: 2009-09-03。

北京自然科学基金(No.2092010), 北京市教委(No.KM200810028009)及北京市留学归国人员择优重点项目(2007)资助。

*通讯联系人。E-mail: niefm@mail.cnu.edu.cn

第一作者: 聂峰梅, 女, 45 岁, 博士, 副教授; 研究方向: 配位化学及生物无机化学。

prokaryotic cell and stroma of mitochondria. It has been proved by X-ray crystallography that the manganese in the Mn-SODs from *Bacillus stearothermophilus*^[1], *Thermus thermophilus*^[5] and humans^[6], is five-coordinated in a trigonal-bipyramidal geometry with a N_3O_2 coordination sphere and is ligated by three histidine residues, one aspartic acid residue and a water molecule^[7]. The manganese is trivalent in the enzymes and can be reduced to the divalent state without any loss of enzymatic activity^[8].

The synthesis and characterization of manganese complexes to model the structure, reactivity, and spectroscopy of Mn-SODs in its various oxidation states, with various ligand types, have contributed substantially to our understanding of the role and mechanism of manganese interaction in SODs^[9–12].

The tetradentate tripodal ligand, tris(2-benzimidazolymethyl)amine (ntb), similar to the histidine imidazole in coordination aspects, shows great potential to mimic the properties of SODs. Reports on the synthesis and spectroscopic characterization of Mn(II) complexes with ntb have appeared in the literatures^[13–17]. In this article, we have succeeded in preparing and characterizing two new pyridinecarboxylate Mn(II) complexes which bear structural similarities to the active sites of Mn-SODs.

1 Experimental

1.1 Reagents and measurements

All reagents were obtained from commercially available sources and used without further purification. The ligand ntb was prepared according to the previously reported procedure^[18]. Elemental analysis (C, H, N) was performed by Perkin-Elmer 240 elemental analyzer. The diffraction data were collected on Bruker P4 diffractometer and Saturn724+ diffractometer. IR spectrum was recorded in a Bruker TENSOR 27 model FTIR spectrophotometer with KBr pellets.

Caution: Perchlorate salts are potentially explosive

and should be handled with great care.

1.2 Synthesis of $[Mn(ntb)(nic)]ClO_4 \cdot H_2O$ (**1**)

To a stirred suspension of ntb (0.042 g, 0.1 mmol) in 20 mL of methanol was added $Mn(ClO_4)_2 \cdot 6H_2O$ (0.037 g, 0.1 mmol), followed by a mixture of nicotinic acid (0.013 g, 0.1 mmol) and triethylamine (0.011 g, 0.1 mmol) in 20 mL methanol. The resulting solution was stirred for 8 h and then allowed to evaporate under room temperature. Yield: 68%. Anal. Calcd for $C_{30}H_{27}ClMnN_8O_7$ (%): C, 51.28; H, 3.85; N, 15.95. Found(%): C, 51.22; H, 4.35; N, 15.66. IR: ν_{as} : 1557 cm^{-1} , ν_s : 1394 cm^{-1}

1.3 Synthesis of $[Mn(ntb)(pic)]ClO_4 \cdot CH_3OH \cdot 2H_2O$ (**2**)

To a stirred suspension of ntb (0.204 g, 0.5 mmol) in 40 mL of methanol was added $Mn(ClO_4)_2 \cdot 6H_2O$ (0.181 g, 0.5 mmol), followed by a mixture of picolinic acid (0.062 g, 0.5 mmol) and piperidine in 20 mL of methanol. The resulting solution was stirred for four hours and then allowed to evaporate under room temperature. Yield: 74%. Anal. Calcd for $C_{31}H_{33}ClMnN_8O_9$ (%): C, 49.47; H, 4.39; N, 14.89. Found (%): C, 48.91; H, 4.27; N, 15.22. IR: ν_{as} : 1542 cm^{-1} , ν_s : 1374 cm^{-1}

1.4 X-ray crystallography

Single-crystal X-ray experiments were performed using Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) on a Bruker P4 diffractometer and Saturn724 + diffractometer equipped with graphite monochromator for complexes **1** and **2** respectively and multi-scan technique was employed. The structure was solved primarily by direct methods and refined on F^2 by full-matrix least-square methods using SHELXL-97. All the non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms attached to carbon atoms were fixed at their ideal positions and those attached to nitrogen atoms were located in the Fourier maps. Details of crystal parameters, data collection and structure refinement are given in Table 1.

CCDC: 725796, **1**; 725797, **2**.

Table 1 Crystallographic data and structures refinements for complexes for complexes **1** and **2**

Complex	1	2
Empirical formula	$C_{30}H_{27}ClMnN_8O_7$	$C_{31}H_{33}ClMnN_8O_9$
Formula weight	701.99	752.04

Continued Table 1

Temperature / K	293(2)	93(2)
System	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a / nm	1.002 47(13)	1.025 90(13)
b / nm	1.256 40(15)	1.296 70(16)
c / nm	1.303 33(13)	1.454 82(17)
α / ($^\circ$)	83.470(8)	72.525(7)
β / ($^\circ$)	78.701(9)	72.041(6)
γ / ($^\circ$)	76.701(10)	69.880(6)
V / nm ³	1.562 5(3)	1.687 3(4)
Z	2	2
θ range for data collection / ($^\circ$)	2.12~25.11	3.02~27.50
Crystal size / mm	0.3×0.4×0.4	0.33×0.33×0.17
D_c / (g·cm ⁻³)	1.492	1.48
μ / cm ⁻¹	0.569	0.536
$F(000)$	722	778
2θ range / ($^\circ$)	4.24~50.22	6.04~55.00
Limiting indices	$-11 \leq h \leq 1, -14 \leq k \leq 14, -15 \leq l \leq 15$	$-12 \leq h \leq 13, -16 \leq k \leq 16, -18 \leq l \leq 18$
Reflec. collect / unique (R_{int})	6 536 / 5 504 (0.027 3)	13 975 / 7 432 (0.021 6)
Reflections observed [$I > 2\sigma(I)$]	3 804	6 272
GOF on F^2	1.074	0.999
Data / restraints / parameters	5 504 / 0 / 424	7 432 / 14 / 514
R_1 and wR_2 [$I > 2\sigma(I)$]	$R_1=0.070$ 5, $wR_2=0.133$ 8	$R_1=0.040$ 1, $wR_2=0.095$ 2
R indices (all data)	$R_1=0.104$ 7, $wR_2=0.148$ 0	$R_1=0.049$ 7, $wR_2=0.102$ 1
Largest diff. peak hole / (e·nm ⁻³)	986 and -766	682 and -392

2 Results and discussion

2.1 [Mn(ntb)(nic)]ClO₄·H₂O (1)

The cation structure of complex **1** is shown in Fig. 1. Selected bond lengths and angles are summarized in Table 2.

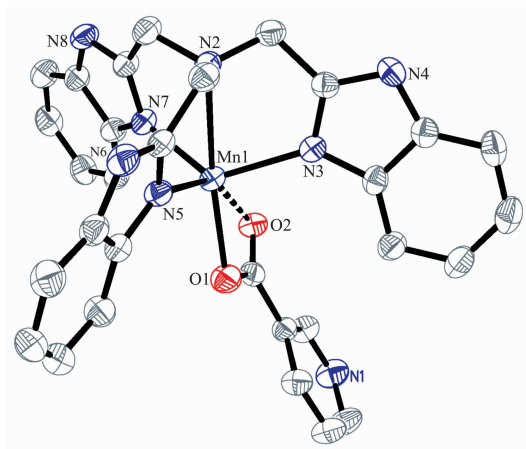


Fig.1 Cation structure of complex **1** (30% probability displacement ellipsoids)

Complex **1** consists of one [Mn(ntb)(nic)]⁺ cation, one perchlorate anion and one lattice water molecule. The Mn(II) center is five-coordinated with four nitrogen atoms from ligand ntb and one oxygen atom from the carboxylate group of nicotinate anion. The coordination geometry of Mn(II) ion can be described as distorted trigonal-bipyramidal. The trigonal plane is occupied by three ligating nitrogen atoms of the benzimidazole groups with Mn(1) being 0.065 5 nm out of the plane. The bond distances are 0.214 9(4) nm for Mn(1)-N(7), 0.215 8(4) nm for Mn(1)-N(3) and 0.216 9(4) nm for Mn(1)-N(5). The angles of the trigonal plane are 100.37(15) $^\circ$ for N(7)-Mn(1)-N(5), 106.40(15) $^\circ$ for N(3)-Mn(1)-N(5) and 125.78(15) $^\circ$ for N(7)-Mn(1)-N(3), respectively. The axial positions are occupied by one nitrogen atom N(2) from ntb and one carboxylate oxygen atom O(1) of nicotinate with bond length to be 0.252 9(4) nm for Mn(1)-N(2) and 0.212 0(4) nm for Mn(1)-O(1). The

Table 2 Bond length (nm) and bond angle ($^{\circ}$) of the complex **1** and **2**

Complex 1					
Mn(1)-O(1)	0.212 0(4)	Mn(1)-N(5)	0.216 9(4)	Mn(1)-O(2)	0.259 4(4)
Mn(1)-N(7)	0.214 9(4)	Mn(1)-N(2)	0.252 9(4)	Mn(1)-N(3)	0.215 8(4)
O(1)-Mn(1)-N(7)	122.71(16)	O(1)-Mn(1)-O(2)	54.57(13)	N(5)-Mn(1)-N(2)	71.71(14)
O(1)-Mn(1)-N(3)	100.79(15)	N(7)-Mn(1)-O(2)	91.30(13)	N(3)-Mn(1)-N(2)	71.38(14)
N(7)-Mn(1)-N(3)	125.78(15)	N(3)-Mn(1)-O(2)	89.17(14)	O(1)-Mn(1)-N(2)	161.50(15)
O(1)-Mn(1)-N(5)	95.46(15)	N(5)-Mn(1)-O(2)	148.90(13)	N(7)-Mn(1)-N(2)	73.80(14)
N(7)-Mn(1)-N(5)	100.37(15)	N(2)-Mn(1)-O(2)	139.39(13)	O(2)-C(6)-O(1)	122.9(5)
N(3)-Mn(1)-N(5)	106.40(15)				
Complex 2					
Mn(1)-O(1)	0.2144 3(13)	Mn(1)-N(2)	0.2192 7(16)	Mn(1)-N(1)	0.2540 6(16)
Mn(1)-N(4)	0.2177 5(15)	Mn(1)-N(8)	0.2286 5(16)	Mn(1)-N(6)	0.2191 8(16)
O(1)-Mn(1)-N(4)	128.18(6)	O(1)-Mn(1)-N(1)	154.03(5)	C(25)-O(1)-Mn(1)	119.77(12)
O(1)-Mn(1)-N(6)	96.55(5)	N(4)-Mn(1)-N(1)	72.25(5)	O(2)-C(25)-O(1)	124.84(17)
N(4)-Mn(1)-N(6)	132.88(6)	N(6)-Mn(1)-N(1)	70.99(5)	N(2)-Mn(1)-N(8)	155.12(6)
O(1)-Mn(1)-N(2)	89.14(5)	N(2)-Mn(1)-N(1)	73.20(5)	N(4)-Mn(1)-N(8)	86.12(6)
N(4)-Mn(1)-N(2)	90.91(6)	N(8)-Mn(1)-N(1)	128.60(5)	N(6)-Mn(1)-N(8)	94.48(6)
N(6)-Mn(1)-N(2)	105.44(6)	O(1)-Mn(1)-N(8)	73.64(5)		

bond angle of O(1)-Mn(1)-N(2) is $161.50(15)^{\circ}$. The bond length between Mn(1) and the tertiary amine N(2) atom is significantly longer (~ 0.037 nm) than Mn-N (benzimidazole) (average 0.215 9 nm). This significant elongation has also been observed in other manganese complexes of tripodal tetradentate ligands with benzimidazolymethyl group^[19,20].

Intermolecular H-bond of type N-H \cdots O [(N(4)-H(4B) \cdots O(2)=0.287 0(6) nm)] between the NH group of ntb and the uncoordinated carboxylate oxygen atom of nicotinate anion bridges the two adjacent molecules to form a double molecular unit. The double molecular units are further connected via H-bond of type N-H \cdots N [N(6)-H(6A) \cdots N(1)=0.278 4(6) nm] between the NH group of ntb and the nitrogen atom of nicotinate to form a one-dimensional chain structure as shown in Fig.2. All hydrogen bond parameters of complex **1** are listed in Table 3.

The 1D chain is further expanded to a two-dimensional (2D) structure through H-bond interactions involving the NH group of ntb, the water molecules and perchlorate anions as shown in Fig.3. The 2D structure is extended into a 3D structure through weak $\pi \cdots \pi$

stacking of the benzimidazole group of ntb ligand ($\pi \cdots \pi$ 0.373 8 nm).

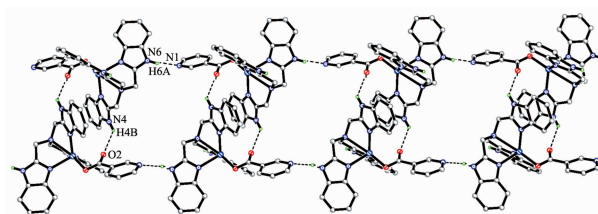


Fig.2 1D chain connected through hydrogen bonding interactions in complex **1**, type of hydrogen bond and its symmetry codes : N(6)-H(6A) \cdots N(1): $x, -1+y, z$; N(4)-H(4B) \cdots O(2): $1-x, 1-y, 1-z$

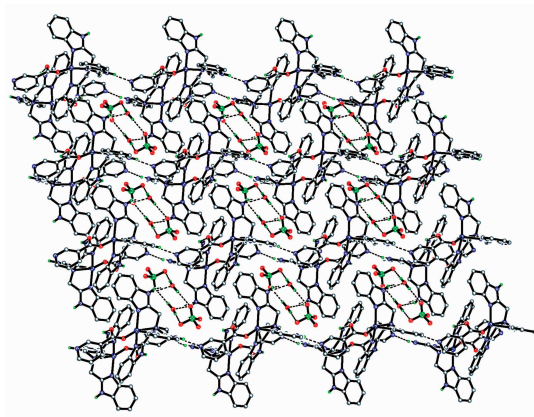


Fig.3 2D structure in complex **1** view along c -axis

Table 3 Hydrogen bond geometry for complexes 1 and 2

D-H...A	$d(\text{H}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^{\circ})$	$d(\text{D}\cdots\text{A}) / \text{nm}$	Symmetry codes
Complex 1				
N(6)-H(6A)···N(1)	0.196 0	160.2	0.278 4(6)	$x, -1+y, z$
N(4)-H(4B)···O(2)	0.223	131.0	0.287 0(6)	$1-x, 1-y, 1-z$
N(8)-H(8A)···O(1W)	0.210	153.9	0.2898(7)	$1+x, -1+y, z$
O(1W)-H(1B)···O(4)	0.215	179.6	0.300 5(10)	$-1+x, y, z$
O(1W)-H(1C)···O(6)	0.207	179.2	0.292 3(9)	$1-x, 2-y, 1-z$
Complex 2				
N(5)-H(5N)···O(2)	0.192 2	145.60	0.269 4(2)	$-1+x, y, z$
O(8)-H(8OA)···O(1)	0.197 8	169.41	0.279 1(2)	x, y, z
O(9)-H(9OB)···O(8)	0.203 2	159.58	0.280 6(2)	$1-x, 1-y, 1-z$
O(8)-H(8OB)···O(9)	0.195 3	160.99	0.274 0(3)	$1+x, -1+y, z$
N(3)-H(3N)···O(8)	0.1894	169.35	0.2764(2)	$1-x, -y, 1-z$
O(9)-H(9OA)···O(7)	0.195 2	176.03	0.278 4(3)	x, y, z

2.2 [Mn(ntb)(pic)]ClO₄·CH₃OH·2H₂O (2)

The structure of complex **2** is shown in Fig.4. Selected bond lengths and angles are summarized in Table 2. All hydrogen bond parameters of complex **2** are listed in Table 3.

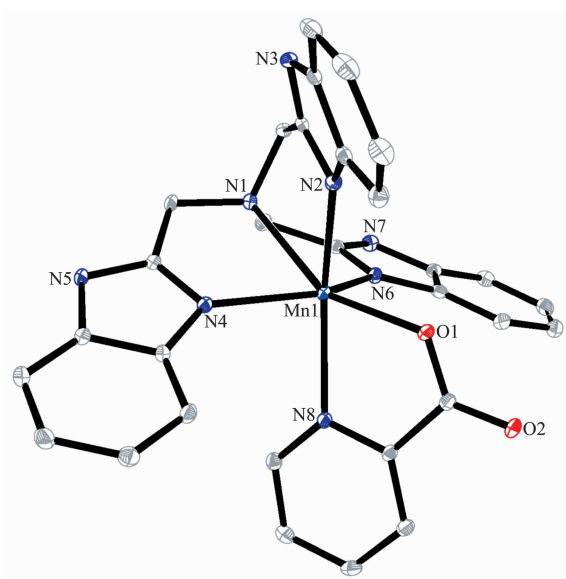


Fig.4 Cation structure of complex **2** (30% probability displacement ellipsoids)

Complex **2** consists of one [Mn(ntb)(pic)]⁺ cation, one perchlorate anion, one methanol and two water molecules. The Mn(II) ion is six-coordinated with N₅O coordination sphere and adopts distorted octahedral coordination geometry. The basal plane is defined by N(1), N(4), N(6) atoms of ntb and O(1) atom from the carboxylate group of picolinate anion, while

the apical sites are occupied by the N(2) atom of ntb and N(8) atom of picolinate anion. In the basal plane, the bond distance of Mn (1)-N (1)=0.254 06 (16) nm, lies *trans*- to O (1) atom, is significant longer than Mn (1)-N (4)=0.217 75(15) nm, Mn(1)-N (6)=0.219 18(16) nm. In the axial position, the bond distances Mn(1)-N(2)=0.219 27(16) nm, Mn(1)-N(8)=0.228 65(16) nm, the bond angle N (2)-Mn (1)-N (8)=155.12 (6)°. The bond distance Mn (1)-N (4) and the angle N (2)-Mn (1)-N(8) reflect the distortions of the coordination octahedron. Other significant distortions are observed in the angles, O(1)-Mn(1)-N(1)=154.03(5)°, N(8)-Mn(1)-N(1)=128.60 (5)°, N(4)-Mn(1)-N(6)=132.88(6)°.

A one dimensional chain structure (Fig.5) is formed through intermolecular H-bond interactions between the NH group of ntb and the uncoordinated carboxylate

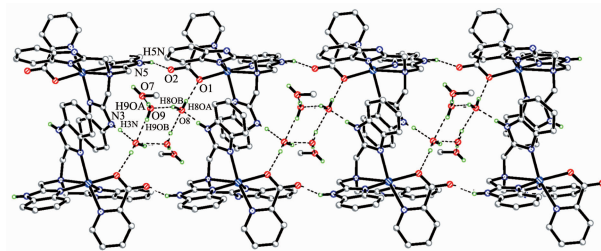


Fig.5 1D chain connected through hydrogen bonding interactions in complex **2**, type of hydrogen bond and its symmetry codes: N(5)-H(5N)···O(2): $-1+x, y, z$; O(8)-H(8OA)···O(1): x, y, z ; O(9)-H(9OB)···O(8): $1-x, 1-y, 1-z$; O(8)-H(8OB)···O(9): $1+x, -1+y, z$; N(3)-H(3N)···O(8); O(9)-H(9OA)···O(7): x, y, z

oxygen atom of picolinate with bond distance N(5)–H(5N)···O(2) to be 0.269 4 nm, and bond angle N(5)–H(5N)···O(2) to be 145.60°. Other hydrogen bonding interactions involving the NH group, the coordinated carboxylate oxygen atom of picolinate, and the water molecules generate the double-molecule one dimensional chain structure. This 1D chain is further extended into a three-dimensional structure through C–H··· π interaction and π ··· π stacking of the benzimidazole group of ligand ntb (π ··· π =0.345 2 nm).

2.3 IR spectrum

Both complexes exhibit a broad band in the 3 000~3 300 cm⁻¹ region, which may be ascribed to hydrogen-bonded ν (O–H) and ν (N–H), and may also include ν (C–H) vibrations. The $\nu_{\text{as}}(\text{COO})$ is assigned to the strong bands at 1 557 cm⁻¹ (**1**) and 1 542 cm⁻¹ (**2**) whereas the $\nu_{\text{s}}(\text{COO})$ is attributed to the 1 394 cm⁻¹ (**1**) and 1 374 cm⁻¹ (**2**) peaks, suggesting the presence of coordinated nicotinate or picolinate group. The strong, fairly broad absorptions at 1 101 cm⁻¹ (**1**) and 1 118 cm⁻¹ (**2**) indicate that ionic perchlorate groups are present. In the free ligand ntb, a strong band is found at *ca.* 1 440 cm⁻¹ along with a weak band at 1 460 cm⁻¹.

References:

- [1] Riley D P. *Chem. Rev.*, **1999**, **99**:2573~2587
- [2] McCord J M, Fridovich I. *Superoxide Dismutase in Metalloproteins*. London: Academic Press, **1977**.
- [3] Fridovich I. *Acc. Chem. Res.*, **1982**, **15**(7):200~205
- [4] FAN Zhi(樊志), WEN Xin(文欣), ZHOU Wei-Hong(周卫红), et al. *Chinese J. Inorg. Chem. (Wuji Huaxue Xuebao)*, **1999**, **15**(5):601~606
- [5] Ludwig M L, Metzger A L, Partridge K A, et al. *J. Mol. Biol.*, **1991**, **219**:335~358
- [6] Borgstahl G E, Parge H E, Hickey M J, et al. *J. Cell*, **1992**, **71**:107~118
- [7] Lah M S, Dixon M M, Partridge K A, et al. *Biochemistry*, **1995**, **34**:1646~1660
- [8] Fee J A, Shapiro E R, Moss T H. *J. Biol. Chem.*, **1976**, **251**:6157~6159
- [8] Yamaguchi K S, Spencer L, Sawyer D T. *FEES. Lett.*, **1986**, **197**:249~252
- [10] Darr D, Zarilla K A, Fridovich I. *Arch. Biochem. Biophys.*, **1987**, **258**:351~355
- [11] Rush J D, Maskos Z, Koppenol W H. *Arch. Biochem. Biophys.*, **1991**, **289**(1): 97~102
- [12] Kitajima N, Osawa M, Tamura N, et al. *Inorg. Chem.*, **1993**, **32**:1879~1880
- [13] Oki A R, Bommarreddy P R, Zhang H M, et al. *Inorg. Chim. Acta*, **1995**, **231**:109~114
- [14] Lah M S, Chun H. *Inorg. Chem.*, **1997**, **36**:1782~1785
- [15] Wu H L, Gao Y C. *J. Coord. Chem.*, **2006**, **59**:137~146
- [16] Xiang D F, Duan C Y, Tan X S, et al. *J. Chem. Soc., Dalton Trans.*, **1998**:1201~1204
- [17] Xiang D F, Tan X S, Hang Q W, et al. *Inorg. Chim. Acta*, **1998**, **277**:21~25
- [18] Cetin N, Rainer W, Johannes B, et al. *Z. Anorg. Allg. Chem.*, **1996**, **622**:329~336
- [19] Takahashi K, Nishida Y, Kida S. *Inorg. Chim. Acta*, **1983**, **77**:185~186
- [20] Takahashi K, Nishida Y, Kida S. *Bull. Chem. Soc. Jpn.*, **1984**, **57**:2628~2633