

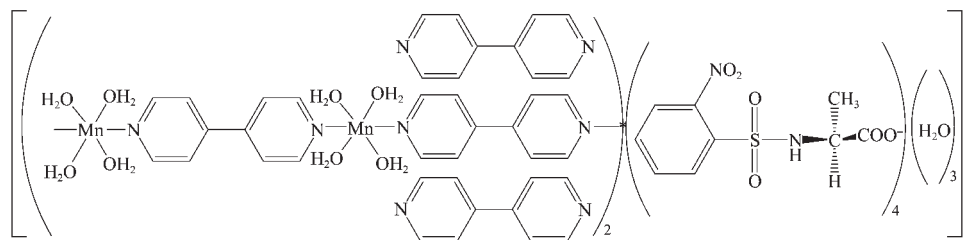
amine acids^[10,11]. 4,4'-bipy ligand is a simple but attractive building block. It can effectively form diverse architecture from 1D to 3D frameworks. One-dimensional chain compounds consisting of metal connected together by 4,4'-bipy ligands are attracting attention because of their specific structural features and their ability to show novel magnetic, unusual nonlinear optical and conductive properties^[12-16].

Taking into account the above-mentioned aspects, herein we report the preparation, crystal structures of a ligand 2-NBS-AlaH and its complex $[\text{Mn}(4,4'\text{-bipy})(\text{H}_2\text{O})_4]_2[(4,4'\text{-bipy})_2(\text{H}_2\text{O})_3(2\text{-NBS-Ala})_4]$ and the preliminary magnetic properties of the 1D complex.

1 Experimental

1.1 General

All reagents used in the syntheses were of analytical grade. C, H and N analysis were determined



Scheme 2

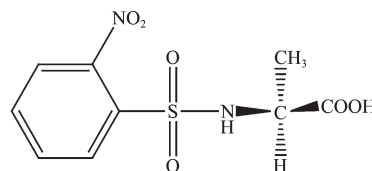
1.2 Synthesis of ligand 1

N-2-Nitrobenzenesulfonyl-*L*- α -alanine acid was prepared according to the method reported in the literature^[17]. 2-NBS-AlaH (1 mmol, 0.275 g) was stirred into 15 mL water and ethanol solution (2:1) about 10 minutes to give a clear solution at room temperature, and then filtered. The colorless crystal was separated from the mother liquor by slow evaporation at room temperature after 10 days. Anal. Calcd. (%) for $\text{C}_9\text{H}_{10}\text{N}_2\text{O}_6\text{S}$: C, 39.27; H, 4.03; N, 10.18. Found (%) C, 39.19; H, 4.10; N, 10.12. IR (KBr pellet, cm^{-1}) spectra: $\nu_{\text{as}}(\text{COO}^-)$ 1719vs, $\nu_{\text{s}}(\text{COO}^-)$ 1546s, $\nu_{\text{as}}(-\text{SO}_2^-)$ 1365m, $\nu_{\text{s}}(-\text{SO}_2^-)$ 1171vs.

1.3 Synthesis of complex 2

The mixture of $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (0.5 mmol, 0.123 g) and 2-NBS-AlaH (1 mmol, 0.275 g) was stirred into 10 mL aqueous solution about 10 minutes to give a clear solution at room temperature. Then the

on a Perkin-Elmer 240 elemental analyzer. The I.R. spectrum was recorded in KBr discs on a Shimadzu IR-408 I.R. spectrophotometer in the 4 000~600 cm^{-1} range. Variable-temperature magnetic susceptibilities were measured using a MPMS-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all constituent atoms. X-ray diffraction data were collected on a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$). The ligand and the complex are shown in the Scheme 1 and 2, respectively.



Scheme 1

pH value of the reaction mixture was adjusted to 6 or so by slow addition of 0.1 $\text{mol} \cdot \text{L}^{-1}$ NaOH solution. After 3 h of stirring at 65 $^{\circ}\text{C}$, 5 mL ethanol solution of 4,4'-bipyridine (0.5 mmol, 0.096 g) was added and the solution was stirred and heated for another 3 h at 65 $^{\circ}\text{C}$, and then filtered. The light pink crystal was separated from the mother liquor by slow evaporation at room temperature after 3 days. Anal. Calcd. (%) for $\text{C}_{76}\text{H}_{90}\text{Mn}_2\text{N}_{16}\text{O}_{35}\text{S}_4$: C, 45.06; H, 4.48; N, 11.06. Found (%) C, 45.20; H, 4.55; N, 11.19. IR (KBr, cm^{-1}) spectra: $\nu_{\text{as}}(\text{COO}^-)$ 1600vs; $\nu_{\text{s}}(\text{COO}^-)$ 1411s, $\nu_{\text{as}}(-\text{SO}_2^-)$ 1358m; $\nu_{\text{s}}(-\text{SO}_2^-)$ 1167vs.

1.4 Single crystal structure determination

X-ray single-crystal diffraction data collection for **1** and **2** was performed with a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) by using θ - ω scan technique at room temperature. The

structures were solved by direct methods with SHELXS-97. A full-matrix least-squares refinement on F^2 was carried out using SHELXL-97. The hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by use of

geometrical restraints. A summary of the crystallographic data is given in Table 1. Selected bond distances and angles are given in Table 2.

CCDC: 601686, **1**; 601455, **2**.

Table 1 A summary of the crystallographic data for complexes 1 and 2

	1	2
Empirical formula	C ₉ H ₁₀ N ₂ O ₆ S	C ₇₆ H ₉₀ Mn ₂ N ₁₆ O ₃₅ S ₄
Formula weight	274.25	2 025.76
Temperature / K	291(2)	295(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a / nm	7.099 8(10)	13.574 1(8)
b / nm	7.433 1(11)	25.666 6(2)
c / nm	11.238 8(16)	14.183 2(9)
β / (°)	103.854(2)	112.221 0(1)
Z	2	2
V / nm ³	5.758 6(1)	4.574 4(5)
D_{cal} / (g·cm ⁻³)	1.582	1.471
Absorption coefficient / mm	0.304	0.461
$F(000)$	284	2 104
θ range / (°)	2.96~27.49	2.38~27.50
Limiting indices (h, k, l)	$-7 \leq h \leq 9, -9 \leq k \leq 9, -14 \leq l \leq 12$	$-17 \leq h \leq 17, -33 \leq k \leq 33, -18 \leq l \leq 18$
Independent reflections	2 455 ($R_{\text{int}}=0.010$ 9)	20 345 ($R_{\text{int}}=0.020$ 1)
Observed reflections	3 487	41 056
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	2 455 / 1 / 161	20 345 / 10 / 1 290
Goodness-of-fit on F^2	1.049	1.021
Final R indices [$I > 2\sigma(I)$]	$R_1=0.025$ 9, $wR_2=0.062$ 6	$R_1=0.037$ 7, $wR_2=0.088$ 5
Largest diff. peak and hole / (e·nm ⁻³)	152 and -223	453 and -375

Table 2 Selected bond lengths (nm) and angles (°) for 1 and 2

1					
S(1)-O(4)	0.142 56(16)	O(1)-C(1)	0.121 7(2)	O(6)-N(2)	0.121 7(3)
S(1)-O(3)	0.142 96(13)	O(2)-C(1)	0.131 7(2)	O(6)-H(6)	0.082 00
S(1)-N(1)	0.162 13(16)	O(2)-H(2)	0.082 00	N(1)-C(2)	0.146 2(2)
S(1)-C(4)	0.179 19(18)	O(5)-N(2)	0.122 1(2)	N(1)-H(1)	0.076(2)
O(4)-S(1)-O(3)	120.10(9)	N(1)-S(1)-C(4)	108.56(8)	O(6)-N(2)-C(9)	117.74(18)
O(4)-S(1)-N(1)	107.41(9)	C(2)-N(1)-S(1)	120.79(12)	O(1)-C(1)-O(2)	123.90(16)
O(3)-S(1)-N(1)	106.70(8)	S(1)-N(1)-H(1)	113.8(16)	O(1)-C(1)-C(2)	123.74(16)
O(4)-S(1)-C(4)	108.47(9)	O(5)-N(2)-O(6)	123.90(17)	O(2)-C(1)-C(2)	112.52(15)
O(3)-S(1)-C(4)	105.18(9)	O(5)-N(2)-C(9)	118.33(16)	N(1)-C(2)-C(1)	112.52(13)
2					
Mn(1)-O(2)	0.205 00(10)	Mn(1)-N(2)	0.220 67(13)	Mn(2)-O(8)	0.208 93(11)
Mn(1)-O(4)	0.205 32(9)	Mn(1)-N(3)	0.220 87(13)	Mn(2)-O(6)	0.20975(11)

Continued Table 2

Mn(1)-O(1)	0.213 97(11)	Mn(2)-O(5)	0.207 58(9)	Mn(2)-N(4)	0.221 82(12)
Mn(1)-O(3)	0.214 47(10)	Mn(2)-O(7)	0.207 57(9)	Mn(2)-N(1) ^a	0.223 77(13)
O(2)-Mn(1)-O(4)	176.83(5)	O(1)-Mn(1)-O(3)	176.21(5)	O(2)-Mn(1)-N(3)	87.36(5)
O(2)-Mn(1)-O(1)	88.90(4)	O(2)-Mn(1)-N(2)	90.77(4)	O(4)-Mn(1)-N(3)	89.76(4)
O(4)-Mn(1)-O(1)	92.56(4)	O(4)-Mn(1)-N(2)	92.17(4)	O(1)-Mn(1)-N(3)	92.86(5)
O(2)-Mn(1)-O(3)	91.11(4)	O(1)-Mn(1)-N(2)	84.53(5)	O(3)-Mn(1)-N(3)	90.92(5)
O(4)-Mn(1)-O(3)	87.62(4)	O(3)-Mn(1)-N(2)	91.68(5)	N(2)-Mn(1)-N(3)	176.83(4)

Symmetry code: ^a $x+1, y, z-1$.

2 Results and discussion

2.1 Crystal structure of the ligand 2-NBS-AlaH

Fig.1 is the ORTEP diagram and atomic numbering scheme of compound **1**. It is noteworthy that there are significant intermolecular hydrogen bonds existing between the compounds. The intermolecular hydrogen bonds occur between two oxygen atoms from neighboring carboxyl group of the 2-NBS-AlaH

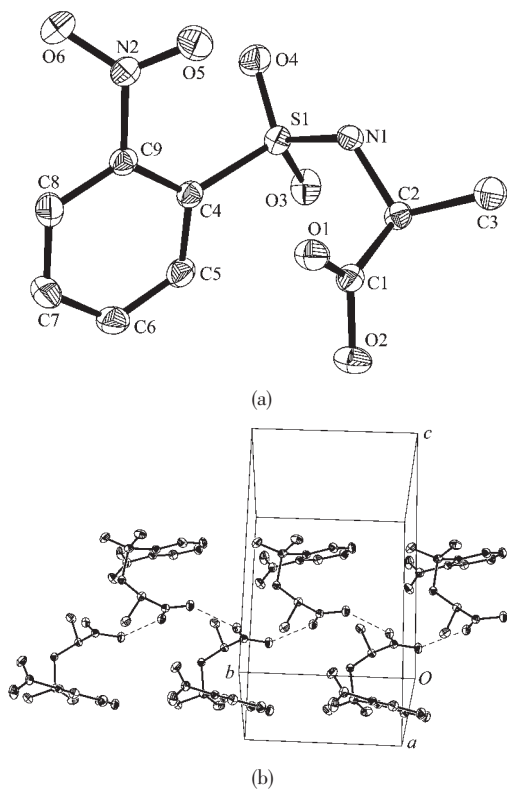
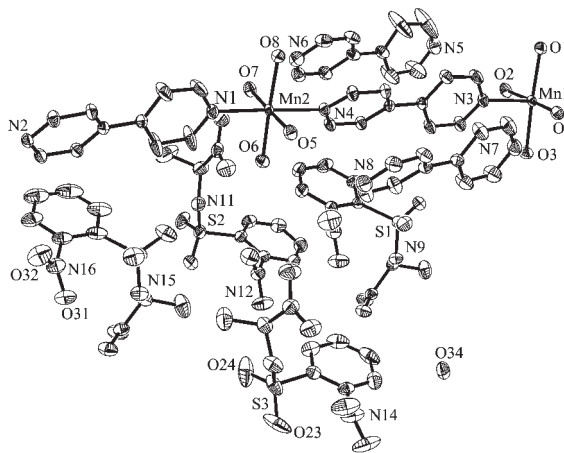
Symmetry code: ^a $-x+2, y+1/2, -z+1$; ^b $-x+2, y-1/2, -z+1$

Fig.1 An ORTEP diagram and atomic numbering scheme of compound: (a) Crystal structure of **1**; (b) Hydrogen-bonding interactions among the ligands, showing that the chain is formed along b axis

(0.273 79(18) nm for $O\cdots O$). Thus, the structure of the compound can be viewed as a 1D chain by the hydrogen bonds along the b axis (Fig.1).

2.2 Crystal structure of complex **2**

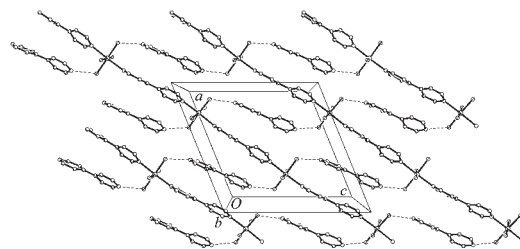
X-ray analysis reveals that the crystal structure consists of coordination cations, counteranions 2-NBS-Ala, uncoordination 4,4'-bipy ligands and lattice water molecules. As shown in Fig.2, 4,4'-bipy ligands act as a μ -bridge and join the Mn atoms into an infinite 1D chain structure. The two pyridyl rings in a 4,4'-bipy ligand are not coplanar (the dihedral angle is 22.3°).



coordination sphere of the complex **2**, there are four counteranions 2-NBS-Ala, two uncoordination 4, 4'-bipy molecules, and three lattice water molecules.

A remarkable feature of complex **2** is that there exist extensive hydrogen bonding interactions involving the 2-NBS-Ala as well as coordinated and free water molecules and 4,4'-bipy molecules (Table 3). Coordination water molecules are hydrogen bonded to the free 4,4'-bipy, lattice water and 2-NBS-Ala. There are two uncoordinating 4,4'-bipy molecules around each coordinating 4,4'-bipy molecules. However, the three 4,4'-bipy molecules are not parallel to each other. The dihedral angles between pyridyl rings (N3, C11 to C15), (N4, C16 to C20) of the coordinating 4,4'-bipy molecules and pyridyl rings (N7, C31 to C35), (N6 C26 to C30) of the uncoordinating 4, 4'-bipy molecules are 9.1° , 7.1° respectively, and their average interplane distance is 0.359 1, 0.369 8 nm respectively (Fig.1 and Fig.3). The distance is subject to π - π stacking interactions.

As shown in Fig.4, the adjacent 1D chains form a 2D framework by uncoordinating 4,4'-bipy molecules via π - π stacking interactions and $O_w-H\cdots N_{4,4'-bipy}$ hydr-



Symmetry code: ^a $x, y, z-1$; ^b $-x+1, y+1/2, -z+1$; ^c $x-1, y, z$; ^d $x, y, z+1$; ^e $-x+1, y+1/2, -z+1$; ^f $x, y+1, z+1$

Fig.3 2D supramolecular lamellar structure of **2** along the ac plane

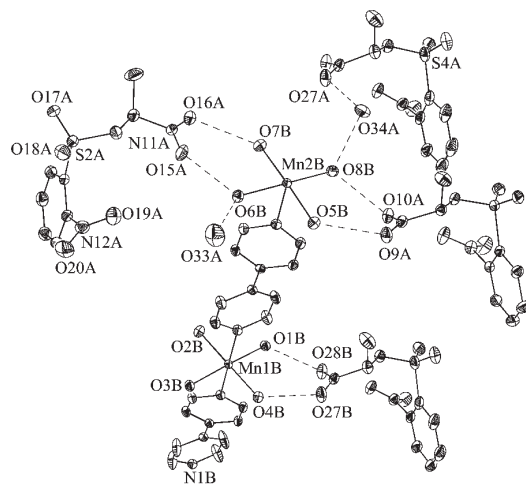


Fig.4 2-NBS-Ala linked to the chain via hydrogen-bonding into supramolecular structure

Table 3 Hydrogen bond lengths (nm) and bond angles ($^\circ$) for **1** and **2**

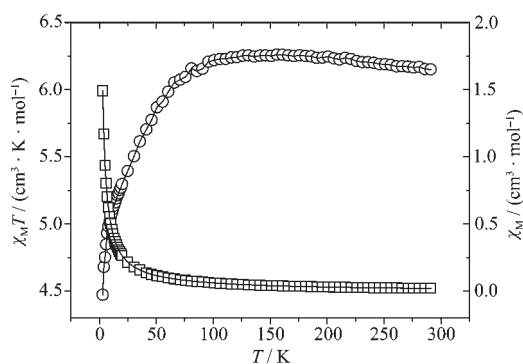
	Donor-H \cdots Acceptor	H \cdots A	D \cdots A	D-H \cdots A
1	O(2)-H(2) \cdots O(1) ^a	0.195	0.273 79(18)	159.7
2	O(8)-H(16W) \cdots O(10) ^b	0.192	0.273 33(15)	169.3
	O(8)-H(15W) \cdots O(34) ^b	0.187	0.269 06(17)	163.3
	O(7)-H(14W) \cdots N(6) ^c	0.190 7(9)	0.274 52(19)	170.2(14)
	O(7)-H(13W) \cdots O(15)	0.272	0.341 36(19)	140.0
	O(7)-H(13W) \cdots O(16)	0.207	0.286 22(16)	154.6
	O(6)-H(12W) \cdots O(15)	0.179	0.263 73(17)	164.6
	O(6)-H(11W) \cdots O(33)	0.190 5(9)	0.272 1(2)	166.7(13)
	O(5)-H(10W) \cdots O(9) ^b	0.192 3(8)	0.273 51(16)	163.0(15)
	O(5)-H(9W) \cdots N(5)	0.198 8(9)	0.279 1(3)	159.8(11)
	O(4)-H(8W) \cdots O(27) ^b	0.190	0.268 29(17)	160.4
	O(4)-H(7W) \cdots N(7)	0.200 1(9)	0.281 0(2)	161.8(12)
	O(3)-H(6W) \cdots O(16) ^d	0.219 4(9)	0.301 95(16)	174.2(17)
	O(3)-H(5W) \cdots O(21) ^e	0.184	0.272 40(17)	171.3
	O(2)-H(4W) \cdots O(22) ^e	0.184 9(9)	0.266 21(18)	164.5(14)
	O(2)-H(3W) \cdots N(8) ^e	0.192 2(8)	0.274 80(18)	169.1(13)
	O(1)-H(2W) \cdots O(28) ^b	0.186 7(8)	0.270 31(16)	169.9(15)
	O(1)-H(1W) \cdots O(35) ^e	0.188	0.270 12(19)	154.0

Symmetry code: ^a $-x+2, y-1/2, -z+1$; ^b $-x+1, y+1/2$; ^c $x, y, z+1$; ^d $x-1, y, z$; ^e $x, y+1, z+1$.

ogen bonds. In addition, a 3D supramolecular framework is formed through hydrogen bonds between 2D lamellar structure and free 2-NBS-Ala.

2.3 Magnetic properties

Variable temperature magnetic susceptibility χ_M measurements (in the range of 2 ~300 K) for **2** were carried out at a magnetic field of 10 000 G on a powdered fresh sample taken from the same uniform batch used for the structural determination, and shown as $\chi_M T$ and χ_M versus T plots in Fig.5. As can be seen from the plots of experimental data, the experimental $\chi_M T$ value at 300 K is $6.15 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, somewhat larger than the spin-only value ($4.38 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, $S = 5/2$) expected for uncouple high-spin Mn(II) ions. Upon cooling down, the $\chi_M T$ value continuously increases, reaching a maximum value of $6.26 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 126 K. This behavior of the $\chi_M T$ curve shows that there exist ferromagnetic interactions in complex **2** (Fig.5). In fact, in order to quantitatively evaluate magnetic interaction on the system, all of our attempts to reproduce the susceptibility data through an isotropic Heisenberg form of interaction were not successful.



Solid line is convenient for observation

Fig.5 Temperature dependence of $\chi_M T$ and χ_M for **2**

References:

- [1] Liu J H, Peng J, Wang E B, et al. *J. Mol. Struct.*, **2000**,**525**: 71~77
- [2] Sigel H, Martin R B. *Chem. Rev.*, **1982**,**82**:385~426
- [3] Appleton T G, Hall J R, Prenzler P D. *Inorg. Chem.*, **1989**, **28**:815~819
- [4] Corradi A B, Lusvardi G, Menabue. *Polyhedron*, **1999**,**18**:1975 ~1982
- [5] Saladini M, Menabue L, Ferrari E, et al. *J. Chem. Soc., Dalton. Trans.*, **2001**:1513~1519
- [6] Liang F P, Cheng M S, Hu R X, et al. *Acta Cryst.*, **2004**,**C60**: m269~m271
- [7] Menabue L, Saladini M. *Inorg. Chem.*, **1991**,**30**:1651~1655
- [8] Iacopino D, Menabue L, Saladini M. *Aust. J. Chem.*, **1999**,**52**: 741~748
- [9] Battistuzzi G, Borsari M, Menabue L, et al. *Inorg. Chem.*, **1996**,**35**:4239~4247
- [10] Corradi A B, Gozzoli E, Menabue L, et al. *J. Chem. Soc., Dalton Trans.*, **1994**:273~278
- [11] Gavioli G B, Borsari M, Pellacani G C, et al. *Inorg. Chem.*, **1988**,**27**:1587~1592
- [12] Plater M J, Foreman M R St J, Slawin A M Z. *Inorg. Chim. Acta*, **2000**,**303**:132~136
- [13] Kitagawa S, Kitaura R, Noro S. *Angew. Chem., Int. Ed.*, **2004**, **43**:2334~2375
- [14] Hagrman P J, Hagrman D, Zubieta J. *Angew. Chem., Int. Ed.*, **1999**,**38**:2638~2684
- [15] Rueff J M, Pillet S, Clauser N, et al. *Eur. J. Inorg. Chem.*, **2002**:895~900
- [16] Hou H W, Wei Y L, Fan Y T, et al. *Inorg. Chim. Acta*, **2001**, **319**:212~218
- [17] McChesney E W, Swann W K. *J. Am. Chem. Soc.*, **1937**,**59**: 1116~1118
- [18] Wang Y H, Feng L Y, Li Y G, et al. *Inorg. Chem.*, **2002**,**41**: 6351~6357
- [19] Li M X, Xie G Y, Gu Y D. *Polyhedron*, **1995**,**14**:1235 ~ 1239
- [20] Nather C, Greve J, Jeß I. *Chem. Mater.*, **2002**,**14**:4536 ~ 4542