

配合物 [1-(4'-bromo-2'-fluorobenzyl)pyridinium]₂[Ni(mnt)₂] 和 [1-(4'-bromo-2'-fluorobenzyl)pyrazinium]₂[Ni(mnt)₂] (mnt²⁻ = maleonitriledithiolate dianion) 的合成及晶体结构

刘玲^{1,2} 谢景力^{*1} 储玉平¹ 田正芳¹ 李一志¹ 任小明¹ 孟庆金¹

(¹ 南京大学配位化学研究所, 配位化学国家重点实验室, 南京 210093)

(² 云南师范大学化学化工学院, 昆明 650092)

本文报道两个含双(马来二氰基二硫烯)镍(II)配合物阴离子的离子对化合物。对阳离子为 1-(4'-溴-2'-氟苄基)吡啶鎓盐时, 生成配合物 1。晶体数据: 三斜晶系, 空间群 $P\bar{1}$, $a = 0.7086(2)$ nm, $b = 1.0968(3)$ nm, $c = 1.1775(3)$ nm, $\alpha = 69.914(5)^\circ$, $\beta = 89.495(5)^\circ$, $\gamma = 74.765(5)^\circ$, $V = 0.8259(4)$ nm³, $Z = 1$ 。对阳离子为 1-(4'-溴-2'-氟苄基)吡嗪鎓盐时, 生成配合物 2。晶体数据: 单斜晶系, 空间群 $P2_1/n$, $a = 0.71554(17)$ nm, $b = 1.4262(3)$ nm, $c = 1.6725(4)$ nm, $\beta = 100.396(4)^\circ$, $V = 1.6788(7)$ nm³, $Z = 4$ 。两个配合物中, 阴离子为拟平面结构, 镍原子均位于对称中心。变换对阳离子上的芳环种类对晶体的堆积结构产生影响。

关键词: 双(马来二氰基二硫烯)配体 镍(II)配合物 鎓盐阳离子 晶体结构

分类号: O614.81*3

Synthesis and Crystal Structure of [1-(4'-bromo-2'-fluorobenzyl)pyridinium]₂[Ni(mnt)₂] and [1-(4'-bromo-2'-fluorobenzyl)pyrazinium]₂[Ni(mnt)₂] Complex (mnt²⁻ = maleonitriledithiolate dianion)

LIU Ling^{1,2} XIE Jing-Li^{*1} CHU Yu-Ping¹ TIAN Zheng-Fang¹

LI Yi-Zhi¹ REN Xiao-Ming¹ MENG Qing-Jin¹

(¹ State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing 210093)

(² College of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650092)

Two complexes [1-(4'-bromo-2'-fluorobenzyl)pyridinium]₂[Ni(mnt)₂] (1) and [1-(4'-bromo-2'-fluorobenzyl)pyrazinium]₂[Ni(mnt)₂] (2) (mnt²⁻ denotes maleonitriledithiolate dianion) have been prepared by reactions of Na₂[Ni(mnt)₂] with the corresponding 1-(4'-bromo-2'-fluorobenzyl)pyridinium bromide and 1-(4'-bromo-2'-fluorobenzyl)pyrazinium bromide salt. The crystallographic data for the complex 1: Triclinic $P\bar{1}$, $a = 0.7086(2)$ nm, $b = 1.0968(3)$ nm, $c = 1.1775(3)$ nm, $\alpha = 69.914(5)^\circ$, $\beta = 89.495(5)^\circ$, $\gamma = 74.765(5)^\circ$, $V = 0.8259(4)$ nm³, $Z = 1$. Complex 2: Monoclinic $P2_1/n$, $a = 0.71554(17)$ nm, $b = 1.4262(3)$ nm, $c = 1.6725(4)$ nm, $\beta = 100.396(4)^\circ$, $V = 1.6788(7)$ nm³, $Z = 4$. In these two complexes, the Ni atom of [Ni(mnt)₂]²⁻ anion lies on an inversion center and complex anion exhibit a quasi-planar structure. The nature and size of cation seems to play an important role in the type of intermolecular interactions as well as the crystal packing in this series of complexes. CCDC: 1, 210340; 2, 210339.

Keywords: bis(maleonitriledithiolate) ligand nickelate (II) complex onium salt cation
crystal structure

收稿日期: 2003-05-03。收修改稿日期: 2003-07-08。

国家自然科学基金资助项目(No. 29771017, 29831010)。

* 通讯联系人。

第一作者: 刘玲, 女, 45 岁, 副教授; 研究方向: 功能配合物及无机化合物合成。

0 Introduction

In the past years, considerable interests have been focused on the study of square-planar $M(\text{dithiolene})_2$ complexes in the areas of conducting and magnetic materials, dyes, non-linear optics, catalysis^[1]. Complexes containing maleonitriledithiolate (*abbr.* mnt) ligand have been studied extensively for its high charge density associated with the delocalised planar π -system enables this series of complexes to have a large body of stacking modes and, consequently, led to different resultant physical properties^[2]. Recently, we have employed a strategy of constructing one-dimensional molecule-based magnets based on ion-pair complex containing $[M(\text{mnt})]^-$ ($M = \text{Ni (III)}, \text{Pt (III)}$; $\text{mnt}^{2-} = \text{maleonitriledithiolate}$) and benzylpyridinium derivative as counterions. Excitedly, varying counterions led to kaleidoscopic magnetic exchange properties although those complexes have extremely similar molecular and stack structures. Versatile magnetic property such as ferromagnetic ordering at 2K, peculiar magnetic transition from ferromagnetic coupling to diamagnetism or from paramagnetic to diamagnetism, spin-Peierls-like transition have been witnessed^[3]. Primary results shown that these great variable magnetic properties may be associated with the different cooperativity. Herein, we report two complexes with the aim to see the affection of substituting the paramagnetic d^7 central metal by diamagnetic d^8 metal on the crystal structure. In addition, we replace the pyridine molecule of benzylpyridinium counterion by pyrazine molecule for a new type of stacking structure should be anticipated because the electronic property of pyrazine is different from that of pyridine.

1 Experimental

1.1 Materials and Methods

Starting materials were purchased from Aldrich Chemical Co. (4-bromo-2-fluorobenzyl bromide and pyrazine), and were used without further purification. 1-(4'-bromo-2'-fluorobenzyl) pyridinium bromide ($[\text{BrFPy}]\text{Br}$) and 1-(4'-bromo-2'-fluorobenzyl) pyrazinium bromide ($[\text{BrFPz}]\text{Br}$), and disodium maleoni-

triledithiolate (Na_2mnt) were synthesized following the published procedures^[4,5].

Elemental analyses were performed with a Perkin-Elmer 240 analytical instrument. IR spectrum was recorded on a 170SX Fourier Transform Infrared Spectrometer (KBr pellet).

1.2 Synthesis of $[1-(4'-\text{bromo-2'-fluorobenzyl})\text{pyridinium}]_2[\text{Ni}(\text{mnt})_2]$ (1)

Complex **1** was prepared by the direct combination of 1 : 2 : 2 mol equiv of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, Na_2mnt and $[\text{BrFPy}]\text{Br}$ in H_2O . A red precipitate given was filtered off, washed by water and dried under vacuum. After dissolved by acetonitrile and the solution stood for about a week, good shaped single crystals suitable for X-ray analysis were obtained. Yield: 87% (Found(%): C, 43.88; H, 2.23; N, 9.69. Calc. for $\text{C}_{32}\text{H}_{20}\text{Br}_2\text{F}_2\text{N}_6\text{NiS}_4$ (%): C, 44.01; H, 2.31; N, 9.62). IR spectra data (cm^{-1}): $\nu(\text{CN})$ 2192.9 vs, $\nu(\text{C}=\text{C})$ of mnt^{2-} 1482.1s.

1.3 Synthesis of $[1-(4'-\text{bromo-2'-fluorobenzyl})\text{pyrazinium}]_2[\text{Ni}(\text{mnt})_2]$ (2)

This complex was synthesized by a stoichiometric mixing of NiCl_2 , Na_2mnt and $[\text{BrFPz}]\text{Br}$ following the above procedure. Yield: 89%. (Found(%): C, 41.35; H, 2.08; N, 12.76. Calc. for $\text{C}_{15}\text{H}_9\text{BrFN}_4\text{Ni}_{0.5}\text{S}_2$ (%): C, 41.17; H, 2.07; N, 12.80). IR (cm^{-1}): $\nu(\text{CN})$ 2206.7 vs, $\nu(\text{C}=\text{C})$ of mnt^{2-} 1485.3m.

1.4 Data Collection, Structure Solution, and Refinement

The red single crystals of the two complexes, have approximate dimensions 0.25 × 0.20 × 0.15mm for **1**, 0.25 × 0.20 × 0.10mm for **2** were selected for X-ray structure measurement. Data were collected on a Siemens Smart CCD area diffractometer using graphite-monochromated $\text{Mo K}\alpha$ radiation ($\lambda = 0.071073\text{nm}$) by ω scans mode within the angular range $2.06^\circ < \theta < 25.00^\circ$ for **1** and $1.89^\circ < \theta < 25.04^\circ$ for **2**. Space group, lattice parameters, and other relevant information are listed in Table 1. The structures were solved by direct methods and refined on F^2 by full-matrix least-square using the SHELXL-97^[6]. All nonhydrogen atoms were refined with anisotropic thermal parame-

Table 1 Crystal Data and Structure Refinement

compound	1	2
color/shape	red/block	red/block
chemical formula	C ₃₂ H ₂₀ Br ₂ F ₂ N ₆ NiS ₄	C ₁₅ H ₉ BrFN ₄ NiO ₅ S ₂
formula weight	873.31	437.65
temperature/K	293(2)	293(2)
wavelength	0.071073	0.071073
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a/nm	0.7086(2)	0.71554(17)
b/nm	1.0968(3)	1.4262(3)
c/nm	1.1775(3)	1.6725(4)
$\alpha/^\circ$	69.914(5)	
$\beta/^\circ$	89.495(5)	100.396(4)
$\gamma/^\circ$	74.765(5)	
volume/nm ³	0.8259(4)	1.6788(7)
Z	1	4
density (calculated)/(g · cm ⁻³)	1.756	1.732
absorption coefficient/mm ⁻¹	3.305	3.254
diffractometer/scan	simens SMART/CCD area detector	
F(000)	434	868
θ range for data collection/°	2.06 to 25.00	1.89 to 25.04
index ranges	-7 ≤ h ≤ 8 -11 ≤ k ≤ 13 -12 ≤ l ≤ 13	-8 ≤ h ≤ 8 -11 ≤ k ≤ 16 -18 ≤ l ≤ 19
reflections collected	4090	8151
observed reflections (I > 2σ)	2353	2133
independent reflections	2849 (R _{int} = 0.0312)	2959 (R _{int} = 0.1127)
refinement method	full-matrix least-squares on F ²	
data/restraints/parameters	2849/0/215	2959/0/215
goodness of fit on F ²	1.033	1.026
final R indices [I > 2σ(I)]	R ₁ = 0.0523, wR ₂ = 0.1336	R ₁ = 0.0467, wR ₂ = 0.1106
R indices (all data)	R ₁ = 0.0585, wR ₂ = 0.1365	R ₁ = 0.0627, wR ₂ = 0.1153
largest diff. peak and hole/(e · nm ⁻³)	1060 and -769	786 and 665

ters. All H atoms were placed in calculated positions, assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic U value of the attached atom, and allowed to ride on their respective parent atoms.

2 Results and Discussion

As for complex 1, it crystallizes in the triclinic space group $P\bar{1}$. The atom arrangements and the numbering system for it are shown in Fig. 1. Selected bond lengths, angles and the hydrogen contacts are listed in Table 2.

The [Ni(mnt)₂]²⁻ anion has a center of symmetry at the nickel atom and two [BrFPy]⁺ ions are related to each other by the symmetry center. Four sulfur atoms

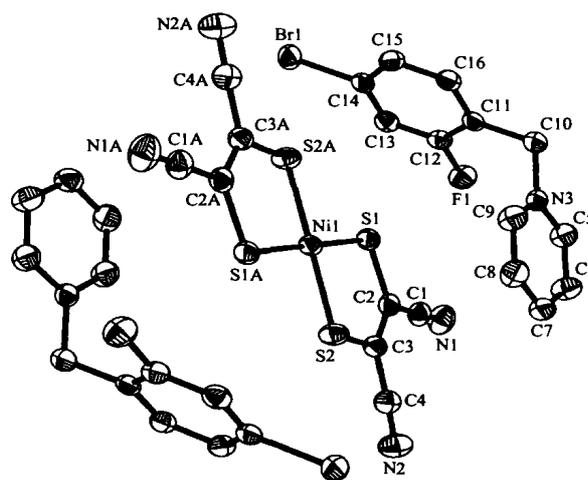


Fig. 1 ORTEP plot (30% probability ellipsoids) showing the molecular structure of [1-(4'-bromo-2'-fluorobenzyl)pyridinium]₂[Ni(mnt)₂] (1)

Table 2 Selected Bond Lengths (nm), Bond Angles (°) of Complex 1

Ni(1)-S(1)	0.21678(12)	Ni(1)-S(2)	0.21625(12)	S(1)-C(2)	0.1731(4)
S(2)-C(3)	0.1723(4)	N(1)-C(1)	0.1140(6)	N(2)-C(4)	0.1139(6)
N(3)-C(9)	0.1317(5)	N(3)-C(5)	0.1341(6)	C(1)-C(2)	0.1421(6)
S(2)-Ni(1)-S(1)	91.64(4)	S(2)-Ni(1)-S(1)#1	88.36(4)	C(2)-S(1)-Ni(1)	103.29(14)
N(2)-C(4)-C(3)	178.1(5)	N(3)-C(5)-C(6)	120.7(4)		

Symmetry codes: #1: $-x+1, -y+1, -z+1$.

define a plane, and the nickel atom is square-planar geometry. The complex dianion is not completely planar, the five-membered nickel-containing ring are slightly puckered, as that have been found for other $[M(mnt)_2]^{2-}$ structures^[7]. A dihedral angle of 12.5° between the planar NiS_4 group and the $N(1)C(1)C(2)C(3)C(4)N(2)$ (mnt^{2-}) mean plane is found and this led to a chair conformation. The terminal nitrogen atom of CN groups are tipped out of the coordination plane, with the deviation of 0.05924nm for N(1) atom, 0.07933nm for N(2) atom, respectively. The S-Ni-S bond angle within the five-membered ring is 91.6° , the two inequivalent Ni-S bond distances are 0.2168nm and 0.2163nm, respectively.

As for the $[BrFPy]^+$ cation, the dihedral angles between the $N(3)-C(10)-C(11)$ reference plane and the aryl rings are 113.5° for phenyl ring, 118.6° for pyridine ring, these values are mildly larger than the corresponding Ni(III) complex^[3a]. In addition, the phenyl ring is nearly vertical to the pyridine ring with a dihedral angle of 99.2° . As could be noted, its cations and anions possess the stacking structure with well-separated column along the direction of a -axis (Fig. 2).

As for complex 2, it crystallizes in the monoclinic space group $P2_1/n$. An ORTEP drawing with the atom labeling of the molecular unit is shown in Fig. 3. Se-

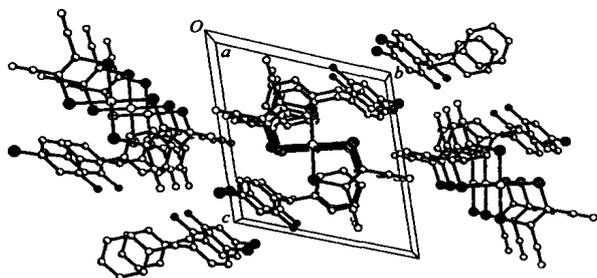


Fig. 2 Packing pattern of complex 1 viewed along a -axis

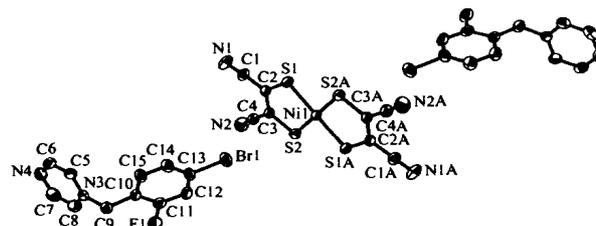


Fig. 3 ORTEP view with non-H atomic numbering scheme for 2; 30% probability thermal ellipsoids are shown

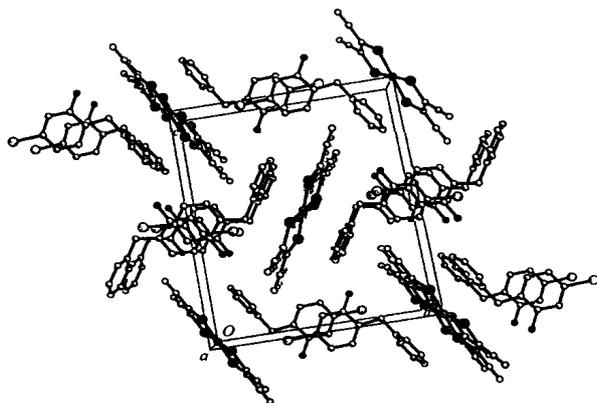
lected bond lengths and bond angles are listed in Table 3.

The molecular structure of 2 is similar to that of 1; the $[Ni(mnt)_2]^{2-}$ anion of 2 also has a center of symmetry at the nickel atom and two $[BrFPz]^+$ ions are related to each other by the symmetry center. The nickel atom is coordinated to four sulfur atoms, and exhibits square-planar coordination geometry. There exists a dihedral angle of 3.8° between the planar NiS_4 group and the $N(1)C(1)C(2)C(3)C(4)N(2)$ (mnt^{2-}) mean plane so as to show a chair conformation. The terminal nitrogen atom of CN groups are tipped out of the coordination plane, with the deviation of 0.01148nm for N(1) atom, 0.01844nm for N(2) atom, respectively. The S-Ni-S bond angle within the five-membered ring is 92.2° , the two inequivalent Ni-S bond distances are 0.2177nm and 0.2163nm, respectively.

As far as the cation in complex 2 is concerned, the dihedral angles between the $N(3)-C(9)-C(10)$ reference plane and the aryl rings are 5.2° for phenyl ring, 81.0° for pyrazine ring, respectively. The pyrazine ring and the phenyl ring make a dihedral angle of 82.7° . Apparently, the conformation of $[BrFPz]^+$ cation in 2 is significantly different from that of 1. It should be noted that its cations and anions are inter-

Table 3 Selected Bond Lengths (nm), Bond Angles (°) of Complex 2

Ni(1)-S(1)	0.21774(10)	Ni(1)-S(2)	0.21630(11)	S(1)-C(2)	0.1721(4)
S(2)-C(3)	0.1728(4)	N(1)-C(1)	0.1133(5)	N(2)-C(4)	0.1137(6)
N(3)-C(9)	0.1478(6)	N(3)-C(5)	0.1321(5)	C(1)-C(2)	0.1439(6)
S(2)-Ni(1)-S(1)	92.22(4)	S(2)-Ni(1)-S(1)#1	87.78(4)	C(2)-S(1)-Ni(1)	102.70(14)
N(2)-C(4)-C(3)	178.4(5)	N(3)-C(5)-C(6)	118.6(5)		

Symmetry codes: #1: $-x, -y+2, -z$.Fig. 4 Packing pattern of 2 in the unit cell, as viewed down *a*-axis

mingled each other as shown in Fig. 4 and this packing pattern is unlike that of complex 1. So it is inferred that varying the kind of aryl ring on counterions have influence the crystal packing positively in this case.

In summary, we have observed two bis(maleonitriledithiolate) nickel (II) complexes described above. The topology and size of the aromatic cation has related to its molecular conformation. Furthermore, the crystal packing of this kind of complexes could be influenced.

References

- [1] (a) Robertson N., Cronin L. *Coord. Chem. Rev.*, **2002**, *227*, 93;
(b) Cassoux P., Valade L., Kobayashi H., Clar R. A., Underhill A. E. *Coord. Chem. Rev.*, **1991**, *110*, 115.
- [2] (a) Coomber A. T., Beljonne D., Friend R. H., Brédas J. L., Charlton A., Robertson N., Underhill A. E., Kurmoo M., Day P. *Nature*, **1996**, *380*, 144;
(b) Pullen A. E., Faulmann C., Pokhodnya K. I., Cassoux P., Tokumoto M. *Inorg. Chem.*, **1998**, *37*, 6714;
(c) Uruichi M., Yakushi K., Yamashita Y., Qin J. *J. Mater. Chem.*, **1998**, *8*, 141;
(d) Arçon D., Lappas A., Margadonna S., Prassides K., Ribera E., Veciana J., Rovira C., Henriques R. T., Almeida M. *Phys. Rev. B*, **1999**, *60*, 4191.
- [3] (a) Xie J. L., Ren X. M., Song Y., Zou Y., Meng Q. J. *J. Chem. Soc. Dalton Trans.*, **2002**, 2868;
(b) Xie J. L., Ren X. M., Song Y., Tong W. J., Lu C. S., Yao Y. G., Meng Q. J. *Inorg. Chem. Commun.*, **2002**, *5*, 395;
(c) Xie J. L., Ren X. M., Song Y., Zhang W. W., Liu W. L., He C., Meng Q. J. *Chem. Commun.*, **2002**, 2346;
(d) Ren X. M., Meng Q. J., Song Y., Lu C. L., Hu C. J., Chen X. Y., Xue Z. L. *Inorg. Chem.*, **2002**, *41*, 5931;
(e) Xie J. L., Ren X. M., He C., Song Y., Meng Q. J., Kremer R. K., Yao Y. G. *Chem. Phys. Lett.*, **2003**, *369*, 41.
- [4] Bulgarevich S. B., Bren D. V., Movshovic D. Y., Finocchiaro P., Failla S. *J. Mol. Struct.*, **1994**, *317*, 147.
- [5] Davison A., Holm R. H. *Inorg. Synth.*, **1967**, *X*, 9.
- [6] SHELXTL, Version 5.10. *Structure Determination Software Programs*, Bruker Analytical X-ray Systems Inc. Madison, Wisconsin, USA.
- [7] Plumlee K. W., Hoffman B. M., Ibers J. A. *J. Chem. Phys.*, **1975**, *63*, 1926.