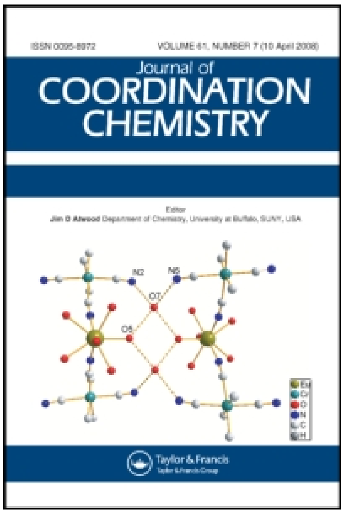

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses and crystal structures of two maleonitriledithiolate complexes containing the 1-(R-benzyl)pyrazinium cation (R = 4'-nitro or 4'-bromo)

Jingli Xie[a]; Xiaoming Ren[a]; Wenwei Zhang[a]; Yizhi Li[a]; Chunlin Ni[a]; Zhaoping Ni[a]; Qingjin Meng[a]; Yuangen Yao[b]
[a] State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, 210093 Nanjing, P.R. China [b] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, 350002 Fuzhou, P.R. China

To cite this Article Xie, Jingli , Ren, Xiaoming , Zhang, Wenwei , Li, Yizhi , Ni, Chunlin , Ni, Zhaoping , Meng, Qingjin and Yao, Yuangen(2003) 'Syntheses and crystal structures of two maleonitriledithiolate complexes containing the 1-(R-benzyl)pyrazinium cation (R = 4'-nitro or 4'-bromo)', Journal of Coordination Chemistry, 56: 16, 1367 — 1374

To link to this Article: DOI: 10.1080/00958970310001624456

URL: http://dx.doi.org/10.1080/00958970310001624456

J. Coord. Chem., Vol. 56, No. 16, 10 November 2003, pp. 1367–1374

Taylor & Francis
Taylor & Francis Group

SYNTHESES AND CRYSTAL STRUCTURES OF TWO MALEONITRILEDITHIOLATE COMPLEXES CONTAINING THE 1-(R-BENZYL)PYRAZINIUM CATION (R = 4′-NITRO OR 4′-BROMO)

JINGLI XIE[a], XIAOMING REN[a], WENWEI ZHANG[a], YIZHI LI[a], CHUNLIN NI[a], ZHAOPING NI[a], QINGJIN MENG[a,]* and YUANGEN YAO[b]

[a]*State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, 210093 Nanjing, P.R. China;* [b]*State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, 350002 Fuzhou, P.R. China*

(Received 6 June 2003; In final form 1 September 2003)

The complexes $[NO_2BzPz]_2[Ni(mnt)_2]$ (**1**) and $[BrBzPz]_2[Pd(mnt)_2]$ (**2**) have been prepared by reaction of Na_2mnt, $NiCl_2 \cdot 6H_2O$ or $PdCl_2$, and the corresponding 1-(R-benzyl)pyrazinium bromide salt (R = 4′-nitro, R = 4′-bromo). Crystallographic data for **1**: monoclinic, $P2_1/n$, $a = 7.3494(15)$, $b = 15.223(3)$, $c = 15.054(3)$ Å, $\beta = 102.42(3)°$, $V = 1644.8(6)$ Å^3, $Z = 2$. Data for **2**: monoclinic, $P2_1/n$, $a = 7.399(2)$, $b = 19.024(4)$, $c = 12.224(2)$ Å, $\beta = 94.62(3)°$, $V = 1715.0(7)$ Å^3, $Z = 4$. In both complexes, the $[M(mnt)_2]^{2-}$ anion has a centre of symmetry at the metal atom and two cations are related to each other by the symmetry centre. The $[M(mnt)_2]^{2-}$ anion exhibits a quasi-planar structure in both complexes, which show similar crystal packing.

Keywords: 1-(4′-Nitrobenzyl)pyrazinium; 1-(4′-Bromobenzyl)pyrazinium; Bis(maleonitriledithiolate)metal(II) complex; Crystal structure

INTRODUCTION

Much effort has been devoted to the study of square planar M(dithiolene)$_2$ complexes in the areas of conducting and magnetic materials, dyes, non-linear optics and catalysis [1]. Complexes containing maleonitriledithiolate (mnt) have been studied extensively as its high charge density associated with a delocalised planar π-system gives rise to a large number of stacking modes and, consequently, differing physical properties [2]. Recently, we reported one-dimensional, molecule-based magnets, based on an ion-pair complex containing $[M(mnt)]^-$ (M = Ni(III), Pt(III); mnt^{2-} = maleonitriledithiolate) and a benzylpyridinium derivative as counterion. Various counterions led to unexpected magnetic exchange properties even though the complexes have

---

*Corresponding author. Fax: +86 25 359 7266. E-mail: mengqj@netra.nju.edu.cn

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970310001624456

extremely similar molecular and stacking structures. Versatile magnetic properties such as ferromagnetic ordering at 2 K, peculiar magnetic transitions from ferromagnetic coupling to diamagnetism or from paramagnetism to diamagnetism, and spin-Peierls-like transitions have been witnessed [3–7]. Herein, we report two complexes with the aim of examining the effect of substituting a paramagnetic d^7 central metal by a diamagnetic d^8 metal on the crystal structure. In addition, we have replaced the pyridine molecule of benzylpyridinium counterion by a pyrazine molecule. A new type of stacking structure may exist in this case because the electronic properties of pyrazine are quite different from those of pyridine.

EXPERIMENTAL

Materials and Preparation

Starting materials were purchased from Aldrich (4-nitrobenzylbromide, 4-bromobenzylbromide, pyrazine), and were used without further purification. [1-(4′-nitrobenzyl)]pyrazinium bromide ($[NO_2BzPz]Br$), [1-(4′-bromobenzyl)]pyrazinium bromide ([BrBzPz]Br) and disodium maleonitriledithiolate (Na_2mnt) were synthesised following published procedures [8,9].

$[NO_2BzPz]_2[Ni(mnt)_2]$ (1)

This compound was prepared by the direct combination of 1 : 2 : 2 mol equivalents of $NiCl_2 \cdot 6H_2O$, Na_2mnt and $[NO_2BzPz]Br$ in H_2O. A red precipitate was filtered off, washed with water and dried under vacuum. Yield: 92%. Found: C, 46.85; H, 2.62; N, 18.09. Calc. for $C_{30}H_{20}N_{10}NiO_4S_4$: C, 46.71; H, 2.61; N, 18.16%.

$[BrBzPz]_2[Pd(mnt)_2]$ (2)

This complex was synthesised as above by mixing stoichiometric amounts of $PdCl_2$, Na_2mnt and [BrBzPz]Br. Yield: 88%. Found: C, 40.48; H, 2.26; N, 12.57. Calc. for $C_{15}H_{10}BrN_4Pd_{0.5}S_2$: C, 40.62; H, 2.27; N, 12.63%.

Crystal Structure Determinations

Good shaped single crystals suitable for X-ray analysis were obtained by diffusing Et_2O into MeCN solutions of **1** or **2** for about a week. Single crystals with approximate dimensions 0.15 × 0.10 × 0.10 mm (for **1**) and 0.15 × 0.10 × 0.10 mm (for **2**) were selected for indexing and intensity data were collected on a Siemens Smart CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71083$ Å) by the ω scan mode in the range $1.93 < \theta < 24.23$ for **1** and $1.98 < \theta < 28.02$ for **2**. Space groups, lattice parameters and other relevant information are listed in Table I. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares methods employing SHELXTL [10]. All non-hydrogen atoms were refined with anisotropic thermal parameters. 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.

TABLE I Crystal data and structure refinement details

	1	*2*
CCDC deposit no.	CCDC-177585	CCDC-197281
Chemical formula	$C_{30}H_{20}N_{10}NiO_4S_4$	$C_{15}H_{10}BrN_4Pd_{0.5}S_2$
Formula weight	771.51	443.50
Temperature, K	293(2)	293(2)
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
Unit cell dimensions	$a = 7.3494(15)$ Å	$a = 7.399(2)$ Å
	$b = 15.223(3)$ Å	$b = 19.024(4)$ Å
	$c = 15.054(3)$ Å	$c = 12.224(2)$ Å
	$\beta = 102.42(3)^\circ$	$\beta = 94.62(3)^\circ$
Volume, Å^3	1644.8(6)	1715.0(7)
Z	2	4
Density (calculated)	1.558 Mg/m^3	1.718 Mg/m^3
Absorption coefficient	0.898 mm^{-1}	3.149 mm^{-1}
$F(000)$	788	872
θ range for data collection	1.93 to 24.23	1.98 to 28.02°
Index ranges	$-8 \le h \le 8$	$-9 \le h \le 9$
	$-15 \le k \le 13$	$-24 \le k \le 21$
	$-17 \le l \le 5$	$-15 \le l \le 15$
Reflections collected	3580	10 549
Independent reflections	2447 ($R_{int} = 0.0247$)	4009 ($R_{int} = 0.0373$)
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	2447/0/223	4009/0/205
Goodness of fit on F^2	1.089	1.073
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0329$, $wR2 = 0.0795$	$R1 = 0.0370$, $wR2 = 0.0768$
R indices (all data)	$R1 = 0.0397$, $wR2 = 0.0817$	$R1 = 0.0656$, $wR2 = 0.0800$
Largest diff. peak and hole	0.222 and -0.275 eÅ^{-3}	0.313 and -0.639 eÅ^{-3}

RESULTS AND DISCUSSION

Crystal Structure

The atomic arrangement and numbering system for **1** are shown in Fig. 1. Fractional atomic coordinates and equivalent isotropic displacement parameters of this complex are listed in Table II. Selected bond lengths and bond angles are given in Table III. The molecule structure is similar to the corresponding species $[NO_2BzPy]_2[Ni(mnt)_2]$, containing the pyridinium cation [11]. The $[Ni(mnt)_2]^{2-}$ anion has a centre of symmetry at the nickel atom and two $[BrBzPz]^+$ ions are related to each other by the symmetry centre. Four sulfur atoms define a plane, and the nickel atom has square planar geometry. The complex dianion is not completely planar, the five-membered nickel-containing ring being slightly puckered, as found in other $[M(mnt)_2]^{n-}$ structures [12]. A dihedral angle of 7.2° 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 evident and this leads to a chair conformation. The terminal nitrogen atoms of CN groups are tipped out of the coordination plane, with deviations of 0.3622 Å for N(1), 0.4371 Å for N(2). The S–Ni–S bond angle in the five-membered rings is 92.4° and the two inequivalent Ni–S bond distances are 2.178 and 2.169 Å, respectively.

As for the $[NO_2BzPz]^+$ cation, the dihedral angles between the N(4)–C(9)–C(10) reference plane and the aryl rings are 37.2° (pyrazine ring) and 70.1° (phenyl ring). In addition, the pyrazine ring is nearly orthogonal to the phenyl ring (dihedral angle

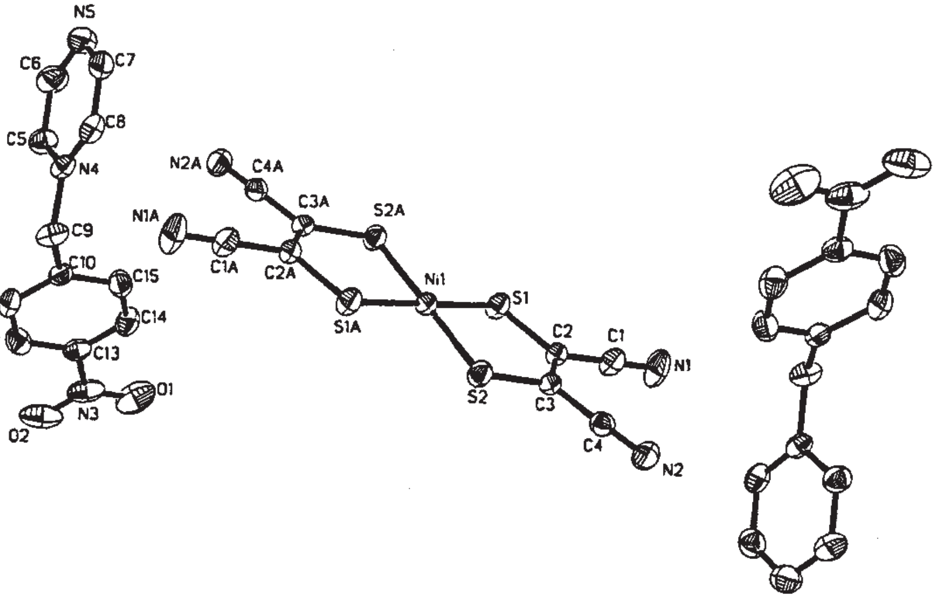

FIGURE 1. ORTEP plot (30% probability ellipsoids) showing the molecule structure of **1**.

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$ Å^2) for $[NO_2BzPz]_2[Ni(mnt)_2]$

Atom	*x/a*	*y/b*	*z/c*	*U*(eq)[a]
Ni(1)	0	5000	0	39(1)
S(1)	1056(1)	3975(1)	−764(1)	50(1)
S(2)	−2826(1)	4842(1)	−782(1)	48(1)
N(1)	−759(3)	2259(2)	−2500(2)	82(1)
N(2)	−5670(3)	3343(2)	−2464(2)	58(1)
N(3)	7981(3)	9689(3)	−561(2)	73(1)
N(4)	6059(3)	8640(2)	3329(1)	44(1)
N(5)	8068(4)	7699(2)	4760(2)	67(1)
C(1)	−826(4)	2848(2)	−2045(2)	53(1)
C(2)	−964(4)	3591(2)	−1476(2)	42(1)
C(3)	−2629(3)	3961(2)	−4179(2)	40(1)
C(4)	−4310(4)	3624(2)	−2037(2)	44(1)
C(5)	7904(4)	8743(2)	3576(2)	55(1)
C(6)	8862(4)	8273(2)	4301(2)	68(1)
C(7)	6249(5)	7631(2)	4512(2)	61(1)
C(8)	5207(4)	8094(2)	3805(2)	53(1)
C(9)	4929(4)	9159(2)	2569(2)	56(1)
C(10)	5882(3)	9285(2)	1787(2)	43(1)
C(11)	6482(4)	10 098(2)	1601(2)	54(1)
C(12)	7213(4)	10 238(2)	845(2)	59(1)
C(13)	7325(3)	9542(2)	286(2)	49(1)
C(14)	6798(4)	8714(2)	470(2)	59(1)
C(15)	6068(4)	8590(2)	1229(2)	59(1)
O(1)	8054(4)	9066(2)	−1051(2)	105(1)
O(2)	8381(3)	10447(2)	−730(2)	91(1)

[a] *U*(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE III Selected bond lengths (Å) and bond angles (°) for $[NO_2BzPz]_2[Ni(mnt)_2]$

Ni(1)–S(2)	2.1693(10)	S(2)–Ni(1)–S(1)#1	87.58(3)
Ni(1)–S(1)	2.1780(7)	S(2)#1–Ni(1)–S(1)#1	92.42(3)
S(1)–C(2)	1.735(3)	C(2)–S(1)–Ni(1)	102.29(9)
S(2)–C(3)	1.728(2)	C(3)–S(2)–Ni(1)	102.74(9)
N(1)–C(1)	1.135(3)		
N(2)–C(4)	1.149(3)		
N(3)–O(1)	1.209(4)		
N(3)–O(2)	1.230(4)		
C(1)–C(2)	1.435(4)		
C(2)–C(3)	1.347(3)		
C(3)–C(4)	1.431(4)		

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

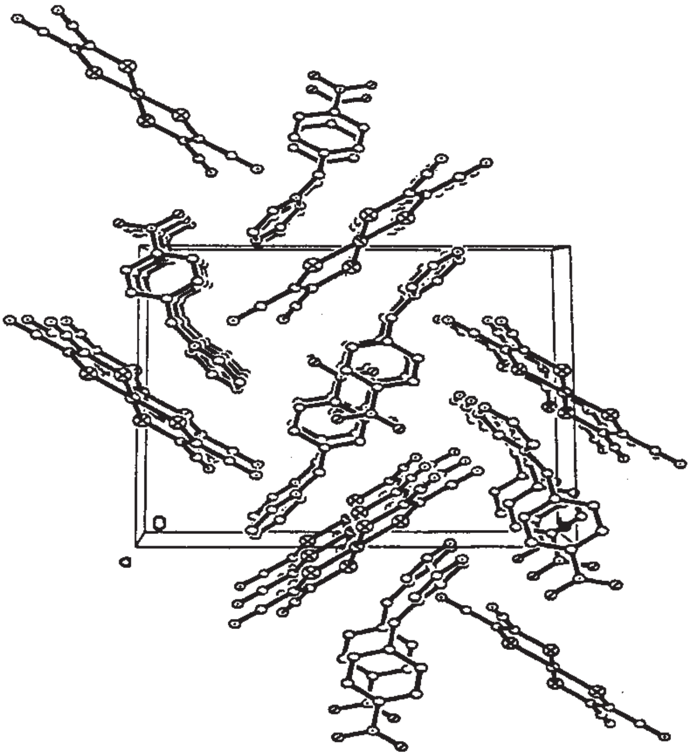

FIGURE 2. The packing diagram of a unit cell for 1 as viewed along the *a*-axis.

90.9°). These values are significantly different from those in the corresponding $[NO_2BzPy]_2[Ni(mnt)_2]$ complex. Cations and anions are interwoven with each other as shown in Fig. 2 and this packing pattern is unlike the alternating ion layers in $[NO_2BzPy]_2[Ni(mnt)_2]$ [11]. It is thus confirmed that the topology of the cation plays an important role in crystal packing.

When the transition metal is palladium, combined with an analogous cation formed by 4-bromobenylbromide and pyrazine, complex $[BrBzPz]_2[Pd(mint)_2]$ (**2**) is prepared. An ORTEP drawing with the atom labelling of the molecular unit is shown in Fig. 3.

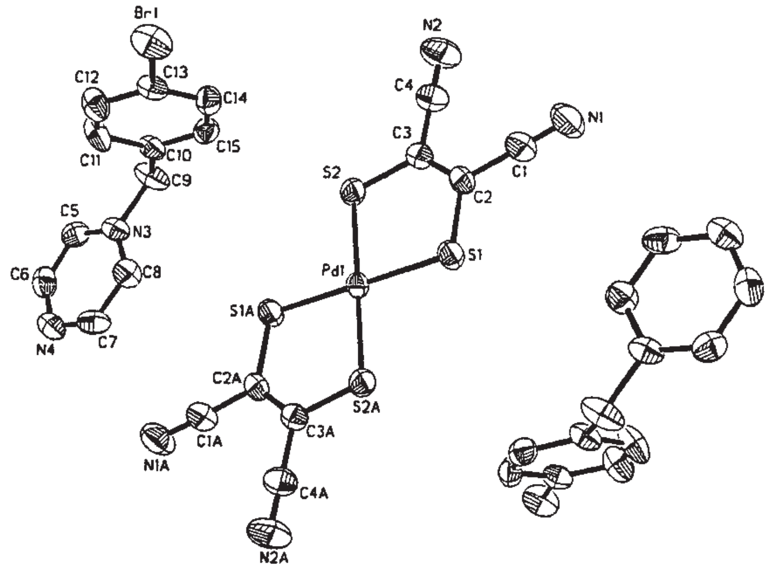

FIGURE 3. ORTEP view with non-H atomic numbering scheme for **2**; 30% probability thermal ellipsoids are shown.

TABLE IV Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$ Å^2) for $[BzBzPz]_2[Pd(mnt)_2]$

Atom	*x/a*	*y/b*	*z/c*	U(eq)[a]
Pd(1)	5000	5000	0	50(1)
Br(1)	6340(1)	6007(1)	5353(1)	89(1)
S(1)	2422(1)	4337(1)	60(1)	64(1)
S(2)	6445(1)	4294(1)	1313(1)	63(1)
N(1)	818(5)	2718(2)	1339(3)	101(1)
N(2)	5710(5)	2693(2)	2883(3)	102(1)
N(3)	13 302(4)	6058(1)	1989(2)	57(1)
N(4)	14 231(6)	7185(2)	785(3)	75(1)
C(1)	1 836(6)	3147(2)	1200(3)	70(1)
C(2)	3127(5)	3686(2)	1002(3)	56(1)
C(3)	4809(5)	3673(2)	1516(3)	55(1)
C(4)	5304(5)	3125(2)	2278(3)	71(1)
C(5)	14 970(5)	6305(2)	2081(3)	68(1)
C(6)	15 393(6)	6872(2)	1478(4)	77(1)
C(7)	12 599(6)	6914(2)	680(3)	77(1)
C(8)	12 092(5)	6348(2)	1273(3)	69(1)
C(9)	12 801(6)	5431(2)	2630(3)	85(1)
C(10)	11 212(5)	5575(2)	3284(3)	60(1)
C(11)	11 181(6)	6157(2)	3967(3)	81(1)
C(12)	9750(6)	6284(2)	4578(3)	76(1)
C(13)	8331(5)	5820(2)	4511(3)	58(1)
C(14)	8337(5)	5239(2)	3863(3)	61(1)
C(15)	9774(5)	5123(2)	3249(3)	59(1)

[a] U(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor.

Fractional atomic coordinates and equivalent isotropic displacement parameters are listed in Table IV. Selected bond lengths and bond angles are given in Table V.

The molecular structure of **2** is similar to that of **1**; the $[Pd(mnt)_2]^{2-}$ anion of **2** is also centrosymmetric and the two $[BrBzPz]^+$ ions are related to each other by the symmetry

TABLE V Selected bond length (Å) and bond angles (°) for $[BrBrPz]_2$ $[Pd(mnt)_2]$

Pd(1)–S(2)	2.2902(10)	S(2)–Pd(1)–S(1)	89.89(4)
Pd(1)–S(1)	2.2926(10)	S(2)–Pd(1)–S(1)#1	90.11(4)
S(1)–C(2)	1.743(4)	C(2)–S(1)–Pd(1)	101.91(12)
S(2)–C(3)	1.724(4)	C(3)–S(2)–Pd(1)	102.06(12)
N(1)–C(1)	1.133(5)		
N(2)–C(4)	1.130(4)		
C(1)–C(2)	1.435(5)		
C(2)–C(3)	1.348(5)		
C(3)–C(4)	1.426(5)		

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

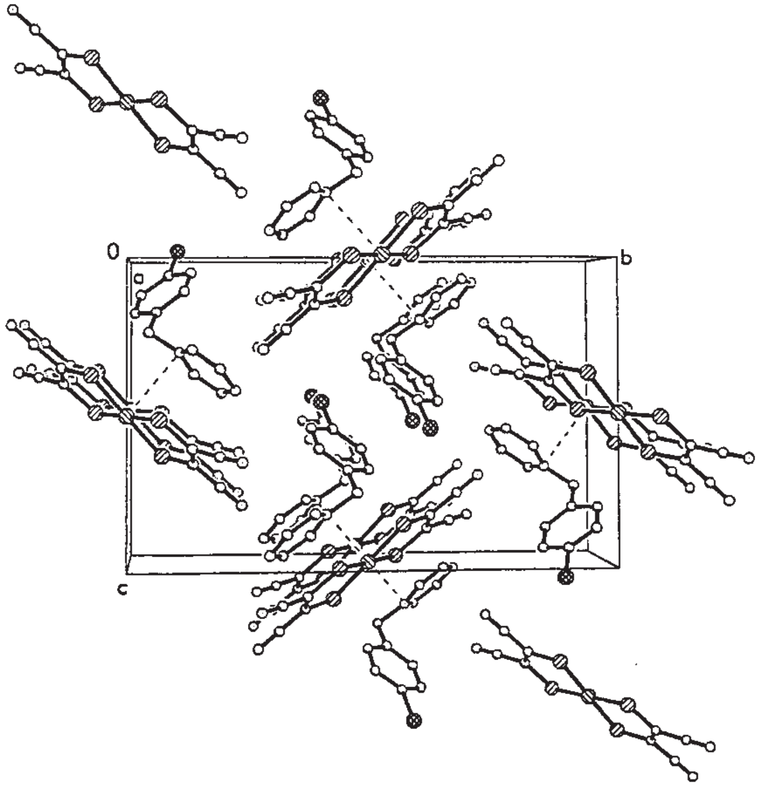

FIGURE 4. Packing of **2** in the unit cell, as viewed down the *a*-axis.

centre. A dihedral angle of 3.7° is seen 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 also tipped out of the coordination plane, with a deviation of 0.2418 Å for N(1) and 0.1920 Å for N(2). The S–Ni–S bond angle in the five-membered ring is 89.89° and the two inequivalent Ni–S bond distances are 2.2902 and 2.2926 Å.

For the $[BrBzPz]^+$ ion in complex **2**, however, dihedral angles between the N(3)–C(9)–C(10) reference plane and the aryl rings are 56.1° (pyrazine ring) and 49.9° (phenyl ring). The pyrazine ring and the phenyl ring make a dihedral angle of 84.6°. It should be noted that cations and anions are arranged as shown in Fig. 4 to give a packing pattern similar to that of complex **1**. Thus it is inferred that variations of substituent groups in the *para*-position of the benzyl group and central metal ion have little influence on crystal packing.

Infrared Spectra

In the IR spectrum of complex **1**, bands due to ν(C–H) of aromatic rings are seen at 3064 (sh), 3059 (s) cm^{-1}. Bands at 2216 (sh), 2199 (vs) cm^{-1} are assigned to ν(C≡N) of nitrile groups. Bands at 1636 (s), 1609 (m) and 1528 (s) can be assigned to ν(C=N), ν(C=C) of the pyrazine ring and phenyl ring and bands at 1530 and 1348 cm^{-1} originate from $\nu_{as}(NO_2)$ $\nu_s(NO_2)$; (C=C) of mnt^{2-} is at 1495 (vs) and the band at 862 (m) results from ν(C–S).

As for complex **2**, the bands in the range 3068–3132 cm^{-1} are assigned to the C–H stretching in the aromatic rings. A very strong characteristic ν(C≡N) band is found in 2211 cm^{-1} with a shoulder at 2214.3 cm^{-1}. The ν(C=N), ν(C=C) bands for the pyrazine and phenyl rings located at 1635 (s), 1607 (m) and 1527 (s) cm^{-1} (C=C) of mnt^{2-} is at 1498 (vs) and the band at 859 (m) results from ν(C–S). Bands at 578 and 543 cm^{-1} originate from ν(Br–C).

Acknowledgements

Financial support from the National Natural Science Foundation (No. 2017022, No. 29831010), Jiangsu Science and Technology Department and The Center of Analysis of Nanjing University is acknowledged.

Supplementary Material

Full lists of crystallographic data are available from the authors upon request.

References

[1] N. Robertson and L. Cronin, *Coord. Chem. Rev.* **227**, 93 (2002).

[2] A.T. Coomber, D. Beljonne, R.H. Friend, J.L. Brédas, A. Charlton, N. Robertson, A.E. Underhill, M. Kurmoo and P. Day, *Nature* **380**, 144 (1996).

[3] J.L. Xie, X.M. Ren, Y. Song, Y. Zou and Q.J. Meng, *J. Chem. Soc., Dalton Trans.* 2868 (2002).

[4] J.L. Xie, X.M. Ren, Y. Song, W.J. Tong, C.S. Lu, Y.G. Yao and Q.J. Meng, *Inorg. Chem. Commun.* **5**, 395 (2002).

[5] J.L. Xie, X.M. Ren, Y. Song, W.W. Zhang, W.L. Liu, C. He and Q.J. Meng, *Chem. Commun.* 2346 (2002).

[6] X.M. Ren, Q.J. Meng, Y. Song, C.L. Lu, C.J. Hu, X.Y. Chen and Z.L. Xue, *Inorg. Chem.* **41**, 5931 (2002).

[7] J.L. Xie, X.M. Ren, C. He, Y. Song, Q.J. Meng, R.K. Kremer and Y.G. Yao, *Chem. Phys. Lett.* **369**, 41 (2003).

[8] S.B. Bulgarevich, D.V. Bren, D.Y. Movshovic, P. Finocchiaro and S. Failla, *J. Mol. Struct.* **317**, 147 (1994).

[9] A. Davison and R.H. Hom, *Inorg. Synth.* **10**, 9 (1967).

[10] SHELXTL, Version 5.10. Structure Determination Software Programs (Bruker Analytical X-ray Systems Inc., Madison, Wisconsin, USA).

[11] X.M. Ren, Y. Xun, Q.J. Meng, C.J. Hu, C.S. Lu and H.Q. Wang, *Chem. Crystallogr.* **30**, 91 (2000).

[12] K.W. Plumlee, B.M. Hoffman and J.A. Ibers, *J. Chem. Phys.* 63, 1926 (1975).