Syntheses and crystal structures of two new nickel 1,2,5-thiadiazole-3, 4-dithiolate complexes as benzylpyridinium salts

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SYNTHESES AND CRYSTAL STRUCTURES OF TWO NEW NICKEL 1,2,5-THIADIAZOLE-3, 4-DITHIOLATE COMPLEXES AS BENZYLPYRIDINIUM SALTS

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Two new complexes, $[BrBzPy]_2[Ni(tdas)_2]$ (**1**) and $[BrFBzPy]_2[Ni(tdas)_2]$ (**2**), have been prepared by reaction of disodium 1,2,5-thiadiazole-3,4-dithiolate (Na_2tdas), $NiCl_2 \cdot 6H_2O$ and 1-(4′-bromobenzyl) pyridinium bromide (BrBzPyBr) or 1-(4′-bromo-2′-fluorobenzyl)pyridinium) bromide (BrFBzPyBr). Crystallographic data for **1**: monoclinic, $P2_1/c$, $a = 11.333(1)$, $b = 12.602(1)$, $c = 12.267(1)$ Å, $\beta = 115.65(1)°$, $V = 1579.4(18)$ Å^3, $Z = 4$. Data for **2**: triclinic, $P\bar{1}$, $a = 7.437(2)$, $b = 10.382(2)$, $c = 11.330(2)$ Å, $\alpha = 110.07(3)$, $\beta = 92.58(3)$, $\gamma = 93.32(3)°$, $V = 818.5(2)$ Å^3, $Z = 1$. In the complexes, the $[Ni(tdas)_2]^{2-}$ anion exhibits a *quasi*-planar structure. The topology of the countercation results in different stacks of molecules in the complexes.

Keywords: 1-(4′-bromobenzyl)pyridinium; 1-(4′-bromo-2′-fluorobenzyl)pyridinium; (1,2,5-thiadiazole-3,4-dithiolate)nickel(II) complex; Crystal structure

INTRODUCTION

Although bis-1,2-ditholene metal complexes are well known, there has been growing interest in them due to their extensive applications in molecular materials showing magnetic, superconducting and optical properties [1,2]. One of these complexes is $M(tdas)_2^{n-}$ (tdas = 1,2,5-thiadiazole-3,4-dithiolate), which has been used as an analogue of dmit (1,3-dithiol-2-thione-4,5-dithiolate) complexes [3]. Some of the complexes in the solid state show interesting magnetic properties with unusual phase transitions and electroconductive properties [4,5]. We have recently developed a new class of transition metal complexes containing as counterion a benzylpyridinium derivative, $[RBzPy]^+[M(mnt)_2]^-$, and found that the topology and size of the countercation in these complexes may play an important role in controlling the stacking pattern of

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anions and cations; this can further influence the magnetic properties of the complexes [6–13]. With the aim of obtaining some information on [RBzPy]$^+$ effects on crystal packing and strength of intermolecular interactions in M(tdas)$_2$ complexes, we report the syntheses and X-ray structures of two new nickel(II) 1,2,5-thiadiazole-3,4-dithiolate complexes containing 1-(4′-bromobenzyl)pyridinium and 1-(4′-bromo-2′-fluorobenzyl)-pyridinium cations.

EXPERIMENTAL

Materials

4-Bromo-2-fluorobenzyl bromide and 4-bromobenzyl bromide were purchased from Aldrich Chemical Company and used as received. The sodium salts of 1,2,5-thiadiazole-3,4-dithiolate, 1-(4′-bromobenzyl)pyridinium bromide and 1-(4′-bromo-2′-fluorobenzyl)pyridinium bromide were synthesized by procedures described in the literature [14,15].

Physical Measurements

Elemental analyses were run on a Perkin Elmer 240 instrument. Infrared spectra were recorded on an IF66V FT-IR spectrophotometer (400–4000 cm^{-1} region) using KBr pellets.

Syntheses

[BrBzPy]$_2$[Ni(tdas)$_2$] (**1**): This compound was prepared by the direct reaction of 1:2:2 mol equivalents of NiCl$_2 \cdot$6H$_2$O, Na$_2$mnt and 1-(4′-bromobenzyl)pyridinium bromide in methanol. A red precipitate was filtered off, washed with methanol and dried under vacuum. Brown crystals were obtained by recrystallization from methanol. Yield: 92%. Anal. Calc. for C$_{14}$H$_{11}$N$_3$Ni$_{0.5}$BrS$_3$(%): C, 39.41; H, 2.60; N, 9.85. Found: C, 39.26; H, 2.71; N, 9.78.

[BrFBzPz]$_2$[Ni(tdas)$_2$] (**2**): This compound was prepared using a procedure similar to that for Complex **1**, but with BrFBzPyBr instead of BrBzPrBr. Yield: 90%. Anal. Calc. for C$_{28}$H$_{20}$N$_6$NiBr$_2$F$_2$S$_6$(%): C, 37.81; H, 2.27; N, 9.45. Found: C, 37.74; H, 2.32; N, 9.38.

Crystal Structure Determination

Brown, single crystals of both salts suitable for X-ray analysis were grown from CH$_3$OH by slow evaporation of the solvent during about 2 weeks. Single crystals having approximate dimensions $0.30 \times 0.25 \times 0.20$ mm (for **1**) and $0.30 \times 0.20 \times 0.20$ mm (for **2**) were selected for indexing. Intensity data were collected on a Siemens Smart CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by the ω scan mode within the angular range $2.0 < \theta < 27.0$ for **1** and $1.9 < \theta < 26.0$ 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 techniques, using the SHELXTL program [16].

TABLE I   Crystal data and structure refinement details

Compound	1	2
CCDC deposit no.	CCDC-227063	CCDC-227062
Chemical formula	$C_{14}H_{11}BrN_3Ni_{0...5}S_3$	$C_{28}H_{20}BrFN_6NiS_6$
Formula weight	426.70	889.39
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions (Å, °)	$a = 11.333(1)$	$a = 7.438(1)$
	$b = 12.602(1)$	$b = 10.382(2)$
	$c = 12.267(1)$	$c = 11.330(2)$
		$\alpha = 110.07(1)$
	$\beta = 115.64(2)$	$\beta = 92.57(3)$
		$\gamma = 93.32(1)$
Volume (Å)^3	1579.4(18)	818.5(2)
Z	4	1
Density (calculated),	$1.795\,Mg\,m^{-3}$	$1.804\,Mg\,m^{-3}$
Absorption coefficient (mm^{-1})	$3.573\,mm^{-1}$	$3.460\,mm^{-1}$
Diffractometer/scan	Siemens SMART/CCD area detector	
$F(000)$	852	442
θ range for data collection (°)	2.0 to 27.0	1.9 to 26.0
Index ranges	$-11 \le h \le 14$	$-8 \le h \le 9$
	$-12 \le k \le 16$	$-11 \le k \le 12$
	$-15 \le l \le 13$	$-11 \le l \le 13$
Reflections collected	8974	4443
Independent reflections	3431 ($R_{int} = 0.048$)	3142($R_{int} = 0.024$)
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	3431/0/196	3142/0/205
Goodness of fit on F^2	1.065	1.019
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0402$, $wR_2 = 0.0858$	$R_1 = 0.0320$, $wR_2 = 0.0838$
R indices (all data)	$R_1 = 0.0795$, $wR_2 = 0.0777$	$R_1 = 0.0379$, $wR_2 = 0.0823$
Largest diff. peak and hole e Å^{-3}	0.77 and -0.91	0.91 and -0.91

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.

RESULTS AND DISCUSSION

Crystal Structure

Complex **1** crystallizes in the monoclinic space group $P2_1/c$. Its molecular geometry and the numbering of the atoms are shown in Fig. 1. Fractional atomic coordinates and equivalent isotropic displacement parameters are listed in Table II. Selected bond-lengths and angles are listed in Table III. The nickel(II) ion is situated at a center of symmetry and is square planar. Two [BrBzPy]$^+$ ions are related to each other by the symmetry center. The Ni(tdas)$_2^{2-}$ion is not completely planar; the five-membered nickel-containing rings are slightly puckered with an average Ni–S bond distance of 2.195 Å. The S–Ni–S bond angles are 93.4° and 86.6°, similar to values found for other Ni(tdas)$_2^{2-}$ structures [17]. The [BrBzPz]$^+$ cation adopts a conformation where both the phenyl and pyridine rings are twisted with respect to the C(9)–C(8)–N(3)
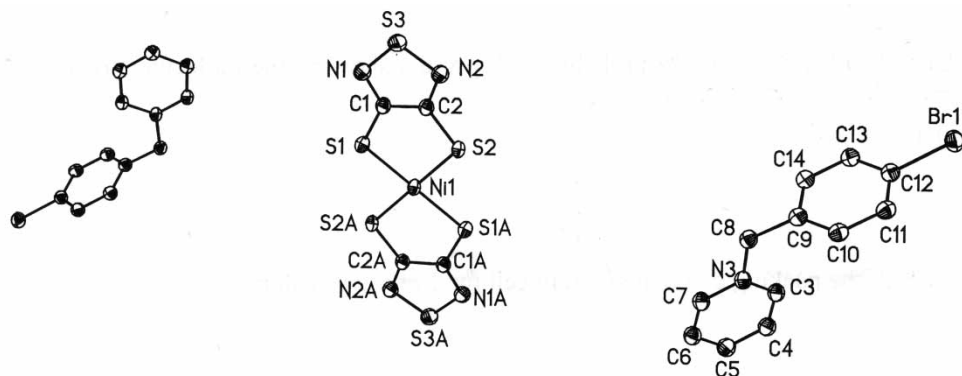
FIGURE 1 ORTEP plot (30% probability ellipsoids) showing the molecular structure and atom numbering scheme of **1**.

TABLE II Atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for [BrBzPz]$_2$[Ni(tdas)$_2$]

Atom	x/a	y/b	z/c	U(eq)[a]
Ni(1)	1/2	0	1/2	0.0373(2)
S(1)	0.31127(9)	−0.08087(7)	0.44287(9)	0.0424(3
S(2)	0.42269(8)	0.11529(7)	0.35101(8)	0.0383(3)
S(3)	0.03022(10)	0.06790(9)	0.14827(10)	0.0603(4)
N(1)	0.0820(3)	−0.0229(2)	0.2556(3)	0.0515(12)
N(2)	0.1698(3)	0.1301(3)	0.1817(3)	0.0509(11)
N(3)	0.7883(3)	0.8641(2)	0.4015(3)	0.0414(11)
Br(1)	0.68728(4)	1.14614(3)	−0.11521(4)	0.0584(2)
C(1)	0.2090(4)	−0.0069(3)	0.3195(3)	0.0450(12)
C(2)	0.2581(3)	0.0801(3)	0.2777(3)	0.0447(12)
C(3)	0.9016(3)	0.8800(3)	0.3957(3)	0.0445(12)
C(4)	1.0155(4)	0.8426(3)	0.4875(3)	0.0490(14)
C(5)	1.0128(4)	0.7901(4)	0.5811(4)	0.0512(16)
C(6)	0.8959(4)	0.7752(3)	0.5870(4)	0.0491(14)
C(7)	0.7846(4)	0.8128(3)	0.4947(3)	0.0442(12)
C(8)	0.6588(3)	0.8973(3)	0.3029(3)	0.0424(12)
C(9)	0.6678(3)	0.9591(3)	0.2034(3)	0.0425(12)
C(10)	0.6816(3)	1.0680(3)	0.2091(3)	0.0452(12)
C(11)	0.6873(3)	1.1245(3)	0.1146(3)	0.0452(12)
C(12)	0.6808(3)	1.0707(3)	0.0152(3)	0.0425(12)
C(13)	0.6646(3)	0.9631(3)	0.0057(3)	0.0434(12)
C(14)	0.6583(3)	0.9078(3)	0.1001(3)	0.0431(12)

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

reference plane. The dihedral angles between the C(9)–C(8)–N(3) reference plane are 93.3° for the phenyl ring and 5.0° for the pyridine ring. The phenyl ring is nearly perpendicular to the pyridine ring with a dihedral angle of 89.1°. The planes defined by S(1)S(2)S(1A)S(2A) with the phenyl ring and pyridine ring make dihedral angles of 108.2° and 29.4°, respectively. The [BrBzPz]$^+$ cation (D) and Ni(tdas)$_2^{2-}$ anion (A) form alternating layers (i.e., of the type …D1D2A1D1D2A2D1D2…) along the c axis of the unit cell (Fig. 2). The Ni···Ni separation between layers of neighboring anions is 8.793 Å, and the S(1) atom of the anion is linked to the C(4) $(1+x, 1+y, z)$ of the cation by hydrogen bonding.

TABLE III   Selected bondlengths (Å) and bond angles (°) for [BrBzPz]₂[Ni(tdas)₂]

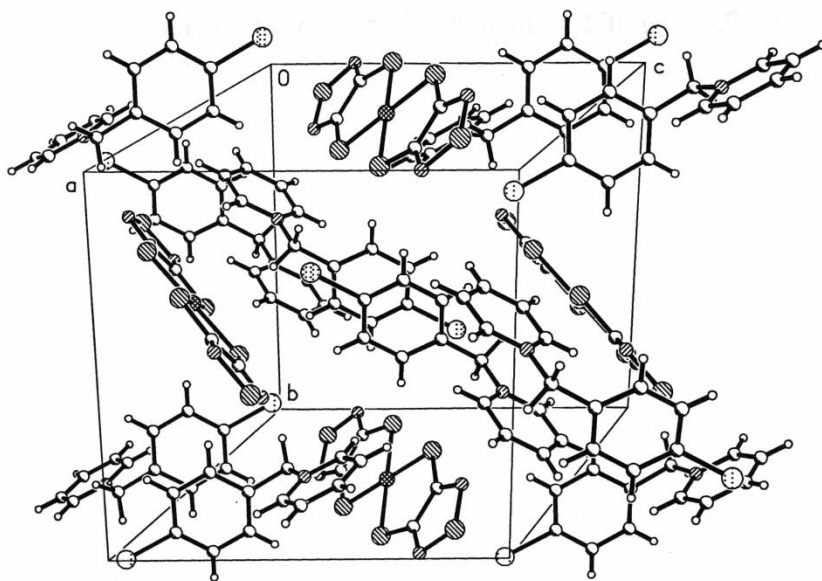|			
Ni(1)–S(1)	2.193(2)	S(1^i)–Ni(1)–S(2)	86.63(4)
Ni(1)–S(2)	2.198(2)	S(1)–Ni(1)–S(2)	93.37(4)
S(1)–C(1)	1.728(3)	Ni(1)–S(1)–C(1)	102.77(15)
S(2)–C(2)	1.741(4)	Ni(1)–S(2)–C(2)	102.32(13)
N(1)–C(1)	1.323(6)		
N(1)–C(2)	1.329(5)		
N(1)–S(3)	1.649(3)		
N(2)–S(3)	1.650(4)		
C(1)–C(2)	1.422(6)		

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

FIGURE 2   Packing diagram in the unit cell of **1**, viewed along the *a* axis.

With the aim of understanding how the cation affects the molecular structure and packing of the complexes, Complex **2**, [BrFBzPy]₂[Ni(tdas)₂], was prepared. An ORTEP drawing with the atom labelling of the molecular unit is shown in Fig. 3. Fractional atomic coordinates and equivalent isotropic displacement parameters of this complex are listed in Table IV. Selected bondlengths and angles are listed in Table V. The coordination geometry of the nickel(II) ion in Complex **2** is essentially similar to that of Complex **1**; S–Ni–S bond angles are 93.7° and 86.3°. Intermolecular hydrogen bonds (C(7)–H(7)···N(2) and C(8)–H(8A)···F(1)) and an intramolecular hydrogen bond (C(11)–H(11)···N(1)) are observed in the crystal structure. These interactions play an important role in the stacking of the ions.

It is worth noting that the average Ni···S bond distance (2.185 Å) in the anion is shorter than that for Complex **1**. There is a dihedral angle of 3.4° between the planar NiS₄ group and the C(1)N(1)S(3)N(2)C(2) (tdas²⁻) mean plane. For the [BrFBzPz]⁺ ion in Complex **2**, the dihedral angle between the C(9)–C(8)–N(3) reference plane and phenyl ring is 96.5°. The angle for the pyridine ring is 71.3°,
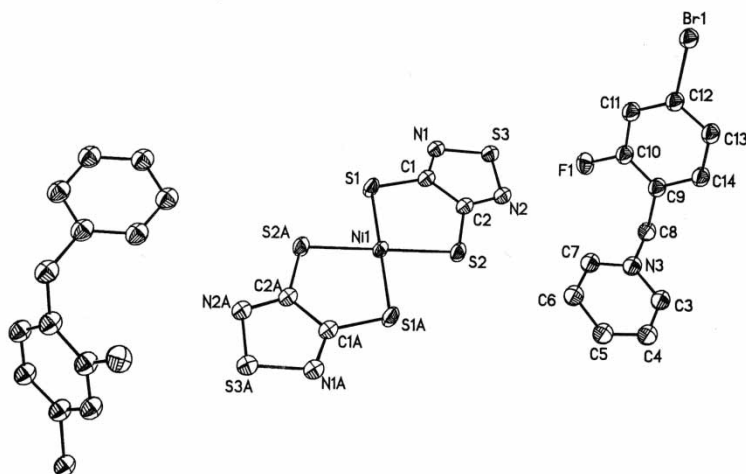
FIGURE 3   ORTEP view with H atom numbering scheme for **2**; 30% probability ellipsoids are shown.

TABLE IV Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for [BrFBzPz]$_2$[Ni(tdas)$_2$]

| Atom	x/a	y/b	z/c	U(eq)[a]
Ni(1)	1/2	0	0	0.0329(2)
S(1)	0.35783(12)	0.90850(9)	0.81381(8)	0.0465(3)
S(2)	0.63607(12)	0.81493(9)	0.98522(8)	0.0477(3)
S(3)	0.46886(12)	0.50637(9)	0.65385(8)	0.0489(3)
N(1)	0.3648(4)	0.6450(3)	0.6584(3)	0.0470(9)
N(2)	0.5859(4)	0.5729(3)	0.7915(3)	0.0469(9)
N(3)	0.8161(4)	0.2652(3)	0.9411(3)	0.0539(11)
Br(1)	1.18947(5)	0.22355(4)	0.39006(4)	0.0554(1)
F(1)	0.6240(3)	0.2297(2)	0.6388(2)	0.0667(8)
C(1)	0.4239(5)	0.7411(3)	0.7632(3)	0.0450(11)
C(2)	0.5495(5)	0.7004(3)	0.8397(3)	0.0449(11)
C(3)	0.9148(5)	0.2566(4)	1.0368(4)	0.0546(12)
C(4)	0.9464(5)	0.3684(4)	1.1445(4)	0.0560(12)
C(5)	0.8733(5)	0.4889(4)	1.1546(4)	0.0570(12)
C(6)	0.7708(5)	0.4965(4)	1.0533(4)	0.0566(12)
C(7)	0.7439(5)	0.3830(4)	0.9477(4)	0.0546(12)
C(8)	0.7840(5)	0.1435(4)	0.8242(4)	0.0546(12)
C(9)	0.8844(5)	0.1607(4)	0.7176(4)	0.0539(11)
C(10)	0.8021(5)	0.2059(4)	0.6300(4)	0.0550(12)
C(11)	0.8863(5)	0.2260(4)	0.5316(4)	0.0545(12)
C(12)	1.0651(5)	0.2002(4)	0.5242(4)	0.0537(11)
C(13)	1.1537(5)	0.1529(4)	0.6069(4)	0.0537(11)
C(14)	1.0638(5)	0.1344(4)	0.7033(4)	0.0537(11)

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

which is markedly different from the situation in Complex **1**. The pyridine ring and the phenyl ring make a dihedral angle of 72.6°. Ni(tdas)$_2$ anions form separated columns along the *c* axis of the crystals as shown in Fig. 4. It is inferred that adding the substituent fluorine group in the *ortho*-position of the benzyl ring of the cation has a significant influence on the crystal packing pattern in these complexes.

TABLE V   Selected bond lengths (Å) and bond angles (°) for [BrFBzPz]$_2$[Ni(tdas)$_2$]

Ni(1)–S(1)	2.186(1)	S(2)–Ni(1)–S(1)	93.74(3)
Ni(1)–S(2)	2.183(1)	S(1)–Ni(1)–S(2^i)	82.26(3)
S(1)–C(1)	1.741(4)	Ni(1)–S(1)–C(1)	102.69(12)
S(2)–C(2)	1.737(3)	Ni(1)–S(2)–C(2)	102.52(12)
N(1)–C(1)	1.133(5)		
N(2)–C(2)	1.130(4)		
N(1)–S(3)	1.660(3)		
N(2)–S(3)	1.654(3)		
C(1)–C(2)	1.424(5)		

Symmetry code: $i = -x+1, y+2, -z+2$.
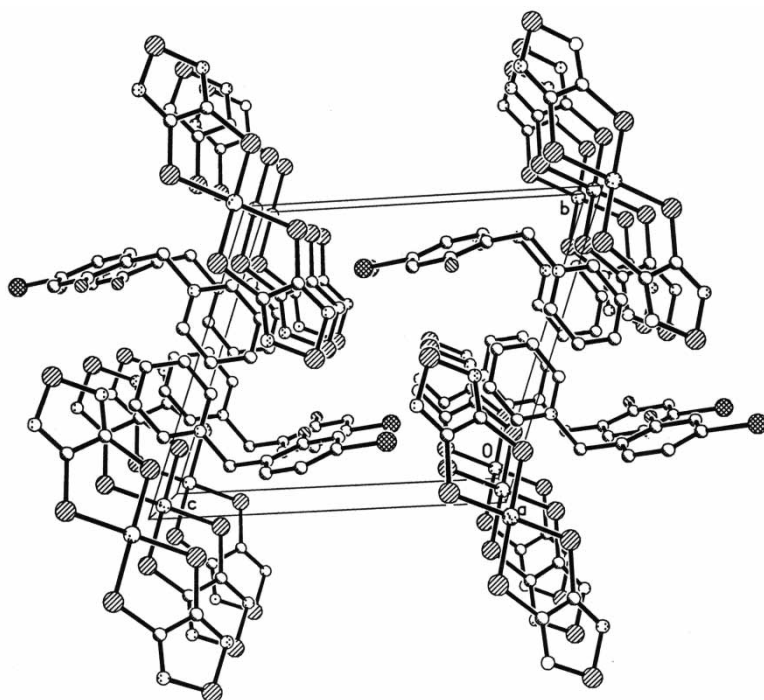
FIGURE 4   Packing of **2** in the unit cell, viewed down the *a* axis.

Infrared Spectra

In the IR spectrum of Complex **1**, ν(C–H) bands of aromatic rings are seen at 3076 (s) and 3046 (s) cm^{-1}. Bands at 1629 (s), 1590 (m) and 1493(s) cm^{-1} can be assigned to ν(C=N) and ν(C=C) of the pyridine and phenyl rings. The band at 579 cm^{-1} originates from ν(C–Br); ν(C=C) of tdas^{2-} is at 1471 (vs) cm^{-1} and the band at 856 (m) cm^{-1} results from ν(C–S).

For Complex **2**, bands at 3081 (s) and 3046 cm^{-1} are assigned to the C–H stretching in the aromatic rings. The ν(C=N) and ν(C=C) bands for the pyridine and phenyl rings are located at 1630 (s), 1605 (m) and 1576 (s) cm^{-1}. Bands at 938 (m) and 598 (s) cm^{-1} originate from ν(F–C) and ν(Br–C); ν(C=C) of mnt^{2-} is at 1481 (vs) cm^{-1} and the band at 876 (m) cm^{-1} results from ν(C–S).

Supplementary Material

Full lists of crystallographic data are available from the Cambridge Crystallographic Data Centre (CCCD-227063 and CCDC-227062).

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