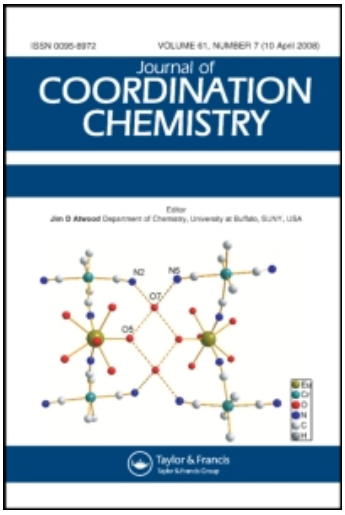

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Preparation and 2D network structure of $[DiClBzMePz]_2[Ni(mnt)_2]$ (DiClBzMePz = 1-(2',4'-dichlorobenzyl)-2-methylpyrazinium, mnt^{2-} = maleonitriledithiolate)

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Preparation and 2D network structure of $[DiClBzMePz]_2[Ni(mnt)_2]$ (DiClBzMePz = 1-(2′,4′-dichlorobenzyl)-2-methylpyrazinium, mnt^{2-} = maleonitriledithiolate)

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The synthesis and crystal structure of a novel ion-pair complex, 1-(2′,4′-dichlorobenzyl)-2-methylpyrazinium-bis(maleonitriledithiolate)nickelate(II), are reported. The compound is triclinic, space group $P\bar{1}$ with $a = 9.079(2)$, $b = 10.154(2)$, $c = 11.243(2)$ Å, $\alpha = 81.58(1)$, $\beta = 69.63(1)$, $\gamma = 68.02(1)^\circ$, $Z = 1$. The $[Ni(mnt)_2]^{2-}$ anion exhibits a relatively planar structure and the cation, $[DiClBzMePz]^+$, adopts a conformation where both the phenyl ring and the pyrazine ring are twisted with respect to the C(10)–C(9)–N(3) reference plane. In the solid state, the cations (D) and anions (A) form a 1D alternating column of the type –D1D2A1D1D2A2D1D2– along the *c* axis through π–π and Ni(1)···N(3) interactions between $Ni(mnt)_2^{2-}$ and $[DiClBzMePz]^+$. Extensive hydrogen bonding further stabilizes a 2D structure.

Keywords: 1-(2′,4′-dichlorobenzyl)-2-methylpyrazinium; Bis(maleonitriledithiolate) nickelate(II); π–π interactions; 2D network structure

1. Introduction

Square-planar $M(dithiolene)_2$ complexes with inorganic and organic cations have been widely studied due to their physical properties and applications in the areas of conducting and magnetic materials, non-linear optics and so on [1, 2]. One of the most studied classes concerns complexes containing $[M(mnt)_2]^{n-}$ (M = Ni, Pd, Pt, mnt^{2-} = maleonitriledithiolate ion). In this series, different counter ions influence

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stacking modes and physical properties [3–5]. This interest, encouraged by the discovery that $NH_4 \cdot Ni(mnt)_2 \cdot H_2O$ possesses ferromagnetic ordering [6], has spurred the development of $M(mnt)_2$ chemistry. Recently, in studies of complexes containing the $Ni(mnt)_2$ anion, it was found that the topology and size of the counter ions play an important role in crystal packing and resulting structural motifs [7–14]. Here we report the synthesis and crystal structure of such a complex containing a pyrazinium cation.

2. Experimental

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

2.1. *Materials and synthesis*

2,4-Bichlorobenzyl bromide and 2-methylpyrazine were purchased from Aldrich and used without further purification. [1-(2′,4′-dichlorobenzyl)]-2-methylpyrazinium bromide ([DiClBzMePz]Br) and disodium maleonitriledithiolate (Na_2mnt) were synthesized following published procedures [15, 16]. $[DiClBzMePz]_2[Ni(mnt)_2]$ was prepared by direct combination of 1 : 2 : 2 molar equivalents of $NiCl_2 \cdot 6H_2O$, Na_2mnt and [DiClBzMePz]Br in H_2O. A red precipitate was filtered off, washed with water and dried under vacuum. Yield: 91%. Anal. Calcd for $C_{32}H_{22}N_8NiCl_4S_4$ (%): C, 45.36; H, 2.62; N, 13.22. Found: C, 45.28; H, 2.65; N, 13.14.

2.2. *Structure determination*

Brown single crystals suitable for X-ray analysis were grown from CH_3CN by slow evaporation during one week. A crystal having approximate dimensions $0.40 \times 0.3 \times 0.20$ mm was selected for indexing and intensity data were collected on a Siemens Smart CCD area detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) with the ω scan mode within the range $1.93 < \theta < 28.05°$. Space group, lattice parameters, and other relevant information are listed in table 1. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques using SHELXTL [17]. All non-hydrogen atoms were refined with anisotropic thermal parameters. H atoms were placed in calculated positions, assigned fixed isotropic displacement parameters equal to 1.2 times the equivalent isotropic U value of the attached atom, and allowed to ride.

3. Results and discussion

In the IR spectrum of the complex, ν(C–H) bands of aromatic rings appear at 3062 and 3034 cm^{-1}. Very strong characteristic bands due to ν(C≡N) of nitrile groups are seen at 2214 and 2198 cm^{-1}. Bands at 1630, 1597, 1568, 1543 and 1480 cm^{-1} can be assigned to ν(C=N) and ν(C=C) of phenyl and pyrazine rings. Bands at 1481, 951,

Table 1. Crystal data and structure refinement details for the complex.

Chemical formula	$C_{32}H_{22}N_8NiCl_4S_4$
Formula weight	847.34
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions (Å, °)	
a	
b	9.079(2)
c	10.154(3)
α	11.243(2)
β	81.58(1)
γ	69.63(1)
Volume (Å^3)	68.02(1)
Z	900.9(3)
Density (calculated) (Mg m^{-3})	1
Absorption coefficient (mm^{-1})	1.562
$F(000)$	430
θ range for data collection (°)	1.93–28.05
Index ranges	$-11 \le h \le 11$, $-7 \le k \le 13$, $-13 \le l \le 14$
Reflections collected	5508, 4021 ($R_{int} = 0.034$)
Data/restraints/parameters	4021/0/224
Goodness of fit on F^2	1.060
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0463$, $wR_2 = 0.0758$
R indices (all data)	$R_1 = 0.0674$, $wR_2 = 0.0787$
Largest diff. peak and hole (e Å^{-3})	0.63 and −0.44

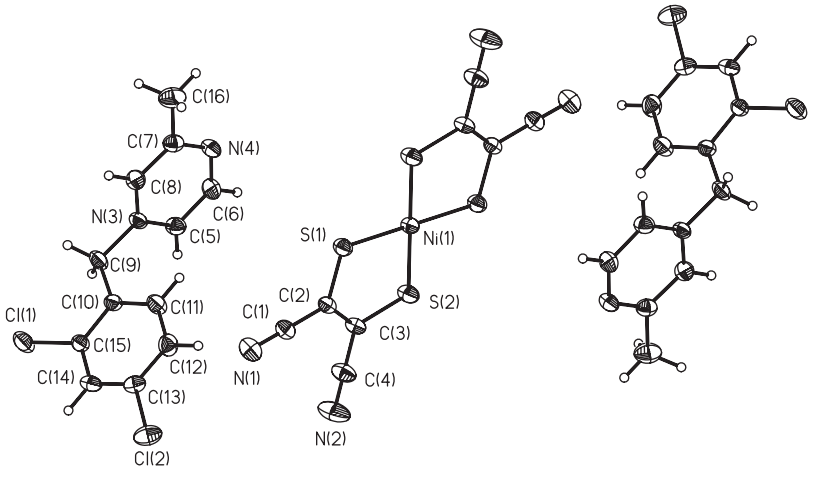

Figure 1. An ORTEP plot (30% probability ellipsoids) showing the molecular structure of the complex.

and 545 cm^{-1} can be assigned to ν(C=C), ν(C–S) and ν(C–Cl). Bands of [DiClBzMePz]$^+$ occur at 710 and 626 cm^{-1}.

An ORTEP diagram of the complex with the atom numbering scheme is depicted in figure 1. Relevant bond lengths and bond angles are listed in table 2. The asymmetric unit consists of a [Ni(mnt)]$^{2-}$ anion and two [DiClBzMePz]$^+$ cations.

Table 2. Selected bond lengths (Å) and bond angles (°) for the complex.

Ni1–S2	2.174(1)	S2–Ni1–S1	92.19(3)
Ni1–S1	2.168(7)	S2#1–Ni1–S1	87.81(3)
S1–C2	1.733(3)	C2–S1–Ni1	103.36(13)
S2–C3	1.746(2)	C3–S2–Ni1	103.28(10)
N1–C1	1.164(5)		
N2–C4	1.153(4)		
C1–C2	1.389(5)		
C2–C3	1.359(5)		
C3–C4	1.391(4)		

Symmetry codes for #1: $-x+1, -y, -z+2$.

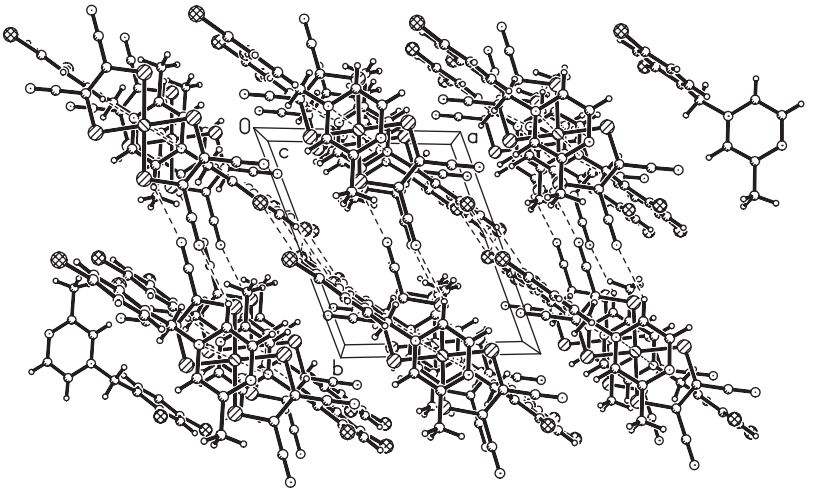

Figure 2. Packing diagram for the complex viewed along the *c* axis.

For $[Ni(mnt)]^{2-}$ anion, four sulfur atoms define a plane and nickel exhibits square-planar coordination geometry. The five-membered nickel-containing rings are slightly puckered, as has been found in other $[Ni(mnt)_2]^{n-}$ structures [18]. CN groups are slightly displaced from the plane; deviations from the plane are 0.0607 Å for N(1) and 0.0543 Å for N(2). The average Ni–S bond distance is 2.171(1) Å and the average S–Ni–S bond angle within the five-membered rings is 90.0°; these compare well with those found in other $[Ni(mnt)]^{2-}$ complexes [19]. It is worth noting that the Ni–S and C–S bond distances within the anion are slightly longer than those of $[Ni(mnt)]^{-}$ complexes [20]. The $[DiClBzMePz]^{+}$ cation adopts a conformation where both the phenyl ring and pyrazine ring are twisted with respect to the C(10)–C(9)–N(3) plane. The phenyl ring and the pyrazine rings are planar. Dihedral angles that pyrazine rings and phenyl rings make with the reference plane are 86.1 and 3.6°, respectively. The phenyl and pyrazine rings make a dihedral angle of 85.2°. The plane defined by S(1)S(2)S(1A)S(2A) makes dihedral angles with the phenyl and pyrazine rings of 87.2 and 2.3°, respectively.

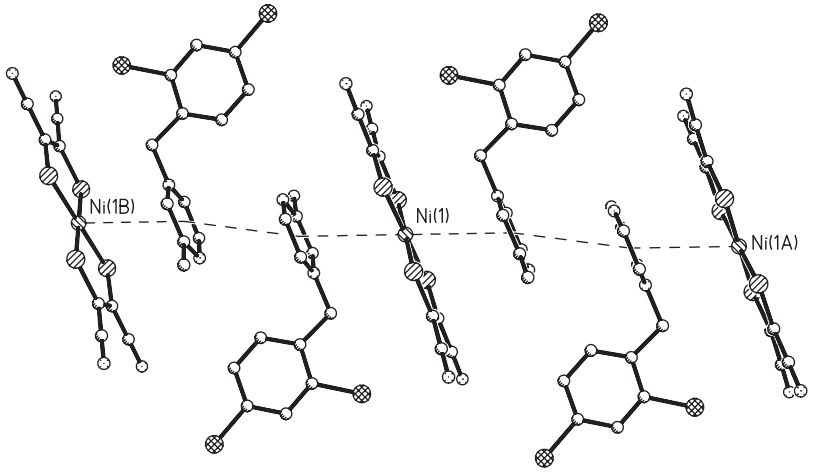

Figure 3. The alternating column of anions and cations in the lattice along the *c* axis.

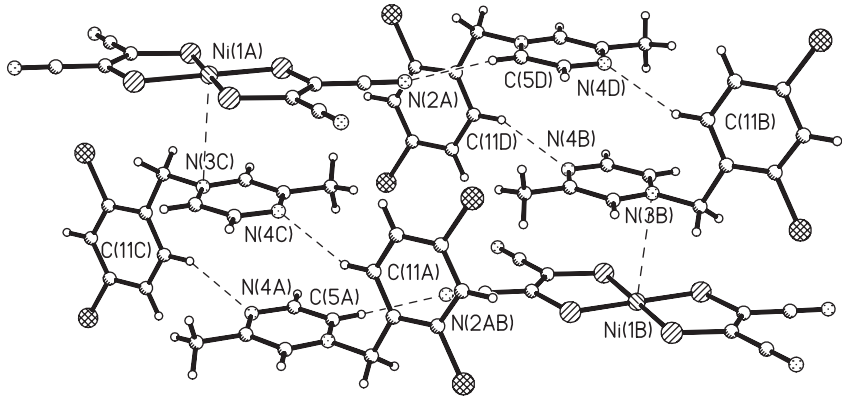

Figure 4. Intermolecular contacts between anions and cations.

In the solid state, $[Ni(mnt)_2]^{2-}$ anions (A) and $[DiClBzMePz]^{+}$ cations (D) are alternately stacked along the *c* axis of the unit cell (figure 2) to form a 1D alternating column of the type –D1D2A1D1D2A2D1D–, in which two anion–cation interactions and one cation–cation interaction are found. The first involves π–π stacking between the planar $[Ni(mnt)_2]^{2-}$ anions and neighbouring pyrazine rings of $[DiClBzMePz]^{+}$ cations with a distance between Ni(1) and the centre of the pyrazine ring of 3.642 Å. In addition, Ni(1)···N(3) interactions are evident with the Ni(1)···N(3) distance being 3.389 Å. Finally, further π–π stacking involves two neighbouring pyrazine rings of the cations with the distance of between N(4) and the centre of pyrazine rings being 3.491 Å, as shown in figures 3 and 4. It should be noted that there are two non-classical hydrogen bonds between anion and cation. The intermolecular contact distance between N(2) and C(5) $(1-x, 1-y, 1-z)$ is 3.390(4) Å, and that between N(4) and C(11) $(1-x, -y, 1-z)$ is 3.444(4) Å. The hydrogen atom distances associated

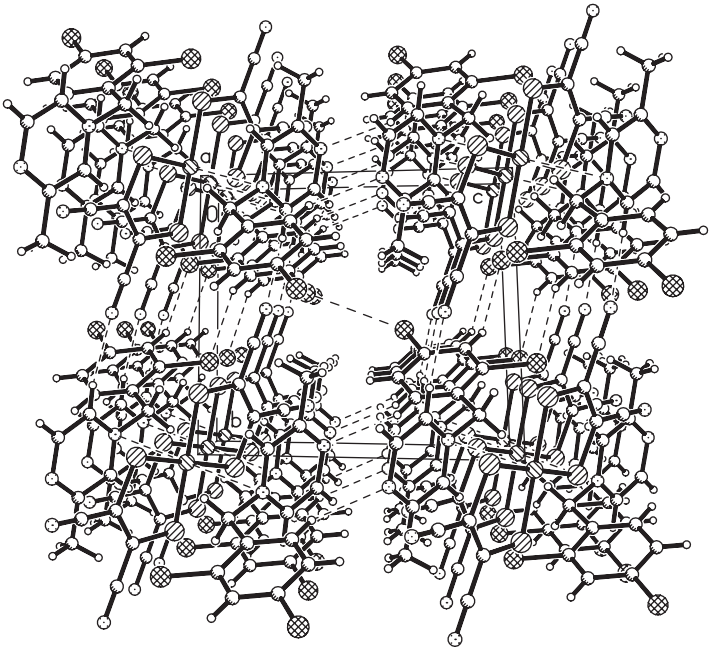

Figure 5. The 2D network structure in the lattice formed by the combination of weak interactions.

with these contacts are N(2)···H(5) 2.560, and N(4)···H(11) 2.580 Å. These distances are indicative of significant van der Waals interactions. The combination of C(5)–H(5)···N(2), C(11)–H(11)···N(4), Ni(1)···N(3) and π–π interactions in the crystal structure generates a 2D network (figure 5).

Supplementary material

Full lists of crystallographic data are available from the Cambridge Crystallographic Data Centre (No. CCDC-226803).

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