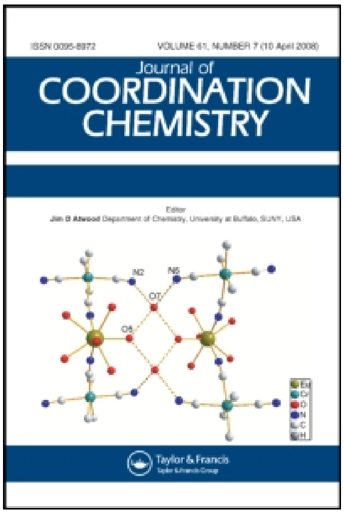

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Preparation, crystal structure and magnetic properties of a maleonitriledithiolate salt of the 1-methyl-3-benzylimidazolium cation with a novel structural motif

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Preparation, crystal structure and magnetic properties of a maleonitriledithiolate salt of the 1-methyl-3-benzylimidazolium cation with a novel structural motif

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A new ion-pair complex, 1-methyl-3-benzylimidazolium bis(maleonitriledithiolato)nickelate(III), has been synthesized and characterized by IR spectroscopy and X-ray crystallography. The compound crystallizes in the triclinic space group $P\bar{1}$ with $a = 13.280(1)$, $b = 14.906(1)$, $c = 17.949(2)$ Å, $\alpha = 108.02(1)$, $\beta = 101.55(1)$, $\gamma = 90.51(1)^\circ$ and $Z = 6$. There are three inequivalent $[Ni(mnt)_2]^-$ anions in the structure of the complex, two of them are stacked along the b axis with an AACC-type repeat unit, the other lies approximately orthogonal to the stack. Anions form three kinds of dimers with short Ni···Ni distances, leading to such strong spin coupling interactions that the complex is diamagnetic.

Keywords: 1-Methyl-3-benzylimidazolium; Bis(maleonitriledithiolato)nickelate(III) complex; X-Ray structure; Magnetic properties

1. Introduction

Transition metal complexes of maleonitriledithiolate (mnt) have been widely investigated because of their novel electronic, optical and magnetic properties and, especially, the discovery of ferromagnetic ordering in $(NH_4)[Ni(mnt)_2] \cdot H_2O$ below 4.5 K in 1996 has stimulated renewed attention on $M(mnt)_2$ based compounds [1–5]. Our previous work on a series of complexes formed by $[M(mnt)]^{n-}$ and benzylpyridinium derivatives has shown that these complexes exhibit low-dimensional character in structure and magnetism. The stacking $[Ni(mnt)_2]^-$ anions can be tuned by systemically varying the substituents of the aryl ring and thus lead to versatile magnetic exchange properties [6–14]. In order to get further information on the role

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of the counter ions and low-dimensional properties in these complexes, we adopted a strategy using a five-membered ring (imidazole) instead of the six-membered ring (pyridine) in the cation. Here we report the synthesis, crystal structure and magnetic properties of a nickel(III) mnt complex using the 1-methyl-3-benzylimidazolium cation.

2. Experimental

2.1. *Measurements*

Elemental analyses for carbon, hydrogen and nitrogen were performed on a Perkin-Elmer 240 instrument. Infrared spectra were obtained with KBr pellets in the 4000–400 cm^{-1} region using an IFS66VFT-IR spectrophotometer. Magnetic susceptibilities were determined down to the liquid nitrogen temperature on a CAHN–2000 Faraday magnetometer.

2.2. *Materials and preparation*

All chemicals and solvents were of reagent grade and were used without further purification. 1-Methyl-3-benzylimidazolium bromide ([BzIm]Br) [15] and disodium maleonitriledithiolate (Na_2mnt) [16] were synthesized following published procedures.

2.2.1. [BzIm]$_2$[Ni(mnt)$_2$]. This compound was prepared by the direct combination of 1 : 2 : 2 mol equivalents of $NiCl_2.6H_2O$, Na_2mnt and [BzIm]Br in H_2O. A red precipitate was filtered off, washed with water and dried under vacuum. Yield: 89% (Found: C, 52.49; H, 3.86; N, 16.32. Calc. for $C_{30}H_{26}N_8NiS_4$: C, 52.56; H, 3.82; N, 16.35%).

2.2.2. [BzIm] [Ni(mnt)$_2$]. A MeCN solution (10 cm^3) of I_2 (150 mg, 0.59 mmol) was slowly added to a MeCN solution (20 cm^3) of [BzIm]$_2$[Ni(mnt)$_2$] (0.69 mg, 1.0 mmol), and stirred for 20 mins. MeOH (90 cm^3) was then added, and the mixture allowed to stand overnight. The microcrystals that formed were filtered off, washed with MeOH and dried under vacuum. Yield: 87% (Found: C, 44.51; H, 2.58; N, 16.34. Calc. for $C_{19}H_{13}N_6NiS_4$: C, 44.54; H, 2.56; N, 16.40%). IR (cm^{-1}): 3138(m), 3107(w), 3080(m), 2204(vs), 1560(m), 1459(m), 1155(s), 715(s).

2.3. *Structure determination of the title compound*

Suitably sized single crystals of the title compound were obtained upon slow evaporation of a MeOH solution of the compound at room temperature. A dark-red single crystal of the title complex, having approximate dimensions $0.30 \times 0.20 \times 0.20\,mm^3$, was selected for X-ray structure measurements. All measurements were made on a Siemens Smart CCD area detector equipped with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å) using the ω-2θ scan mode. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. All H atoms were placed in calculated positions, assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic U

Table 1. Space group, lattice parameters, and other relevant crystallographic information.

Chemical formula	$C_{19}H_{13}N_6NiS_4$
Formula weight	512.30
Temperature, K	293(2)
Wavelength, Å	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions, Å, °	$a = 13.280(1)$ $\alpha = 108.02(1)$ $b = 14.906(1)$ $\beta = 101.55(1)$ $c = 17.949(2)$ $\gamma = 90.51(1)$
Volume, Å^3	3300.8(6)
Z	6
Density (calculated), mg m^{-3}	1.546
Absorption coefficient, mm^{-1}	1.280
Diffractometer/scan	Simens SMART/CCD area detector
$F(000)$	1566
θ range for data collection, °	1.8 to 25.0
Index ranges	$-13 \leq h \leq 15$, $-17 \leq k \leq 17$ $-21 \leq l \leq 21$
Reflections collected	16530
Independent reflections	11432 [$R_{\text{int}} = 0.062$]
Absorption correction	Empirical
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	11432/0/814
Goodness of fit on F^2	1.004
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0435$, $wR2 = 0.0914$
R indices (all data)	$R1 = 0.0643$, $wR2 = 0.0952$
Largest diff. peak and hole	0.50 and −0.49 e Å^{-3}

value of the attached atom, and allowed to ride on their respective parent atoms. All calculations were performed using the Bruker SHELXTL program [17]. Space group, lattice parameters, and other relevant information are listed in table 1.

3. Results and discussion

3.1. *IR characterization*

In the IR spectrum of the complex, ν(C−H) bands of aromatic rings are found at 3138, 3107, 3080 and 715 cm^{-1}. The very strong, characteristic band due to ν(C≡N) of nitrile groups is seen at 2204 cm^{-1}. Bands at 1459 and 1560 cm^{-1} can be assigned to ν(C=N) and ν(C=C) of the benzimidazole ring and phenyl rings. Bands at 1455 can be assigned to ν(C−N) of the imidazole rings.

3.2. *Crystal structure*

The title complex crystallizes in the triclinic space group $P\bar{1}$. An ORTEP diagram of the asymmetric unit with the atom numbering scheme is shown in figure 1. Relevant bond lengths and angles are listed in table 2. There are three inequivalent [BzIm]$^+$ cations and three inequivalent [Ni(mnt)$_2$]$^-$ anions in the strucure of the complex. In the anions, the nickel atom exhibits square-planar geometry with four sulfur atoms. The five-membered, nickel-containing rings are slightly puckered, as found for other [M(mnt)$_2$]$^{n-}$ structures [18]. The average S–Ni–S bond angle in the five-

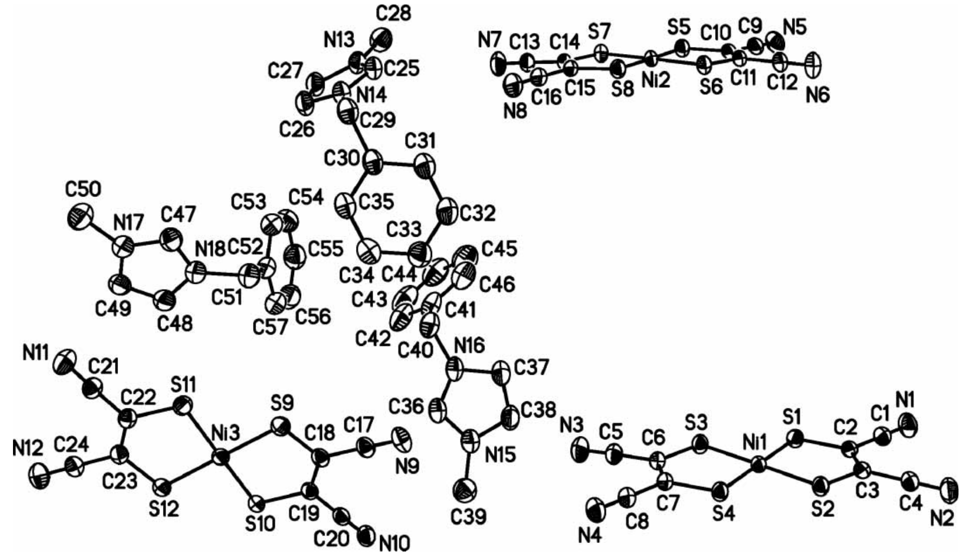

Figure 1. ORTEP diagrams (30% probability ellipsoids) of the asymmetric unit with the atom numbering scheme.

Table 2. Relevant bond lengths (Å) and angles (°).

Ni1–S1	2.146(1)	Ni1–S2	2.141(1)
Ni1–S3	2.146(1)	Ni1–S4	2.145(1)
Ni2–S8	2.143(1)	Ni2–S7	2.139(1)
Ni2–S6	2.138 (1)	Ni2–S5	2.138(1)
Ni3–S10	2.138(1)	Ni3–S12	2.143(1)
Ni3–S9	2.146(1)	Ni3–S11	2.139(1)
S1–Ni1–S2	92.21(4)	S3–Ni1–S4	92.40(4)
S5–Ni2–S6	92.58(4)	S7–Ni2–S8	92.89(4)
S11–Ni3–S12	92.05(4)	S9–Ni3–S10	92.34(4)
N14–C29–C30	111.2(3)	N16–C40–C41	111.0(4)
N18–C51–C52	112.2(3)		

membered rings is 92.41(4)°. The average Ni–S bond distance is 2.142 (1) Å, slightly shorter than that in the $[Ni(mnt)_2]^-$ complex with pyridinium cations [7–14]. Actually, the anion is not planar and the CN groups bend away from the plane defined by the four sulfur atoms. The $[BzIm]^+$ cations, adopts a conformation where both the benzene ring and imidazole rings are twisted to the reference plane defined by N14–C29–C30, N16–C40–C41, and N18–C51–C52, respectively.

In the solid state, two of the Ni groups are stacked along the *b* axis with an AACC-type repeat unit. This gives rise to three different overlaps characterized by different short contacts between the stacked molecules (see figures 2 and 3). AA′ overlap and CC′ overlap are based on a nickel-over-sulfur arrangement with different short S···Ni contacts. AC overlap involves a nickel-over-nickel arrangement with short Ni···Ni and S···S contacts to form an AC dimer. There is another non-equivalent $[Ni(mnt)_2]^-$ unit (B, in figure 3), lying approximately orthogonal to the stack and forming a BB dimer with short Ni···Ni, Ni···S and S···S contacts. The anions connect with neighbouring ones to form a 2D-network via Ni···Ni, Ni···S and S···S

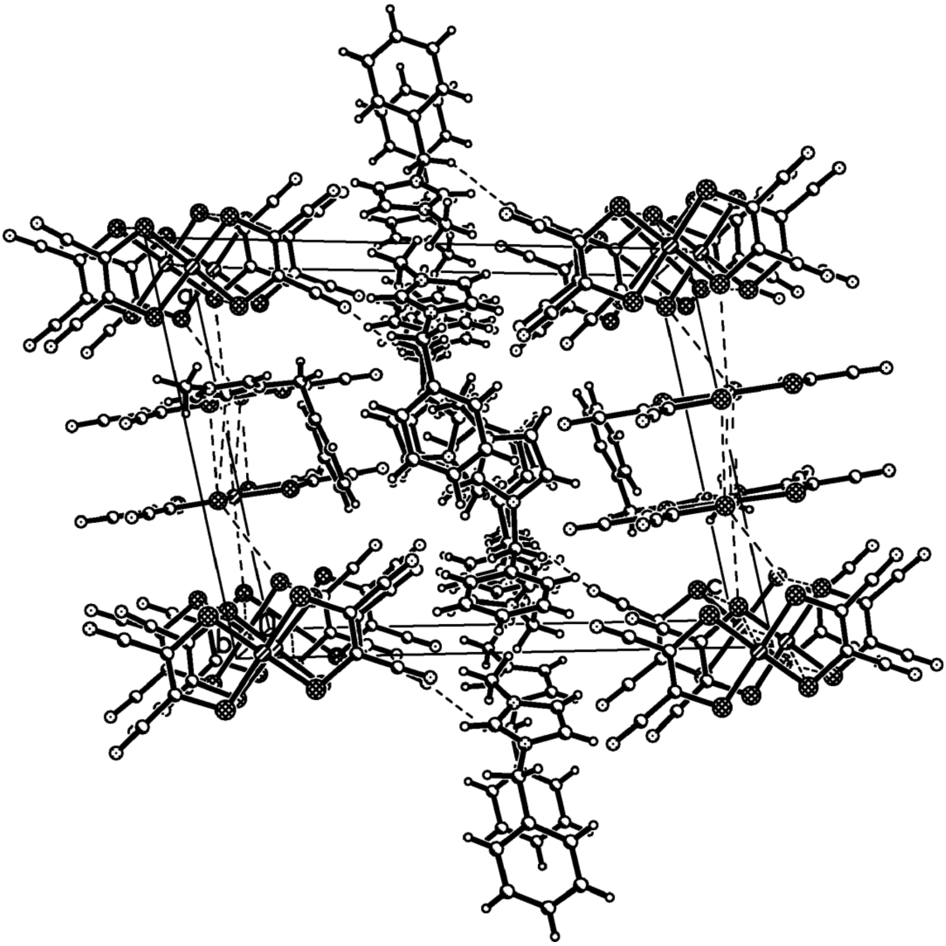

Figure 2. Structure of the title complex viewed along the *b* axis.

interactions (see figure 3). By close inspection of the 2D-network, 12 anions constitute a cyclic dodecamer (ACCABBACCABB). Two [MeBzBzim]$^+$ cations located at the centre of the cyclic dodecamer form an anion–cation mixed-layer in the structure. Other cations lying between the mixed-layers form a cationic layer (see figure 2). The layers are stacked along the *c* axis. To the best of our knowledge, the stacking model in the title complex is unique in the chemistry of [M(mnt)$_2$]$^-$; such complexes with planar aromatic counterions nearly always adopt an arrangement of [M(mnt)$_2$]$^-$ in segregated or mixed stacks, except in the case of [Etpy][Ni(mnt)$_2$] [3], which has a similar structure to the title complex but shows a CAC-type arrangement in [M(mnt)$_2$]$^-$ stacks. In addition, some non-classical hydrogen bonds are found in the complex; contacts and angles are listed in table 3.

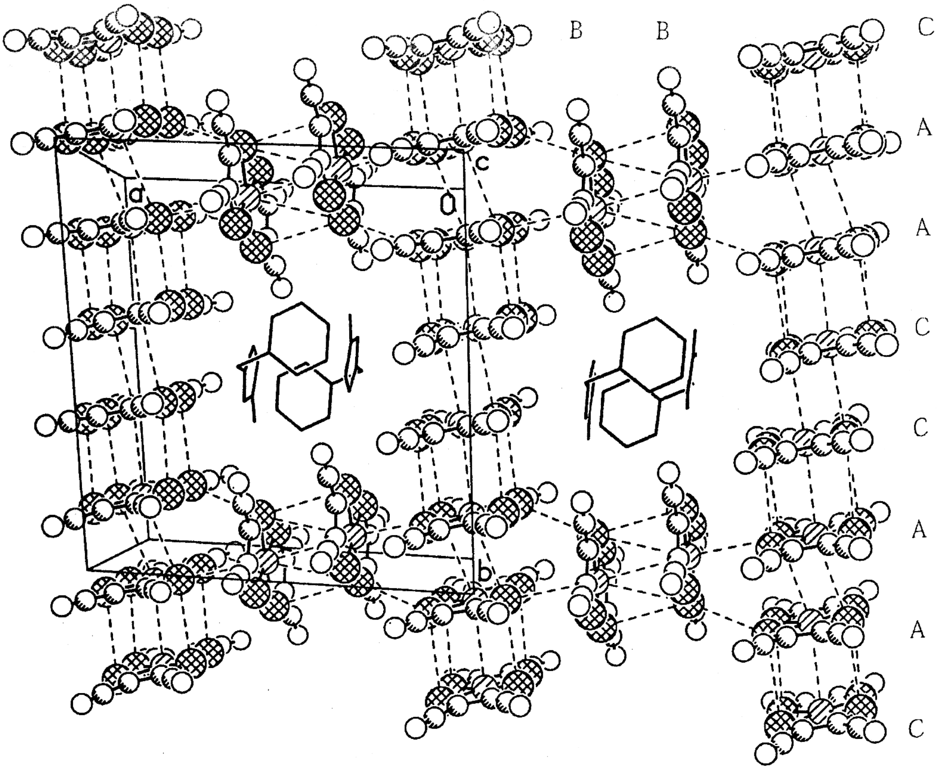

Figure 3. Molecular packing scheme of the complex showing the 2-D network generated via Ni···Ni, Ni···S and S···S interactions.

Table 3. Hydrogen-bonding geometry (Å, °).

D–H···A	D–H	H···A	D–H···A	Degree
C27–H27···N6$^{\mathrm{i}}$	0.9300	2.6200	3.495(6)	157.00
C37–H37···N6$^{\mathrm{ii}}$	0.9300	2.5200	3.179(5)	128.00
C40–H40B···N8$^{\mathrm{iii}}$	0.9700	2.5400	3.383(5)	145.00
C47–H47···N10$^{\mathrm{iv}}$	0.9300	2.2900	3.191(5)	162.00

Symmetry codes: (i) x, y, $1+z$; (ii) $1-x$, $1-y$, $-z$; (iii) $1-x$, $1-y$, $1-z$; (iv) x, $-1+y$, z.

3.3. *Magnetic susceptibility*

The magnetic susceptibility of the title complex has been investigated in the temperature range 75–300 K. The quite short Ni–Ni distances of the dimers lead to such strong spin coupling interactions that the complex is diamagnetic.

Supplementary material

Full lists of crystallographic data are available from the Cambridge Crystallographic Data Center (No. CCDC-232679).

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