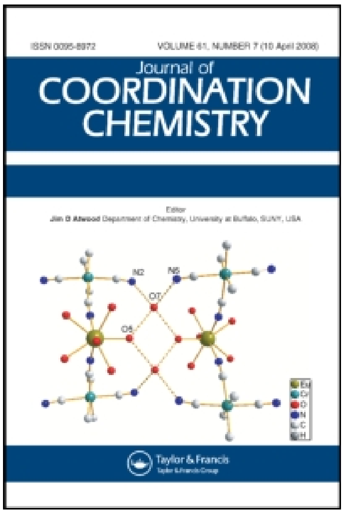

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Synthesis, crystal structure and magnetic properties of a new ion-pair complex benzyltriphenylphosphinium-bis(maleonitriledithiolato)nickel

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Synthesis, crystal structure and magnetic properties of a new ion-pair complex benzyltriphenylphosphinium-bis(maleonitriledithiolato)nickel

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The crystal structure of a new ion-pair complex, benzyltriphenylphosphinium-bis(maleonitrile-dithiolato)nickel (**1**) ([BzTPP][Ni(mnt)$_2$]) was determined. The Ni(mnt)$_2^-$ anions and [BzTPP]$^+$ cations of complex **1** stack into well-segregated columns in the solid state, and the Ni(III) ions form a one-dimensional alternating chain with Ni$\cdots$Ni distances between 4.192 and 4.386 Å within a Ni(mnt)$^{2-}$ anion through Ni$\cdots$S, S$\cdots$S or $\pi\cdots\pi$ interactions. Anion–anion, anion–cation and cation–cation contacts may play important roles in crystal packing and stabilizing. Variable-temperature magnetic susceptibilities of **1** in the temperature range 75–300 K have been interpreted in terms of a simple dimer model approximation ($H = 2JS_AS_B$). Complex **1** exhibits a strong antiferromagnetic interaction, with $g = 1.93$ and $J = -273.1\,\text{cm}^{-1}$.

Keywords: Benzyltriphenylphosphinium; Bis(maleonitriledithiolate)nickelate(III) complex; Crystal structure; Antiferromagnetic interaction

1. Introduction

Considerable interest in maleonitriledithiolate (mnt^{2-}) transition metal complexes exist because of their applications as magnetic, nonlinear optical and conducting materials [1–4]. In particular, the discovery in 1996 of the ferromagnetic complex $NH_4 \cdot Ni(mnt)_2 \cdot H_2O$, containing the Ni(mnt)$_2^-$ ion, stimulated study on Ni(mnt)$_2$ complexes as building blocks for new molecular magnets [5]. Considerable efforts have been directed towards preparing organic cations to tune the stacking pattern of the Ni(mnt)$_2^-$ anion to obtain molecular materials with unusual magnetic properties [6–9]. Recently, we have synthesized and structurally characterized a series of ion-pair complexes [RbzPy]$^+$[M(mnt)$_2$]$^-$ ([RbzPy]$^+$ = derivatives of benzylpyridinium, M = Ni or Pt), and

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found that these complexes exhibit versatile magnetic properties such as ferromagnetic ordering at low temperature [10], meta-magnetism [11], magnetic transition from ferromagnetic coupling to diamagnetism [12], spin-Peierls-like transitions [13, 14], weak ferromagnetic coupling due to spin canting [15, 16], and magnetic switching from paramagnetic to diamagnetic [17]. With a view to examining the effects of some larger organic cations on the stacking pattern and magnetic properties of $Ni(mnt)_2$ complexes, in this study we have succeeded in synthesizing the first $Ni(mnt)_2$ complex with the substituted benyltriphenylphosphinium cation $[BzTPP][Ni(mnt)_2]$ (**1**) and investigating its crystal structure and magnetic properties.

2. Experimental

2.1. *Reagents and preparation of the complex*

All reagents and chemicals were purchased from commercial sources and used as received. Benzyltriphenylphosphinium bromide ([BzTPP]Br) was prepared by a literature method [18]. A similar method for preparing $[Bu_4N]_2[Ni(mnt)_2]$ was used to prepare $[BzTPP]_2[Ni(mnt)_2]$ [19].

An acetone solution ($10\,cm^3$) of I_2 (160 mg, 0.62 mmol) was added slowly to an acetone solution ($50\,cm^3$) of $[BzTPP]_2[Ni(mnt)_2]$ (1046 mg, 1 mmol) and the mixture was stirred for 3 h. MeOH ($90\,cm^3$) was then added, and the mixture allowed to stand overnight; 578 mg of black microcrystals formed and were filtered off, washed with MeOH and dried in vacuum (yield: 83.5%). Anal. Calcd for $C_{33}H_{22}N_4NiPS_4$(%): C, 57.24; H, 3.20; N, 8.09. Found: C, 57.10; H, 3.42; N, 7.89. ESI-MS (m/z): 353.3 $[BzTPP]^+$; 338.0 $[Ni(mnt)_2\text{-}H]^-$.

Black single crystals suitable for the X-ray structure analysis were obtained by evaporating a solution of complex **1** in MeCN and *i*-PrOH (1 : 1 v/v) over about 2 weeks at room temperature.

2.2. *Physical methods*

CHN analysis was determined on a Model 240 Perkin Elmer CHN analytical instrument. IR spectra were obtained in the 400–4000 cm^{-1} region with KBr pellets using a VECTORTM 22 FTIR spectrophotometer. Electrospray mass spectra (ESI-MS) were determined on a Finnigan LCQ mass spectrograph, sample concentration ca $1.0\,mmol\,dm^{-3}$. Magnetic susceptibility measurements were carried out down to liquid nitrogen temperatures with a CAHN-2000 Faraday-type magnetometer; diamagnetic corrections for the constituent atoms were made with Pascal's constants.

2.3. *Crystallography*

Determination of the unit cell parameters and data collection for complex **1** were performed on a Smart APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073\,Å$) at 293 K in the range 2.3–26.0. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares, using the Bruker program SHELXTL [20]. All nonhydrogen atoms were refined with anisotropic thermal parameters. All H atoms were placed in calculated positions, assigned fixed

Table 1. Crystallographic data for [BzTPP][Ni(mnt)$_2$] (**1**).

CCDC No.	243509
Color/shape	Black/block
Chemical formula	$C_{33}H_{22}N_4NiPS_4$
Crystal size (mm)	$0.3 \times 0.2 \times 0.1$
Space system	Triclinic
Formula weight	692.49
Space group	$P\bar{1}$
a (Å)	8.240(1)
b (Å)	13.922(2)
c (Å)	14.995(2)
α (°)	100.72(1)
β (°)	103.47(1)
γ (°)	101.57(1)
V (Å^3)	1589.2(4)
Z	2
T (K)	293(2)
ρ_{calc} (g cm^{-3})	1.447
λ (Å)	0.71073
2θ range (°)	$4.6 < 2\theta < 52.0$
μ(Mo Kα) (mm^{-1})	0.954
Reflections collected	8643
Unique reflections, R_{int}	6084, 0.013
Observed data [$I > 2\sigma(I)$]	4902
$R1$	0.0632
$wR2$	0.1108
Largest diff. peak and hole (e Å^{-3})	0.26, −0.37

isotropic displacement parameters 1.2 times the equivalent isotropic U-value of the attached atom, and allowed to ride on their respective parent atoms. Details of the X-ray data collection and structure refinement of complex **1** are given in table 1.

3. Results and discussion

3.1. *Structure of the complex*

Complex **1** crystallizes in the triclinic space group $P\bar{1}$. An ORTEP drawing of **1** with nonhydrogen atomic labeling of the asymmetric unit is shown in figure 1. Selected bond parameters and intermolecular contacts for **1** are listed in table 2. The Ni(III) ion in the Ni(mnt)$_2^-$ anion exhibits the expected square-planar coordination geometry. The CN groups of Ni(mnt)$_2^-$ are tipped slightly out of the plane; the deviations from the plane are 0.1858 Å for N(1), −0.0049 Å for N(2), 0.0279 Å for N(3) and 0.0930 Å for N(4). The average Ni–S distance is 2.136(1) Å, and the average S–Ni–S bond angle within the five-membered rings is 90.00(5)°, in good accord with those found in the complex [Ph$_4$P][Ni(mnt)$_2$] [21]. The [BzTPP]$^+$ cation adopts a conformation in which four phenyl rings are twisted relative to the C(28)–C(27)–P(1) reference plane, with dihedral angles of 53.2, 64.9, 87.9 and 77.3° for the C(9)C(10)C(11)C(12)C(13)C(14), C(15)C(16)C(17)C(18)C(19)C(20), C(21)C(22)C(23)C(24)C(25)C(26) and C(28)C(29) C(30)C(31)C(32)C(33) rings, respectively. The interesting structural features of complex **1** are the presence of anion–anion, anion–cation and cation–cation contacts (figure 2), and Ni(mnt)$_2^-$ ions and the [BzTPP]$^+$ cation stack into well-segregated columns along the crystallographic a axis (figure 3). In an anionic stacking column, the Ni $\cdots$ Ni

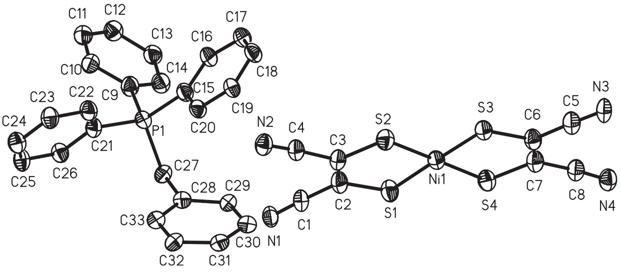

Figure 1. ORTEP plot (30% probability ellipsoids) showing the molecule structure of complex **1**.

Table 2. Selected bond parameters and intermolecular contacts for [BzTPP][Ni(mnt)$_2$] (**1**).

	Bond distance (Å)
Ni(1)–S(1)	2.132(1)
Ni(1)–S(2)	2.143(1)
Ni(1)–S(3)	2.139(1)
Ni(1)–S(4)	2.128(1)
	Bond angle (°)
S(1)–Ni(1)–S(2)	92.68(5)
S(1)–Ni(1)–S(4)	87.12(5)
S(3)–Ni(1)–S(4)	92.50(5)
S(2)–Ni(1)–S(3)	87.70(4)
	Intrachain distance (Å)
Ni···Ni (nearest separation)	4.386, 4.192
Ni···S	3.641, 3.894
S···S	3.701, 3.793
	Interchain distance (Å)
Ni···Ni (nearest separation)	13.566

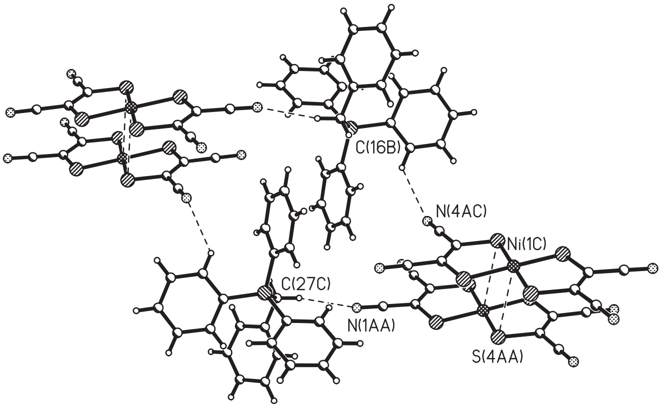

Figure 2. The intermolecular contacts between anions and cations of complex **1**.

distances alternate between 4.192 and 4.386 Å, and the nearest Ni···S and S···S distances are 3.641 and 3.701 Å, respectively. The closest Ni···Ni separation between anion columns is 13.566 Å, which is significantly longer than the Ni···Ni separation within a column. Therefore, each Ni(mnt)$_2^-$ anion can be considered

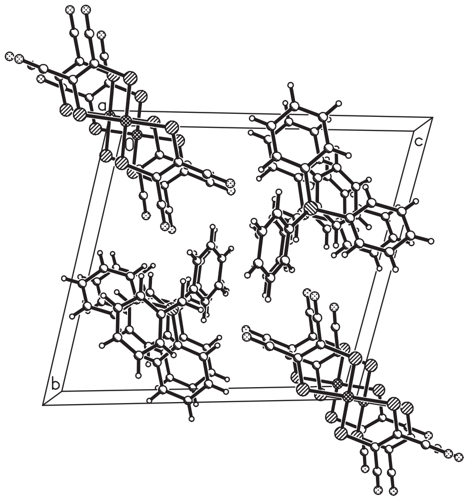

Figure 3. The packing diagram of a unit cell of complex **1** as viewed along the *a*-axis.

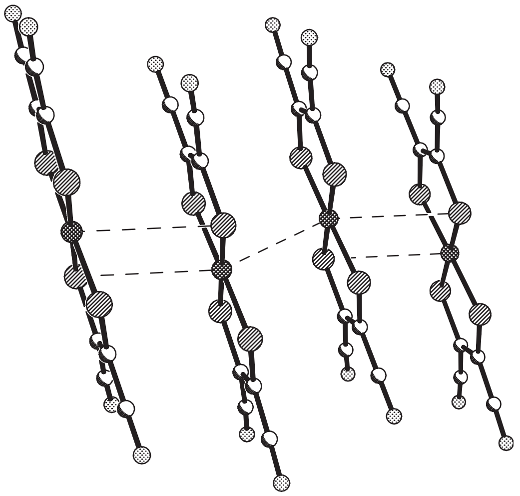

Figure 4. Side view of the anion stacking for complex **1** showing the alternating-space linear chain of $[Ni(mnt)_2]^-$.

as a one-dimensional alternating magnetic chain through intermolecular $Ni \cdots S$, $S \cdots S$ $Ni \cdots Ni$ or $\pi \cdots \pi$ interactions (figure 4). Significant interactions in adjacent cations are the π–π interaction between the conjugated phenyl rings of $[BzTPP]^+$ (the contact distances of C(13) and C(14) atoms of one phenyl ring to the center of neighboring benzene ring are 3.578 and 3.774 Å). It is worth noting that two intermolecular hydrogen bonds between anions and cations were observed in the crystal structure, as shown in figure 2. The intermolecular contacts between N(1) and C(27) $(-x+2, -y+1, -z)$ is 3.541(6) Å, and between N(4) and C(16) $(-x+1, -y, -z)$ 3.292(6) Å, and the hydrogen atoms associated with these atoms have the contacts

N(1)$\cdots$H(27) 2.610 Å and N(4)$\cdots$H(16) 2.580 Å. These anion–anion, anion–cation and cation–cation contacts may play important roles in the crystal packing and stabilization of the complex.

3.2. *IR and electrospray mass spectra*

In the IR spectrum of complex **1**, the bands at 3060.2(w), 3030.3(w) cm^{-1} and 2959.7(w), 2916.6(w) cm^{-1} are assigned to the stretching frequency of C–H in the aromatic rings and methylene, respectively. The very strong $\nu(C\equiv N)$ band is at 2206.9(s) cm^{-1}. The $\nu(C=N)$ and $\nu(C=C)$ bands for the pyridine ring and phenyl ring are located at 1600.7(m), 1587.3(s) and 1494.0(m) cm^{-1}. $\nu(C=C)$ of mnt^{2-} is at 1438.0(s) cm^{-1} and the band at 852.5(m) cm^{-1} results from ν(C–S). The bands at 720.2(m) and 686.5(w) cm^{-1} originate from ν(C–P).

Negative-ion and positive-ion ESI-MS spectra of the complex in MeCN solution show that the mass spectrum is dominated by the 338.0 peak, which is due to $[Ni(mnt)_2\text{-}H]^-$; the peak at 353.3 is assigned to $[BzTPP]^+$.

3.3. *Magnetic susceptibilities*

Variable-temperature magnetic susceptibility measurements of complex **1** performed on a crystalline sample from 298 to 75 K are shown in figure 5 as a plot of $\chi_m T$ *versus* T. Correction for diamagnetism of complex **1** is estimated from Pascal's constants to be -311.62×10^{-6} emu mol^{-1}. The $\chi_m T$ value for **1** is 0.166 emu K mol^{-1} at 300 K, which is significantly less than the calculated spin-only value of 0.375 emu K mol^{-1} for a system composed of noninteracting $g = 2$, $s = 1/2$ spin sites, indicating that there is a strong antiferromagnetic interaction between adjacent $s = 1/2$ Ni(III) spin magnetic centers within the anion chain. When the system cools down, the product $\chi_m T$ decreases rapidly to 0.0136 emu K mol^{-1} at 144 K, and then falls slowly to nearly zero at 75 K. Because of the difference between the Ni$\cdots$Ni distances (4.386 and 4.192 Å) in the nickel(III) ion chains, the magnetic susceptibility data can be

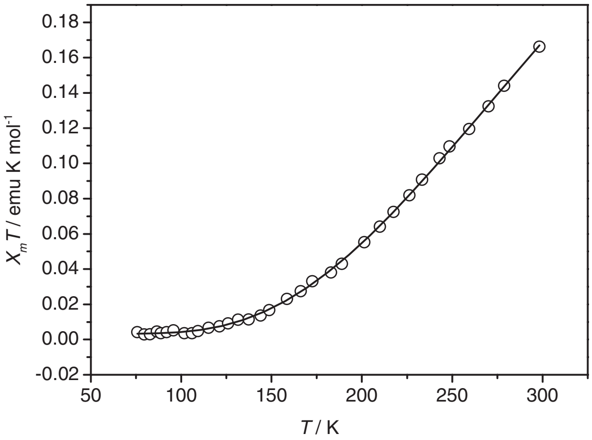

Figure 5. Plot of $\chi_m T$ *vs* T for complex **1**.

analyzed using a simple dimer model approximation (the Hamiltonian being $H = 2JS_AS_B$), equation (1) [22]:

$$\chi_m = (2N\beta^2g^2/kT)\{1/[3 + \exp(-2J/kT)]\}(1-\rho) + (N\beta^2g^2/2kT)\rho \qquad (1)$$

where N, g, k, β and ρ have their usual meanings, and J is the exchange coupling parameter describing the magnetic interaction between any two neighboring $s = 1/2$ spins. The best-fit parameters obtained by least-squares fit are: $g = 1.93$, $J = -273.09\,\text{cm}^{-1}$, $\rho = 4.61 \times 10^{-3}$ and $R = 1.0 \times 10^{-6}$ [R is defined as $\sum(\chi_m T^{\text{calcd}} - \chi_m T_m{}^{\text{obsd}})^2/\sum(\chi_m T^{\text{obsd}})^2$). The low ρ value suggested that the paramagnetic impurities have little effect on the magnetic measurement for **1**. The model provides an excellent fit (the solid line in figure 5a), as indicated by the low value of R.

4. Summary

A novel ion-pair complex [BzTPP][Ni(mnt)$_2$] exhibiting strong antiferromagnetic behavior has been synthesized and its single-crystal structural analysis shows the Ni(mnt)$_2^-$ anion and [BzTPP]$^+$ cations of complex **1** stack into well-segregated columns in the solid state; the anion–anion, anion–cation and cation–cation contacts play important roles in crystal packing and stabilizing. The Ni(III) ions form a one-dimensional zigzag chain within a Ni(mnt)$_2^-$ anion through Ni$\cdots$S, S$\cdots$S, Ni$\cdots$Ni or $\pi\cdots\pi$ interactions. The variable-temperature magnetic susceptibilities of **1** were measured over the 75–300 K range and the results reveal that **1** exhibits strong antiferromagnetic behavior.

Supplementary material

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

Acknowledgements

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