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Synthesis, crystal structure and magnetic property of a novel ion-pair nickel(III) complex containing 1,2-benzenedithiolate

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A new ion-pair complex [1-(4-nitrobenzyl)pyridinium][Ni(bdt)$_2$] (1), in which bdt^{2-} = 1,2-benzenedithiolate, has been synthesized and characterized. The X-ray structure analysis shows that the anions are centrosymmetric, the two non-equivalent anions form different uniform-spaced stacking pattern and the weak H-bonding interactions of C–H···S were observed in 1. The temperature dependence of magnetic susceptibilities of 1 indicates ferromagnetic behavior in the antiferromagnetic exchange system, which may arise from spin-canting. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: nickel(III) thiolate complex; crystal structure; magnetism; spin-canting

INTRODUCTION

In recent years, transition metal bis(dithiolene) complexes, with their square-planar coordination geometry, have been used widely as building blocks for conducting and magnetic materials.[1,2] These complexes can be seen as the inorganic analogs of TTF-type donors, which so far have provided the largest number of known organic conductors and superconductors, where the central C=C bond is replaced by a transition metal. In fact, these inorganic complexes have frontier orbitals that are isolobal with the corresponding TTF analogs. Depending on the metal and on the oxidation state, these complexes can present different magnetic moments. Furthermore, the choice of the transition metal provides access to a diversity of different ground states. These are important features for the study and design of molecular materials with specific magnetic properties such as spin-Peierls transition, valence-ordering, spin-charge separation states, charge-density-wave states and spin-density-wave states.[3–6]

In our previous research, using benzylpyridinium derivatives ([RBzPy]$^+$) as the counter-cation of [M(mnt)$_2$]$^-$ (M = Ni, Pd and Pt), a series of ion-pair compounds with segregated columnar stacks of cations and anions was prepared.[7–11] The quasi-one- dimensional magnetic nature of these complexes was attributed to intermolecular π-orbital interactions within the anionic columns. Furthermore, for some complexes, spin-Peierls-like transition was observed.[10,11] Our present research interest is devoted to the molecular self-assembly of magnets from [Ni(dbt)$_2$]$^-$ ion owing to its molecular and electronic structure resembling [Ni(mnt)$_2$]$^-$ ion. It is expected to obtain new series of molecular magnets with peculiar magnetic phase transition via incorporation of the benzylpyridinium derivatives into a [Ni(dbt)$_2$]$^-$ spin system. Herein, we report the synthesis, crystal structure and magnetic properties of a novel complex consisting of [Ni(dbt)$_2$]$^-$ and benzylpyridinium derivatives.

EXPERIMENTAL

Materials and measurements

All commercially available chemicals are of reagent grade and used as received without further purification. Benzene-1,2-dithiol was purchased from TCI Chemicals; 1-(4-nitrobenzyl)pyridinium bromide ([NO$_2$BzPy]Br) was synthesized following the published procedure.[12] Elemental analyses of C, H and N were carried on a Perkin-Elmer

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240C Elemental Analyzer at the Analysis Center of Nanjing University. A Bruker FS66V FT IR spectrophotometer was used, and the measurements were made by the KBr disk method. ^{1}H NMR spectra were recorded on a Bruker Avance 500 spectrometer in DMSO-d_6 at room temperature.

Synthesis of complex 1

Under argon atmosphere at room temperature, benzene-1,2-dithiol (284 mg, 2 mmol) was added to a solution of sodium metal (92 mg, 4 mmol) in 25 ml of absolute methanol. A solution of $NiCl_2 \cdot 6H_2O$ (240 mg, 1 mmol) in methanol was added, resulting in the formation of a muddy red-brown color. Following this, [NO_2BzPy]Br (599 mg, 2 mmol) was added and the mixture allowed to stand with stirring for 1 h, and then stirred for 24 h in air. The color of the mixture gradually turned green, indicating oxidation from a dianionic species to the more stable monoanionic form. The precipitate was washed with absolute methanol and ether and then dried. The crude product was recrystallized twice from methylene chloride to give black needles in ca. 76% yield. Anal. calcd for $C_{24}H_{19}N_2O_2S_4Ni$: C, 52.00; H, 3.45; N, 5.05. Found: C, 52.04; H, 3.47; N, 5.07. IR (cm^{-1}): 3041 (w), 2957 (s), 2856 (m), 1485 (s), 1421 (s), 1225 (m), 739 (m), 667 (s). ^{1}H NMR: δ (ppm) 9.31 [2H, CHC(NO_2)CH], 8.62(1H, ArH, pyridine ring), 8.15 [2H, CH(C)CH, phenyl ring], 7.61, 7.29 (4H, $C_6H_4S_2$), 5.92 [4H, $(CH)_2N(CH)_2$, pyridine ring], 2.61 (2H, CH_2N).

X-Ray crystallography

The crystallographic data collections for complex **1** were carried out on a Bruker Smart Apex II CCD with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K using the ω-scan technique. The data were integrated using the SAINT program,[13] which also corrected the intensities for Lorentz and polarization effect. An empirical absorption correction was applied using the SADABS program.[14] The structures were solved by direct methods using the program SHELXS-97 and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package.[15,16] The hydrogen atoms were generated geometrically. All calculations were performed on a personal computer with the SHELXL-97 crystallographic software package.[16] The details of the crystal parameters, data collection and refinement for four compounds are summarized in Table 1. Selected bond lengths and angles for complex **1** are listed in Table 2. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC–656509. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystallographic data for complex **1**

	1
Empirical formula	$C_{24}H_{19}N_2O_2S_4Ni$
Formula weight	554.36
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	7.026(3)
b (Å)	12.377(5)
c (Å)	14.735(6)
α (deg)	73.057(6)
β (deg)	84.964(6)
γ (deg)	81.940(8)
V(Å^3)	1212.2(8)
Z	2
D_{calc} (g cm^{-3})	1.519
μ (mm^{-1})	1.170
T (K)	293
F(000)	570
Reflections collected	5760
Unique reflections	4123
R_{int}	0.1072
Goodness-of-fit on F^2	1.034
$R_1{}^a/wR_2{}^b$ [$I > 2\sigma(I)$]	0.0514/0.1294
R_1/wR_2 [all data]	0.0682/0.1464
Largest difference peak and hole (e Å^{-3})	0.439/−0.548

[a] $R = \Sigma \| F_o| - |F_c\| / \Sigma |F_o|$. [b] $R_w = |\Sigma w(|F_o|^2 - |F_c|^2| / \Sigma |w(F_o)^2|^{1/2}$, where $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$. $P = (F_o{}^2 + 2F_c{}^2)/3$.

Table 2. Selected bond lengths (Å) and angles (deg) for **1**

Ni(1)–S(1)	2.1500(13)	Ni(1)–S(2)	2.1483(13)
Ni(2)–S(3)	2.1572(14)	Ni(2)–S(4)	2.1482(14)
S(1)–C(13)	1.742(5)	S(2)–C(18)	1.741(4)
S(3)–C(19)	1.737(5)	S(4)–C(24)	1.735(5)
C(13)–C(18)	1.404(6)	C(19)–C(24)	1.407(6)
S(2)–Ni(1)–S(1)	91.87(5)	S(2)^a –Ni(1)–S(1)	88.13(5)
C(13)–S(1)–Ni(1)	104.80(15)	C(18)–S(2)–Ni(1)	105.47(15)
S(4)–Ni(2)–S(3)	91.55(5)	S(4)^b –Ni(2)–S(3)	88.45(5)
C(19)–S(3)–Ni(2)	105.26(15)	C(24)–S(4)–Ni(2)	105.31(16)

Symmetry transformation used to generate equivalent atoms:
[a] −x + 2, −y, −z + 2; [b] −x + 2, −y, −z + 1.

Magnetic measurements

Variable-temperature magnetic susceptibility measurements were carried on a Quantum Design MPMS-XL7 SQUID magnetometer at an applied field of 2000 Oe using crystalline samples of **1** in the range of 1.8–300 K. The magnetic susceptibilities of the complex were corrected by Pascal constants and diamagnetism of the holder.

RESULTS AND DISCUSSION

Crystal structure of complex 1

The X-ray crystallographic structure analysis of **1** reveals that it crystallizes in triclinic form with space group $P\bar{1}$.

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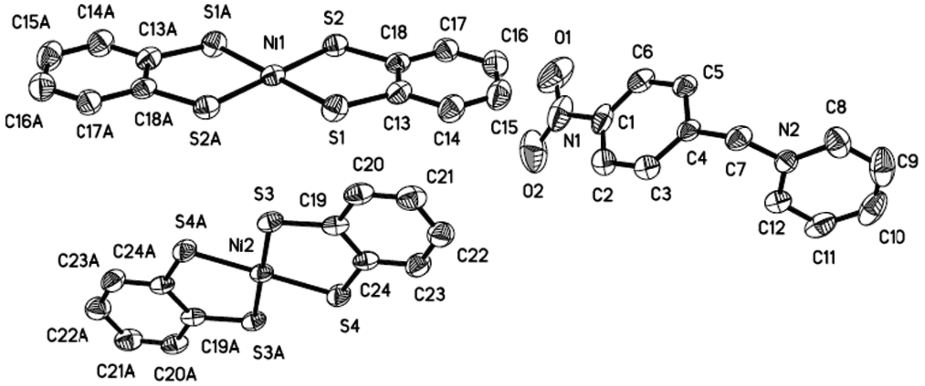

Figure 1. ORTEP plot of **1** showing local coordination environment of Ni(III) with thermal ellipsoids at 30% probability. Hydrogen atoms are omitted for clarity. Symmetry operations: $-x+2$, $-y$, $-z+2$ for S1A, S2A, C13A, C14A, C15A, C16A, C17A and C18A; $-x+2$, $-y$, $-z+1$ for S3A, S4A, C19A, C20A, C21A, C22A, C23A and C24A.

As shown in Fig. 1, the asymmetric unit of **1** contains two different, independent halves of centrosymmetric $[\mathrm{Ni(bdt)_2}]^-$ anions, and one $[\mathrm{NO_2BzPy}]^+$ cation. The nickel atoms are each surrounded by four sulfur atoms in square-planar geometry, which is markedly different from a spiro compound $\mathrm{Si(bdt)_2}$.[17] As for the Ni(1)-containing unit, the Ni(1)–S(1) and Ni(1)–S(2) distances are 2.1500(13) and 2.1483(13) Å, respectively. The values are in agreement with the analogous $[\mathrm{Ni(bdt)_2}]^-$ complex reported.[18] The S–Ni–S bond angle within the five-member ring is 91.87(5)°, which is slightly larger than that observed in complex with substituent groups on benzene rings.[19] There exists a dihedral angle of 1.32° between C(13)C(14)C(15)C(16)C(17)C(18)S(1)S(2) (abbr. $\mathrm{C_6S_2}$) and the Ni(1)S(1)S(2) planes, so the anion adopts an envelope conformation, and the Ni(1) atom deviates by 0.024 Å from a $\mathrm{C_6S_2}$ plane. In Ni(2)-containing unit, the Ni–S bonds cover the range from 2.1482(14) to 2.1572(14) Å and the S–Ni–S bond angle within the five-member ring is 91.55(5)° which is in agreement with that of Ni(1)-containing unit. The Ni(2) atom deviates by 0.077 Å from C(19)C(20)C(21)C(22)C(23)C(24)S(3)S(4) plane and the angle between $\mathrm{C_6S_2}$ and the Ni(2)S(3)S(4) planes is 2.92°. The $\mathrm{Ni(1)C_6S_2}$ and $\mathrm{Ni(2)C_6S_2}$ planes are nearly perpendicular to each other with the dihedral angle of 78.34°. In the 1-(4-nitrobenzyl)pyridinium cation, the dihedral angles of the N(2)–C(4)–C(7) reference plane are 80.58° for the phenyl ring and 41.62° for the pyridine ring, respectively. The phenyl ring and the pyridine ring make a dihedral angle of 77.62°.

The molecule packing of the two anion units in **1** differs (Fig. 2). The Ni(1)-containing units stack in a side-by-side fashion, in which the anions with uniform spaced arrangements form a one-dimensional (1-D) chain along the *a*-axis, and the shortest distance between adjacent Ni(III) ions is 7.026 Å. Conversely, the Ni(2)-containing units stack in a face-to-face fashion with an alternating arrangement of $[\mathrm{Ni(bdt)_2}]^-$ anions and $[\mathrm{NO_2BzPy}]^+$ cations such that the pyridine ring moiety of the cation lies above the phenyl ring moiety of the corresponding Ni(2)-containing units and vice versa. The shortest distance between adjacent Ni(III) ions is 7.026 Å as well. Between the most adjacent Ni(1)-containing and Ni(2)-containing units, a Ni···Ni distance of 7.367 Å is found. The Ni(1)-containing anion and the $[\mathrm{NO_2BzPy}]^+$ cation are held together via non-normal C(7)–H(7B)···S(2)$(1-x, 1-y, 2-z)$ H-bonding interactions to consolidate the structure.

Magnetic property of complex 1

The temperature dependence of the magnetic susceptibility for the powdered sample of **1** was measured in the range 1.8–300 K in the form of the $\chi_M T$ vs T curve, where χ_M is the molar magnetic susceptibility (Fig. 3). Its magnetic behavior may be divided into three parts on their temperature dependence. The value of $\chi_M T$ at 300 K is estimated at 0.378 emu K mol^{-1}, and is nearly equal to that of spin-only of one $S = 1/2$ spin per formula unit. The $\chi_M T$ values decrease continuously upon cooling until 215 K, indicating the presence of antiferromagnetic exchange between metal centers. Then, the $\chi_M T$ values increase gradually between 215 and 7 K and reach a maximum at approximately 7 K ($\chi_M T = 0.393$ emu K mol^{-1}), exhibiting ferromagnetic coupling behavior. The magnetic behavior in the temperature range 300–7 K may arise from the spin-canting mechanism. Spin-canting arises through a Dzyaloshinsk–Moriya interaction, which minimizes the coupling energy when two spins are perpendicular to one another. Furthermore, it should be fulfilled when canting spins in the solid state are not related by a center of inversion.[20] Based on its crystal structure, it is worth noting that the two non-equivalent Ni(III) ions do not relate to each other through an inversion center, and thus there may exist incomplete cancellation of spins between Ni(1)-containing and Ni(2)-containing units. When the temperature is below 7 K, the $\chi_M T$ values decrease quickly and drop to 0.302 emu K mol^{-1} at extremely low temperatures, and this phenomenon may originate from magnetization saturation effect.[21] The data over the entire temperature are best fit by the Bonner–Fisher model for a uniformly spaced chain of $S = 1/2$ spin,[22] Eqn (1),

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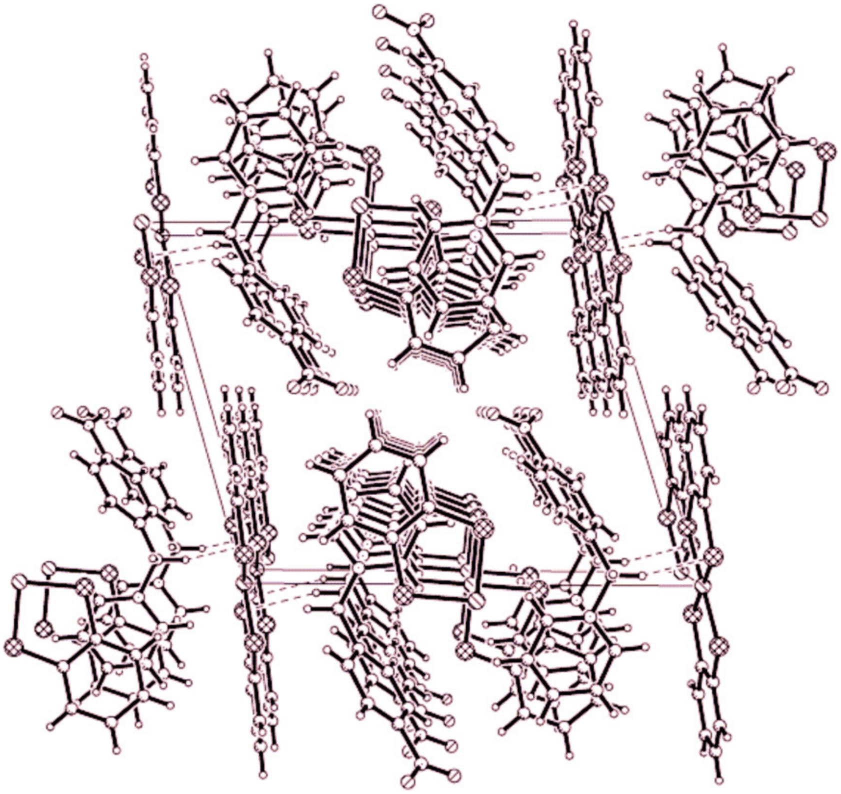

Figure 2. The packing diagram of the complex **1** along *bc* plane. The hydrogen bonds are indicated by dashed lines. This figure is available in colour online at www.interscience.wiley.com/AOC.

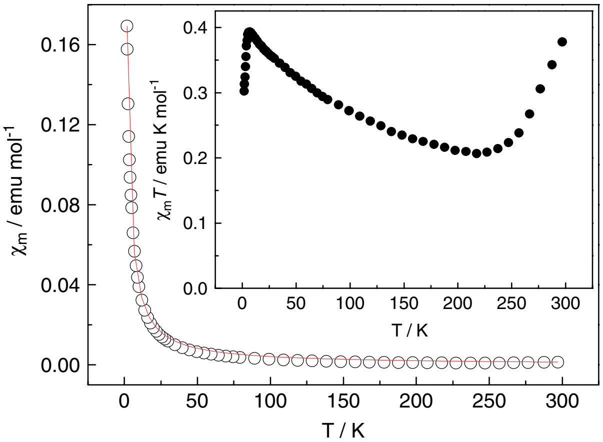

Figure 3. Temperature independence of the the χ_M values for complex **1**. The solid line represents the best fit. Inset: temperature dependence of the $\chi_M T$ values for complex **1**. This figure is available in colour online at www.interscience.wiley.com/AOC.

for $H = -2JS_1S_2$[23] with $z = J/k_BT$.

$$\chi_M = \frac{Ng^2\mu_B^2}{k_BT}\left(\frac{0.25 + 0.74975z + 0.075235z^2}{1 + 0.9331z + 0.172135z^2 + 0.757825z^3}\right) \quad (1)$$

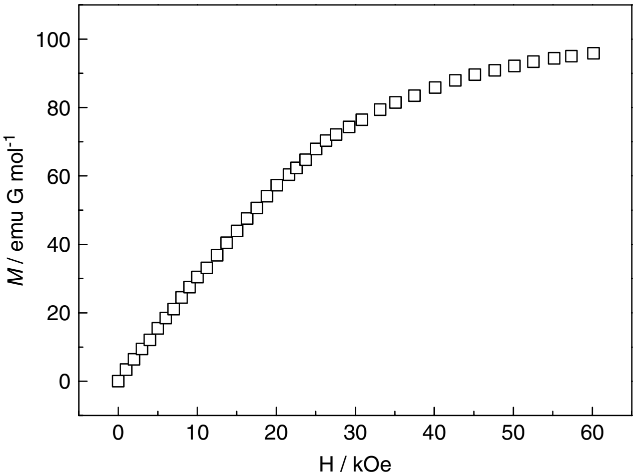

Figure 4. M–H curve of complex **1** measured at 1.8 K.

A fit of the data to eqn (1) gives $J = -12.01$ cm^{-1} and g = 2.11. So complex **1** behaves as a one-dimensional chain with appreciable antiferromagnetic interactions between the $S = 1/2$ Ni(III) spin carriers. As shown in Fig. 4, the field dependence of the magnetization (0–60 kOe) measured at 1.8 K shows that the highest magnetization of approximately 96 emu G mol^{-1} is significantly smaller than the theoretical

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saturation value of 5585 emu G mol^{-1}, supporting the spin-canted structure for this complex.[20,24]

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