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Synthesis, Crystal Structure, and Magnetic Property of a New Nickel(III) Complex Constructed from 1,2-Benezedithiolate

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The new complex, [IBzPyCH$_3$][Ni(bdt)$_2$] (1), has been synthesized and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction, in which [IBzPyCH$_3$]$^+$ = 1-(4-iodobenzyl)-3-methylpyridinium and bdt^{2-} = 1,2-benzenedithiolate. The X-ray structure analysis shows that the anions are centrosymmetric, the two nonequivalent anions form different uniform-spaced stacking pattern and the weak H-bonding interactions of C-H$\cdots$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.

Keywords crystal structure, magnetism, nickel(III) thiolate complex, spin-canting

INTRODUCTION

In the past decades, one-dimensional (1-D) compounds have been attracting widespread attention because they show novel physical properties such as Peierls transition, spin-Peierls transition, charge density wave (CDW) states, spin density wave (SDW) states, molecular bistability, molecular magnetic nanowire properties, etc.[1–5] In addition, 1-D compounds have also stimulated theoretical investigations. One of the most studied classes of 1-D transition metal complexes is the complexes containing M(mnt)$_2^-$ (M = Ni(III), Pd(III) or Pt(III)) ions. In these compounds, the constituent planar anions M(mnt)$_2^-$ form columnar stack structures, in which intermolecular d_{z2}or π orbital interactions result in 1-D electronic nature.[6–9] Usually, the topology and size of the counter cation in M(mnt)$_2^-$ complexes may play an important role in controlling the stacking pattern of anions and cations, which further influence the physical properties of these complexes.

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 have been prepared.[4,5] 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.[5] More recently, we devoted our research interest on the molecular magnets self-assembly from [Ni(bdt)$_2$]$^-$ ion due to its molecular and electronic structure resemble [Ni(mnt)$_2$]$^-$ ion, which is expected to obtain new series of molecular magnets with peculiar magnetic phase transition via incorporating the benzylpyridinium derivatives into [Ni(bdt)$_2$]$^-$ spin system. Herein, we report synthesis, crystal structure, and magnetic properties of a novel complex consisting of [Ni(bdt)$_2$]$^-$ and 1-(4-iodobenzyl)-3-methyl-pyridinium.

EXPERIMENTAL

Materials and Measurements

All commercially available chemicals are of reagent grade and used as received without further purification. Solvents were purified by standard methods prior to use. 1-(4-iodobenzyl)-3-methylpyridinium bromide ([IBzPyCH$_3$]Br) was synthesized following the published procedure.[6] Elemental analyses (C, H and N) were performed on a Vario EL III elemental analyzer. The IR spectrum as a KBr disk was recorded on a Nicolet Avatar 360 FT-IR spectrometer. Magnetic susceptibility data on polycrystalline sample were collected over the temperature range of 2–300 K using a MPMS7 magnetometer (Quantum

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TABLE 1
Crystal data for (**1**)

Complex	(1)
Formula	$C_{25}H_{21}INS_4Ni$
FW	649.28
Size (mm^{-3})	0.26 × 0.20 × 0.12
Crystal system	Triclinic
Space group	P-1
a (Å)	7.3222(14)
b (Å)	12.267(2)
c (Å)	14.628(3)
α(°)	98.425(2)
β (°)	98.466(2)
γ (°)	96.216(3)
Volume(Å^3)	1274.2(4)
Z	2
T (K)	296(2)
Wavelength (Å)	0.71073
D_{calcd} ($mg{\cdot}m^{-3}$)	1.692
F(000)	646
θ (°)	1.43–25.00
Reflections collected	6282
Independent reflections	4392 [$R_{int} = 0.0695$]
Data/parameters	4392/293
Goodness of fit on F^2	1.091
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0559$, $wR_2 = 0.1776$
R indices (all data)	$R_1 = 0.0694$, $wR_2 = 0.1957$
Large diff. peak and hole (e Å^{-3})	1.524 and –1.913

$R_1| = |\Sigma||F_o| - |F_c||/\Sigma|F_o|$. $wR_2 = |\Sigma w(|F_o|^2 - |F_c|^2)|/\Sigma|w(F_o)^2|^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$. $P = (F_o^2 + 2F_c^2)/3$.

Design) in an external field of 2000 Oe, and the diamagnetism was corrected by Pascal constants.[7]

Synthesis of [IBzPyCH$_3$][Ni(bdt)$_2$] (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 $NiCl_2{\cdot}6H_2O$ (237 mg, 1 mmol) in methanol was added, resulting in the formation of a muddy red-brown color. Following this, [IBzPyCH$_3$]Br (780 mg, 2 mmol) was added and the mixture was allowed to stand with stirring for 1 h, and then stirred for 24 h with the presence of atmosphere. 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 dark green block crystals in ca. 77% yield. Anal. calcd for $C_{25}H_{21}INS_4Ni$: C, 46.24; H, 3.26; N, 2.16; S, 19.75. Found: C, 46.22; H, 3.29; N, 2.18; S, 19.77. IR (cm^{-1}): 3055 (w), 2953 (s), 2846 (m), 1484 (s), 1423 (s), 1227 (m), 737 (m), 665 (s).

DATA COLLECTION, STRUCTURAL DETERMINATION, AND REFINEMENT

Crystal Structure Determination

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 296(2) K using the ω-scan technique. The data were integrated by using the SAINT program,[8] which also did the intensities corrected for Lorentz and polarization effect. An empirical absorption correction was applied using the SADABS program.[9] The structures were solved by direct methods using the program SHELXS-97and all non-hydrogen atoms were refined anisotropically on F^2 by the full-matrix least-squares technique with SHELXL-97.[10,11] The hydrogen atoms were generated geometrically. The details of the crystal parameters, data collection and refinement for **1** are summarized in Table 1. Selected bond lengths and bong angles for complex **1** are listed in Table 2. Crystallographic data for the two complexes have been deposited with Crystallographic Data Center (CCDC 668713).

RESULTS AND DISCUSSION

Structure Description of the Complex

The X-ray crystallographic structure analysis of **1** reveals that it crystallizes in triclinic with space group P-1. As shown in Figure 1, the asymmetric unit of **1** contains two different, independent halves of centrosymmetric [Ni(bdt)$_2$]$^-$ anions, and one [IBzPyCH$_3$]$^+$ cation. The nickel atoms are each surrounded by four sulfur atoms in square-planar geometry, which is markedly different from a spiro compound Si(bdt).$_2$[12] As for the Ni(1)-containing unit, the Ni(1)-S(1) and Ni(1)-S(2) distances are 2.1470(16) and 2.1562(16) Å, respectively. The values are in agreement with the analogous [Ni(bdt)$_2$]$^-$ complex reported.[13]

TABLE 2
Selected bond lengths (Å) and bond angles (°) for (**1**)

Ni(1)-S(1)	2.1470(16)	Ni(1)-S(2)	2.1562(16)
Ni(2)-S(3)	2.1504(17)	Ni(2)-S(4)	2.1447(15)
S(1)-C(1)	1.747(6)	S(2)-C(6)	1.745(6)
C(1)-C(6)	1.390(8)	S(3)-C(7)	1.732(6)
S(4)-C(12)	1.749(7)	C(7)-C(12)	1.381(9)
S(1)-Ni(1)-S(2)	91.59(6)	S(1)-Ni(1)-S(2)#1	88.41(6)
S(4)-Ni(2)-S(3)	91.79(6)	S(4)#2-Ni(2)-S(3)	88.21(6)
C(1)-S(1)-Ni(1)	104.7(2)	C(6)-S(2)-Ni(1)	105.1(2)
C(7)-S(3)-Ni(2)	105.5(2)	C(12)-S(4)-Ni(2)	104.1(2)

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

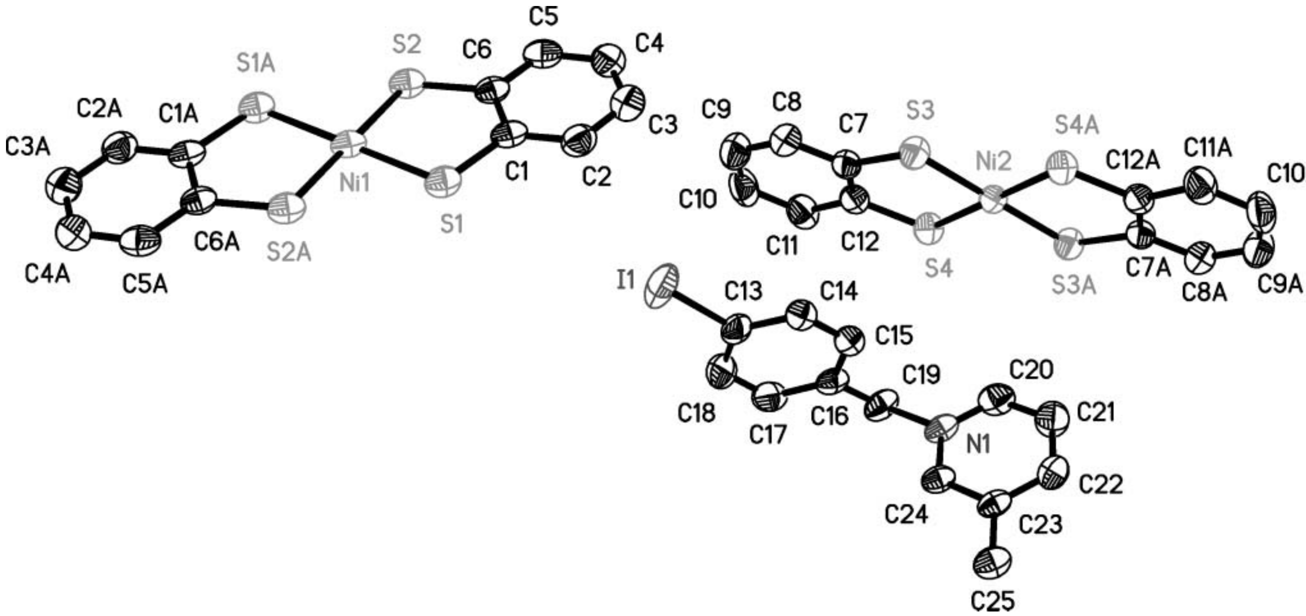

FIG. 1. ORTEP representation of complex (**1**) with 30% thermal ellipsoids. Hydrogen atoms have been omitted for clarity.

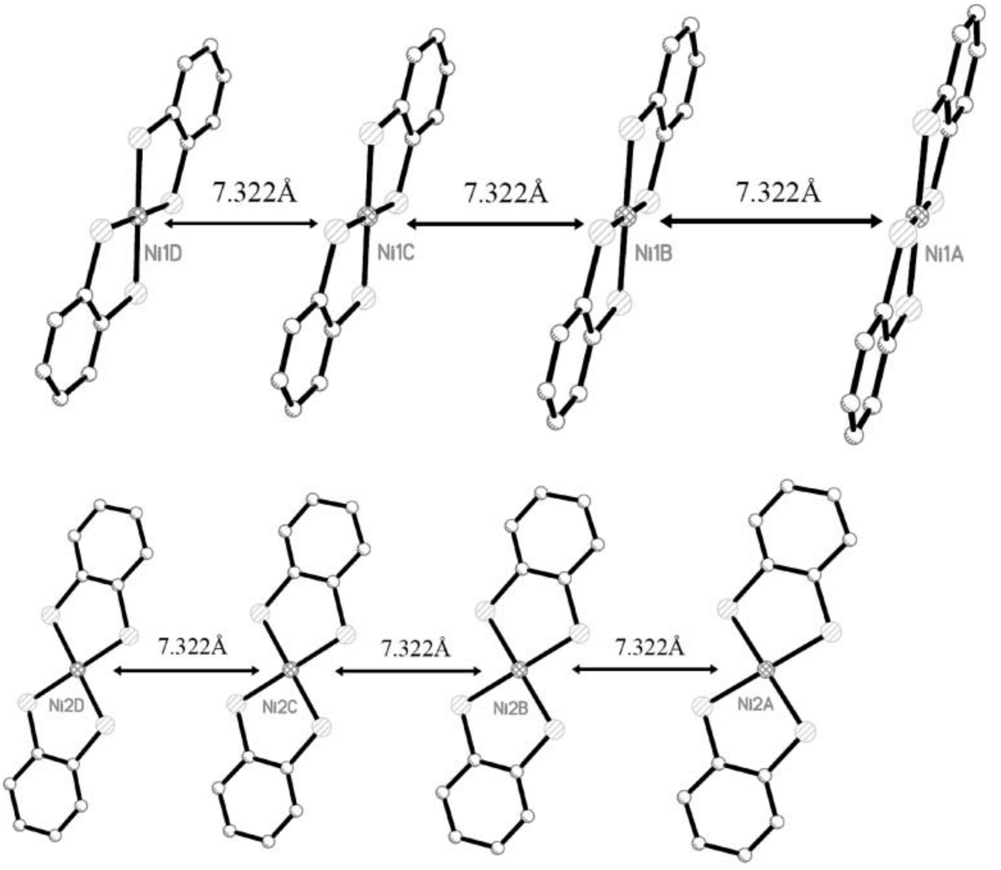

FIG. 2. The molecule packing diagram of two different $\mathrm{Ni(bdt)}_2^-$ anions with the Ni· · ·Ni distances of 7.322 Å.

The S-Ni-S bond angle within the five-member ring is 91.59(6)°, which is slightly larger than that observed in complex with substituent groups on benzene rings.[14] There exists a dihedral angle of 6.91° between C(1)C(2)C(3)C(4)C(5)C(6)S(1)S(2) (abbr. 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 0.181 Å from C_6S_2 plane. In Ni(2)-containing unit, the Ni-S bonds cover the range from 2.1447(15) to 2.1504(17) Å and the S-Ni-S bond angle within the five-member ring is 91.79(6)° which is in agreement with that of Ni(1)-containing unit. The Ni(2) atom deviates 0.013 Å from C(7)C(8)C(9)C(10)C(11)C(12)S(3)S(4) plane and the angle between C_6S_2 and the Ni(2)S(3)S(4) planes is 1.24°. The Ni(1)C_6S_2 and Ni(2)C_6S_2 planes are nearly perpendicular to each other with the dihedral angle of 74.74°. In the 1-(4-iodobenzyl)-3-methylpyridinium cation, the dihedral angles of the N(1)-C(19)-C(16) reference plane are 42.85° for phenyl ring, 63.19° for pyridine ring, respectively. The phenyl ring and the pyridine ring make a dihedral angle of 86.94°.

The molecule packing of two anion units in **1** is different from each other (Figure 2). The Ni(1)-containing units stack in face to face fashion with an alternating arrangement of $[Ni(bdt)_2]^-$ anion and $[IBzPyCH_3]^+$ cation such that the pyridine ring moiety of cation lie above the phenyl ring moiety of the corresponding Ni(1)-containing units and vice versa and the shortest distance between adjacent Ni(III) ions is 7.322 Å. Conversely, the Ni(2)-containing units stack in side by side fashion, in which the anions with uniform spaced arrangements to form one dimensional (1-D) chain along *a*-axis. The shortest distance between adjacent Ni(III) ions is 7.322 Å, too. Between the most adjacent Ni(1)-containing and Ni(2)-containing units, a Ni···Ni distance of 7.314 Å is found. Ni-containing anion and $[IBzPyCH_3]^+$ cation are held together via non-normal C(19)-H(19B)···S(2)(-1+x, 1+y, z) and C(20)-H(20)···S(4)(-x, 2-y, 2-z) H-bonding interactions to consolidate the structure (Figure 3). The stacking pattern of **1** is different from that of the reported,[15] since variation of the substituents of pyridine ring would be expected to affect the conformation of the cation in this series of complexes.

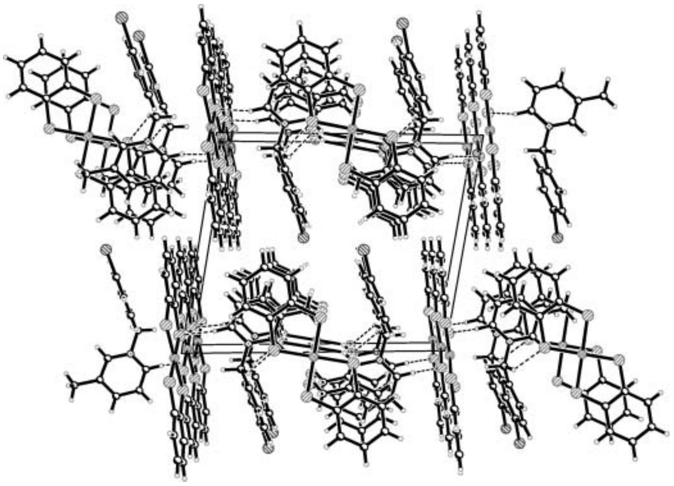

FIG. 3. The packing diagram of the complex (**1**) along *bc* plane. The hydrogen bonds are indicated by dashed lines.

Magnetic Property

The temperature dependence of the magnetic susceptibility for the powdered sample of **1** was measured in the range of 2-300 K in the form of the $\chi_M T$ versus T curve, where χ_M is the molar magnetic susceptibility (Figure 4). 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 0.368 emu K mol^{-1}, and is smaller than that of spin-only of one $S = 1/2$ spin per formula unit. The $\chi_M T$ values decrease continuously upon cooling until 194 K, indicating the presence of antiferromagnetic exchange between metal centers. Then, the $\chi_M T$ values increase gradually between 194 and 18 K and reaches a maximum at approximately 18 K ($\chi_M T = 0.406$ emu K mol^{-1}) exhibiting ferromagnetic coupling behavior. The magnetic behavior in the temperature range 300-18 K may arise from 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.[16] Based on its crystal structure, it is worth noting that the two nonequivalent 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 18 K, the $\chi_M T$ values decrease quickly and drop to 0.296 emu K mol^{-1} at extremely low temperatures and this phenomenon may origin from magnetization saturation effect.[17] The data over the entire temperature are best fit by the Bonner-Fisher model for

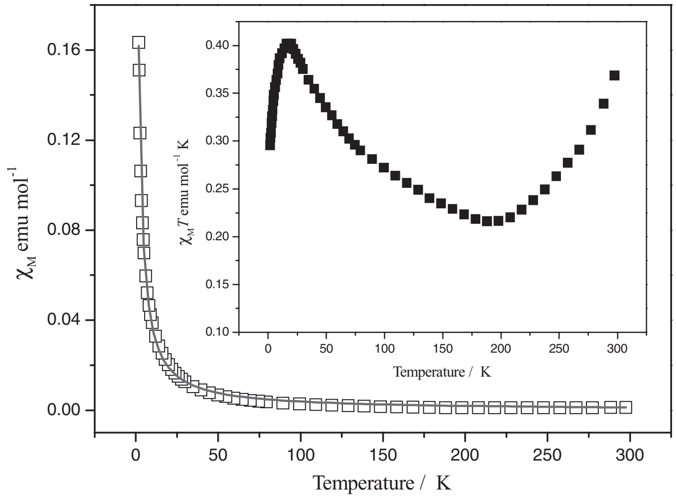

FIG. 4. Temperature independence of the the χM values for complex (**1**). The solid line represents the best fit. Inset: temperature dependence of the χMT values for complex (**1**).

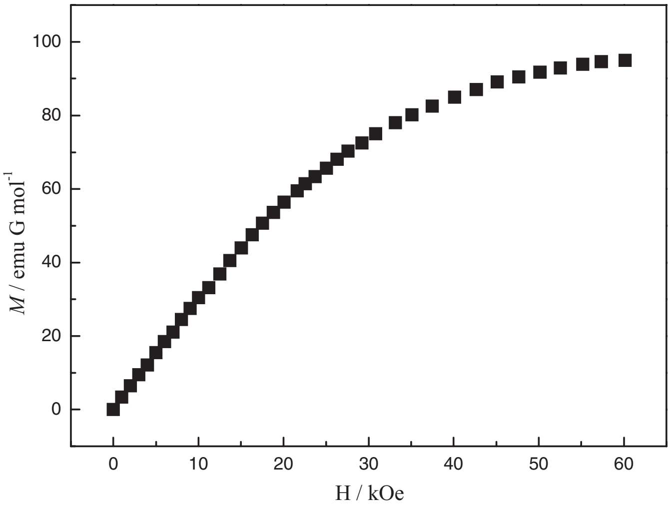

FIG. 5. M-H curve of complex (**1**) measured at 2 K.

a uniformly spaced chain of S = 1/2 spin[18] Equation (1) for $H = -2JS_1S_2$[19] with z $= J/k_BT$.

$$\chi_m = \frac{Ng^2\mu_B^2}{k_BT}\left(\frac{0.25 + 0.74975_Z + 0.075235_{Z^2}}{1 + 0.9331_Z + 0.172135_{Z^2} + 0.757825_{Z^3}}\right) \quad [1]$$

A fit of the data to Equation (1) gives J = -1.39 cm^{-1} and g = 2.02. So complex **1** behaves as a 1-D chain with appreciable antiferromagnetic interactions between the S = 1/2 Ni(III) spin carriers. As shown in Figure 5, the field dependence of the magnetization (0 - 60 kOe) measured at 2 K shows the highest magnetization of approximately 95 emu G mol^{-1} is significantly smaller than the theoretical saturation value of 5585 emu G mol^{-1}, supporting the spin-canted structure for this complex.[15]

CONCLUSION

In this contribution, we fabricated a new ion-pair complex containing the [Ni(bdt)$_2$]$^-$ unit. Two nonequivalent anions are stacked in different fashion, i.e., face to face or side by side in the complex. To our best knowledge, this structural motif is unprecedented in the chemistry of [M(bdt)$_2$]$^-$ complexes and is remarkably different from the corresponding [M(mnt)]$^-$ complexes. The magnetic properties of the complex show that the primary exchange process involves antiferromagnetic coupling between nickel centers with a canting of the spins, that is to say, the weak ferromagnetism at a low temperature may be due to a consequence of canted spin antiferromagnetism.

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