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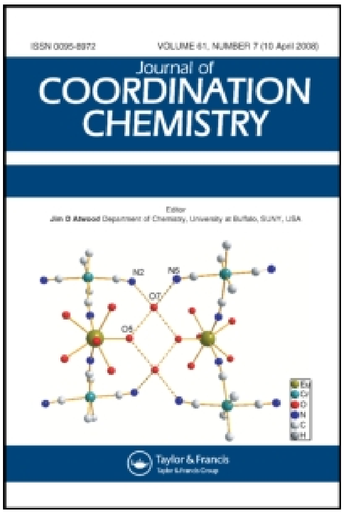

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
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Synthesis, crystal structure and magnetic properties of [1-(2',4'-dichlorobenzyl)-3-methylpyridinium] [Ni(mnt)$_2$] complex (mnt^{2-} = maleonitriledithiolate)

Chunlin Ni[a,b]; Yizhi Li[b]; Zhaoping Ni[b]; Qingjin[b]
[a] College of Chemistry and Life Sciences, China Three Gorges University, 443002 Yichang, P.R. China [b] State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, 210093 Nanjing, P.R. China

To cite this Article Ni, Chunlin , Li, Yizhi , Ni, Zhaoping and Qingjin(2004) 'Synthesis, crystal structure and magnetic properties of [1-(2',4'-dichlorobenzyl)-3-methylpyridinium] [Ni(mnt)$_2$] complex (mnt^{2-} = maleonitriledithiolate)', Journal of Coordination Chemistry, 57: 15, 1321 — 1328

To link to this Article: DOI: 10.1080/00958970412331295246

URL: http://dx.doi.org/10.1080/00958970412331295246

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J. Coord. Chem., Vol. 57, No. 15, 15 October 2004, pp. 1321–1328

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SYNTHESIS, CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES OF [1-(2′,4′-DICHLOROBENZYL)-3-METHYLPYRIDINIUM] [Ni(mnt)$_2$] COMPLEX ($mnt^{2-} =$ MALEONITRILEDITHIOLATE)

CHUNLIN NI[a,b,*], YIZHI LI[b], ZHAOPING NI[b] and QINGJIN MENG[b]

[a]*College of Chemistry and Life Sciences, China Three Gorges University,*
443002 Yichang, P.R. China;
[b]*State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute,*
Nanjing University, 210093 Nanjing, P.R. China

(Received 17 April 2004; Revised 8 August 2004; In final form 27 July 2004)

A new ion-pair complex, [DiClBzMePy][Ni(mnt)$_2$] (**1**) ([DiClBzMePy]$^+$ = 1−(2′4′-dichlorobenzyl)-3-methylpyridinium; mnt^{2-} = maleonitriledithiolate), has been prepared. The Ni(mnt)$_2^-$ anion and [DiClBzMePy]$^+$ cations of Complex **1** stack into well-segregated columns in the solid state, and the Ni(III) ions form a 1D zigzag chain within a Ni(mnt)$_2^-$ anion through Ni···S, S···S and Ni···S···Ni interactions. The anion–anion, anion–cation and cation–cation contacts may play important roles in the crystal packing. Variable temperature magnetic susceptibilities measured at 75–300 K reveal that Complex **1** exhibits antiferromagnetic behavior.

Keywords: 1-(2′,4′-Dichlorobenzyl)-3-methylpyridinium; Bis(maleonitriledithiolate) nickelate(III) complex; X-ray structure; Magnetism

INTRODUCTION

Maleonitriledithiolate (mnt^{2-}) transition metal complexes have been widely investigated mainly because of their versatile structural, chemical and physical properties [1–5]. In particular, the discovery in 1996 of the ferromagnetic complex containing Ni(mnt)$_2^-$, NH_4·Ni(mnt)$_2$·H_2O, stimulated interest in Ni(mnt)$_2$ complexes as building blocks for new molecular magnets [6]. In our recent work on quasi-one-dimensional molecular magnets based on [M(mnt)$_2$]$^-$ building blocks (M = Ni(III), Pt(III)), we have developed a new class of ion-pair complexes [RbzPy]$^+$[Ni(mnt)$_2$]$^-$ ([RbzPy]$^+$ = derivatives of benzylpyridinium) that exhibit versatile magnetic properties such as ferromagnetic ordering at low temperature, magnetic transition from ferromagnetic

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*Corresponding author. E-mail: ctgunicl@163.com

ISSN 0095-8972 print: ISSN 1029-0389 online © 2004 Taylor & Francis Ltd
DOI: 10.1080/00958970412331295246

coupling to diamagnetism, meta-magnetism and spin-Peierls-like transitions [7–13]. In these ion-pair complexes, the prominent structural feature is that the $Ni(mnt)_2^-$ ions and $[RbzPy]^+$ cations stack into well-segregated columns in the solid state. In order to widen the scope of our research and obtain more information on the countercation influence on the stacking pattern and magnetic properties of $Ni(mnt)_2^-$ complexes, in this paper we describe the synthesis, crystal structure and magnetic behavior of the title complex. To the best of our knowledge, this is the first $Ni(mnt)_2^-$ complex containing a substituted benzyl-3-methylpyridinium cation.

EXPERIMENTAL

Reagents and Preparation of the Complex

2,4-Dichlorobenzyl bromide and 3-methylpyridine were purchased from Aldrich and used without further purification. [1-(2′,4′-Dichlorobenzyl)]-3-methylpyridinium bromide ([DiClBzMePy]Br) was prepared by the literature method [14]. Disodium maleonitriledithiolate (Na_2mnt) was synthesized by a published procedure, and a method similar to that for preparing $[Bu_4N]_2[Ni(mnt)_2]$ was used to prepare $[DiClBzMePy]_2[Ni(mnt)_2]$ [15].

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 $[DiClBzMePy]_2[Ni(mnt)_2]$ (845 mg, 1 mmol) and the mixture was stirred for 2 h. MeOH ($90\,cm^3$) was then added, and the mixture allowed to stand overnight; 505 mg of black micro-crystals formed and were filtered off, washed with MeOH and dried in vacuum (yield: 85.3%). Anal. Calcd. for $C_{21}H_{12}N_5NiCl_2S_4$(%): C, 42.59; H, 2.04; N, 11.82. Found: C, 42.52; H, 2.14; N, 11.60. ESI-MS (*m*/*z*): 252.1, $[DiClBzMePy–H]^+$; 337.9, $[Ni(mnt)_2-H]^-$.

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

Physical Measurements

Elemental analyses were carried out with a Perkin Elmer CHN model 240 instrument. IR spectra were recorded using KBr pellets on a VECTORTM 22 FT-IR spectrophotometer in the range $400–4000\,cm^{-1}$. 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 temperature with a CAHN-2000 Faraday-type magnetometer; diamagnetic corrections for the constituent atoms were made with Pascal's constants.

Crystallography

Measurement of Complex **1** was performed on a Smart APEX CCD area detector using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) by ω scan mode within the angle range $2.19 < \theta < 25.0$. Space group, lattice parameters and other relevant information are listed in Table I. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares, using SHELXTL [16]. All nonhydrogen

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TABLE I Crystallographic data and structure refinement for **1**

CCDC deposit no.	CCDC-234948
Color/shape	Black/block
Chemical formula	$C_{21}H_{12}N_5NiCl_2S_4$
Formula weight	592.21
Temperature (K)	293(2)
Wavelength (Å)	0.71073Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	
a (Å)	6.944(1)
b (Å)	24.933(5)
c (Å)	14.130(3)
β deg	99.84(1)
Volume (Å^3)	2410.4(8)
Z	4
Density (calculated) (mg m^{-3})	1.632
Absorption coefficient (mm^{-1})	1.394
Diffractometer/scan	Siemens SMART/CCD area detector
$F(000)$	1196
θ range for data collection	2.19–25.00
Index ranges	$-8 \le h \le 8$ $-29 \le k \le 22$ $-16 \le l \le 16$
Reflections collected	11762
Independent reflections	4230($R_{int} = 0.036$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4230/0/298
Goodness of fit on F^2	1.064
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0605$, $wR2 = 0.1296$
R indices (all data)	$R1 = 0.0769$, $wR2 = 0.1338$
Largest diff. peak and hole (eÅ^{-3})	0.62 and −0.37

atoms were refined with anisotropic thermal parameters. All H atoms were placed in calculated positions, assigned fixed isotropic displacement parameters 1.2 times the equivalent isotropic U value of the attached atom, and allowed to ride on their respective parent atoms.

RESULTS AND DISCUSSIONS

Structure of Complex 1

An ORTEP drawing of Complex **1** with nonhydrogen atomic labeling of the asymmetric unit is shown in Fig. 1. The Ni(III) ion in the $Ni(mnt)_2^-$ anion is coordinated by four S atoms of two mnt^{2-} ligands and exhibits the expected square-planar coordination geometry. The CN groups of the $Ni(mnt)_2^-$ anion are tipped slightly out of the plane; the deviations from the plane are 0.0482 Å for N(1), −0.0738 Å for N(2), 0.1367 Å for N(3) and 0.1004 Å for N(4). The five-membered nickel-containing rings are slightly puckered. The average Ni–S bond distance is 2.144(2) Å, and the average S–Ni–S bond angle within the five-membered rings is 90.01(6)°; these values compare well with those found in other $Ni(mnt)_2^-$ complexes [17]. The $[DiClBzMePy]^+$ cation adopts a conformation where both the phenyl and pyridine rings are twisted relative to the C(12)–C(15)–N(5) reference plane. The phenyl and pyridine rings are planar. The deviations of two Cl atoms from the phenyl ring plane are 0.0781 and −0.0504 Å, and the deviation of C(21) from the pyridine ring plane is 0.0446 Å.

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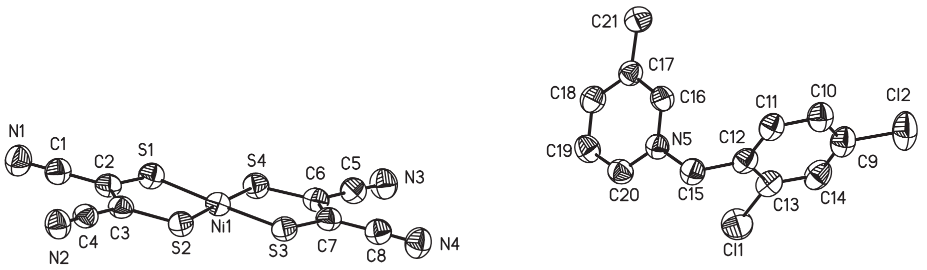

FIGURE 1 ORTEP plot (30% probability ellipsoids) showing the molecule structure of Complex **1**.

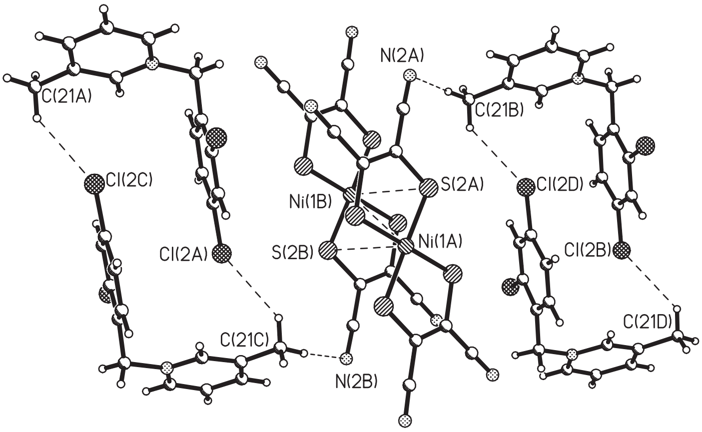

FIGURE 2 The intermolecular contacts between anions and cations of Complex **1**.

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The dihedral angles that the pyridine ring and the phenyl ring make with the C(12)–C(15)–N(5) reference plane are 129.7 and 77.5°, respectively. The phenyl ring and the pyridine ring make a dihedral angle of 79.0°. The planes defined by S(1)–S(2)–Ni(1)–S(3)–S(4) with the phenyl ring and pyridine ring make dihedral angles of 66.7 and 111.1°, respectively.

An interesting structural feature of Complex **1** is the presence of anion–anion, anion–cation and cation–cation contacts (Fig. 2) the Ni(mnt)$_2^-$ ions and the [DiClBzMePy]$^+$ cation stack into well-segregated columns along the crystallographic *a* axis (Fig. 3), and each Ni(mnt)$_2^-$ anion is flanked by four columns of cations. In an anionic column, the Ni···Ni distances alternate between 3.810 and 4.027 Å; the nearest Ni···S and S···S distances are 3.451 and 3.825 Å, respectively. The closest Ni···Ni separation between anion columns is 14.130 Å, significantly longer than the Ni···Ni separation within a column. Therefore, each Ni(mnt)$_2^-$ anion can be considered as a one-dimensional magnetic chain by means of the intermolecular Ni···S, S···S or $\pi \cdots \pi$ interactions. The slipped zigzag configuration of Ni(mnt)$_2{}^-$ anions is displayed in Fig. 4. Within a column of [DiClBzMePy]$^+$ cations, there are two significant interactions in adjacent cations. One interaction is the hydrogen bond between a chlorine atom of the benzene ring on one cation and a hydrogen atom of the methyl group on another cation [C(21)–H(21)···Cl(2), $-x+1$, $-y+1$, $-z$]; and the other is the p–π interaction between the chlorine atom and benzene ring (the contact distance of the Cl atom to the center of the neighboring benzene ring is 3.744 Å). The cation–cation

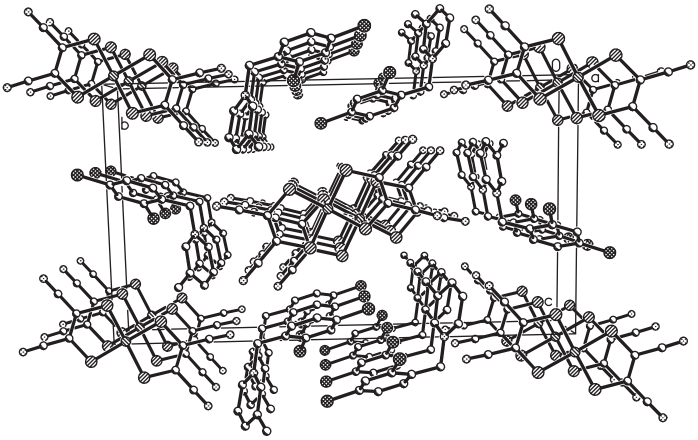

FIGURE 3 The packing diagram of a unit cell for Complex **1** as viewed along the *a*-axis.

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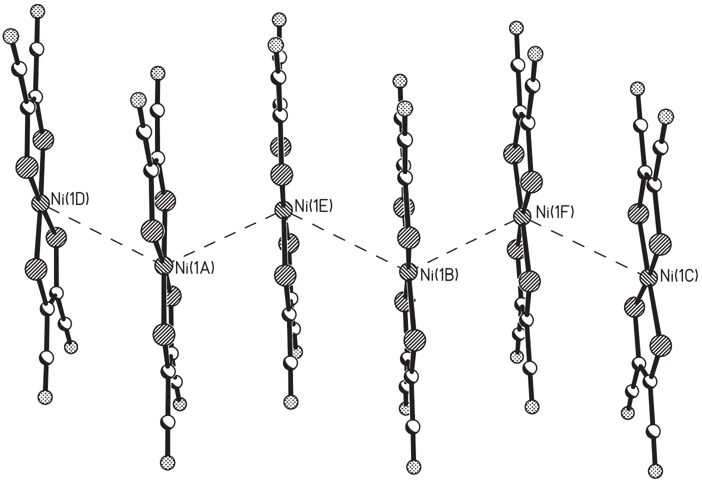

FIGURE 4 Side view of the anions stack of Complex **1** showing the alternating space linear-chain of $[Ni(mnt)_2]^-$.

interactions give rise to a cation column with a rectangular channel extending along the crystallographic *a* axis (Fig. 5). Intermolecular hydrogen bonds between anions and cations were observed in the crystal structure and molecular structure as shown in Fig. 2. The intermolecular contact is the N(2) atom with the C(21) $(x, y+1, z+1)$ atom at 3.534(7) Å; the hydrogen atom associated with these atoms has contact with $N(2)\cdots H(21)$ of 2.620 Å. These anion–anion, anion–cation and cation–cation contacts may play important roles in the crystal packing.

IR Spectra and ESI Mass Spectra

In the IR spectrum of Complex **1**, the bands at 3097 cm^{-1} and 2925 cm^{-1} are assigned to the stretching vibration of C–H in the aromatic rings and methyl group, respectively.

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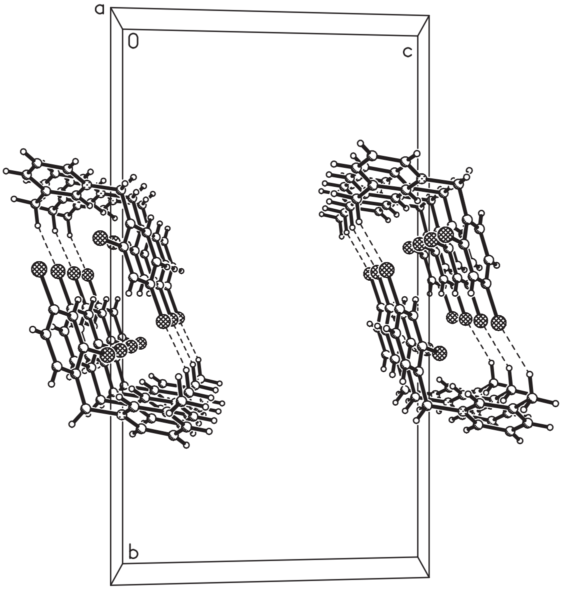

FIGURE 5 Side view of the cation stack of Complex **1** as viewed along the *a*-axis.

The very strong $\nu(C\equiv N)$ band is at $2208\,cm^{-1}$. The $\nu(C=N)$ and $\nu(C=C)$ bands for the pyridine ring and phenyl ring are located at 1632(m), 1589(s), 1564(m) and 1501(s) cm^{-1}. $\nu(C=C)$ of mnt^{2-} is at 1447(s) cm^{-1} and the band at 860(m) cm^{-1} results from ν(C–S). The bands at 679(m) and 600(w) cm^{-1} originate from ν(C–Cl).

The negative-ion and positive-ion ESI-MS spectra of the complex in MeCN solution show that the mass spectrum is dominated by the 337.9 peak, which is due to $[Ni(mnt)_2\text{-}H]^-$; the peak at 252.1 is assigned to $[DiClBzMePy\text{-}H]^+$.

Magnetic Susceptibilities

The magnetic behavior of Complex **1** in the form of χ_m (χ_m is the molar magnetic susceptibility per nickel atom) *vs* *T* in the range 300–75 K is shown in Fig. 6. Corrections for diamagnetism of Complex **1** are estimated from Pascal's constants to be $-266.49\times10^{-6}\,emu\,mol^{-1}$. The effective magnetic moment of Complex **1** is 1.712 μB at 300 K, which is slightly less than the calculated spin-only value of 1.732 μB for a system composed of noninteracting $g=2$, $s=1/2$ spin sites, and falls to 1.540 μB at 75 K. The effective magnetic moment of Complex **1** decreases with the decreasing temperature, which suggests antiferromagnetic interactions between adjacent $s=1/2$ Ni(III) spin magnetic centers within the anion chain. Taking into account the possibility that Complex **1** may act as a uniformly spaced chain of nickel(III) ions from the point of view of structure analysis due to the small difference between two Ni···Ni distances in the nickel(III) ion chains, its magnetic susceptibility data can be analyzed using the theoretical expression ($H=-J(S_iS_{i+1})$) for a uniform chain of local spin $s=1/2$ (Eq. (1)) [18,19]:

$$\chi_m=(N\beta^2g^2/kT)(0.25+0.14994x+0.300094x^2)/(1+1.9862x+0.68854x^2+6.0626x^3) \tag{1}$$

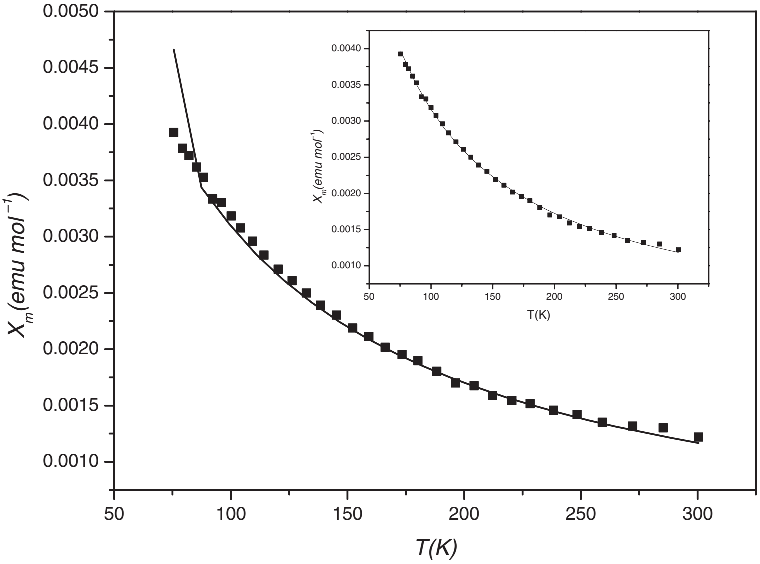

FIGURE 6 Plot of χ_M *versus* T for Complex **1**.

where $x = |J|/kT$ and J is the exchange coupling parameter describing the magnetic interaction between two neighboring $s = 1/2$ spins. The best-fit parameters obtained by least-squares are: $g = 2.00$ $J = -19.85\,\text{cm}^{-1}$ and $R = 1.9 \times 10^{-8}$ [R is defined as $\sum(\chi_m^{\text{calcd}} - \chi_m^{\text{obsd}})^2 / \sum(\chi_m^{\text{obsd}})^2$]. The model provides an excellent fit (the solid line in Fig. 6), as indicated by the low value of R. The magnetic susceptibility data may also be interpreted using the Curie–Weiss law $\chi_m = C/(T - \theta)$, giving a θ value of $-20.09\,\text{K}$, a Curie constant $C = 0.38\,\text{emu}\,\text{K}\,\text{mol}^{-1}$ and $R = 2.7 \times 10^{-5}$.

SUMMARY

A novel ion-pair complex [DiClBzMePy][Ni(mnt)$_2$] exhibiting antiferromagnetic behavior has been synthesized. Single-crystal structural analysis shows that the Ni(mnt)$_2^-$ anions and [DiClBzMePy]$^+$ cations of Complex **1** stack into well-segregated columns in the solid state; the Ni(III) ions form a 1D zigzag chain within a Ni(mnt)$_2^-$ anion through Ni···S, S···S and Ni···S···Ni interactions. The variable temperature magnetic susceptibilities measured over the range 75–300 K reveal that Complex **1** exhibits antiferromagnetic behavior.

Supplementary Material

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

Acknowledgments

We are grateful for the financial support of the National Natural Science Foundation of China (Project No. 20171022) and the Science Foundation of China Three Gorges University.

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