

4-硝基邻苯二硫酚金属镍配合物的合成、结构和性质

温和瑞^{1,2} 李育佳² 王彩凤² 左景林^{*2} 游效曾²

(¹赣南师范学院化学与生命科学系, 赣州 341000)

(²南京大学配位化学国家重点实验室, 南京 210093)

摘要: 合成了4-硝基邻苯二硫酚配体及相应金属镍配合物, $(\text{Bu}_4\text{N})_2[\text{Ni}(\text{nbdt})_2]$ (**1**)和 $(\text{Bu}_4\text{N})[\text{Ni}(\text{nbdt})_2]$ (**2**)(nbdt=4-硝基邻苯二硫酚阴离子), 并通过X-射线单晶结构测定、循环伏安、ESR谱、紫外可见吸收光谱和变温磁化率实验对其结构和性质进行了表征。这两个化合物均为略有变形的平面四方型配合物。配合物**2**是由配合物**1**通过 I_2 氧化制备。配合物**2**含有一个未成对电子, 磁性研究表明由于分子间的自旋耦合使它表现为反铁磁性。

关键词: 5-硝基邻苯二硫酚; 金属镍配合物; 电子顺磁共振; 磁性质

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Syntheses, Structures and Properties of Nickel Complexes with 4-nitro-benzene-1,2-dithiolate Ligand

WEN He-Rui^{1,2} LI Yu-Jia² WANG Cai-Feng² ZUO Jing-Lin^{*2} YOU Xiao-Zeng²

(¹Department of Chemistry and Life Science, Gannan Teachers College, Ganzhou, Jiangxi 341000)

(²State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093)

Abstract: Two new nickel complexes with a new 1,2-dithiolate ligand, $(\text{Bu}_4\text{N})_2[\text{Ni}(\text{nbdt})_2]$ (**1**) and $(\text{Bu}_4\text{N})[\text{Ni}(\text{nbdt})_2]$ (**2**) (nbdt=4-nitro-benzene-1,2-dithiolate), have been synthesized and characterized by X-ray single-crystal structure determination, cyclic voltammetry, ESR, UV/Vis spectra and magnetic susceptibility measurements. Complex **2** was obtained by oxidation of complex **1** with I_2 . The crystal structure determination reveals that the central Ni atoms in complexes **1** and **2** are in slightly distorted square-planar coordination environment. The cyclic voltammetric studies show that there are two oxidation peaks at 0.15 and 0.85 V for complex **1**. The antiferromagnetic interaction dominates the magnetic properties in complex **2**. CCDC: 287714; 287715.

Key words: 4-nitro-benzene-1,2-dithiolate ligand; Nickel complexes; ESR spectra; Magnetic properties

0 Introduction

Metal complexes of 1,2-dithiolene ligands have been intensively studied because of their novel properties and applications in the areas of molecular conducting, magnetic materials, non-linear optics and others^[1,2]. Over the last decade, a large number of new

dithiolene ligands and resultant complexes have been prepared to optimize the molecular properties in an effort to prepare novel and advanced materials^[3-8]. The benzene-1,2-dithiolate (bdt) and toluene-3,4-dithiolate complexes of transition-metal ions were prepared and characterized as early as the 1960s^[9-12]. These complexes have been studied in details because of their

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*通讯联系人. E-mail: zuojl@nju.edu.cn

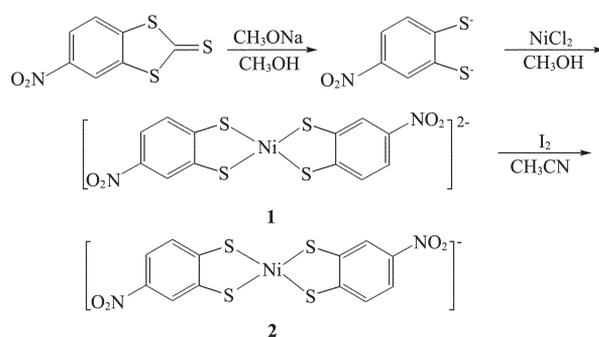
第一作者:温和瑞,男,41岁,教授;研究方向:功能配合物。

easy preparation compared with other bis (dithiolene) complexes and the rich redox and spectral properties. However, the magnetic and conducting properties of $[M(\text{bdt})_2]^{n-}$ have not been undertaken like other similar compounds, such as $[M(\text{mnt})_2]^{n-}$ (mnt=maleonitriledithiolate) and $[M(\text{dmit})_2]^{n-}$ (dmit=2-thioxo-1,2-dithiole-4,5-dithiolate)^[13,14]. This may be due to the perception of poorer intermolecular interactions for these in comparison with the $[M(\text{dmit})_2]^{n-}$ class owing to the reduced number of sulfurs in the $[M(\text{bdt})_2]^{n-}$ complexes. Recently several nickel complexes based on the benzene-1,2-dithiolate unit were synthesized and studied for magnetic properties^[15-18]. As we know, the type of side group on the benzene framework has great effects on the properties of the resulted complex. In order to explore the effects of chemical modification group on the properties of complexes, in this paper we report the syntheses, structures and properties of two new nickel complexes with a new 4-nitro-benzene-1,2-dithiolate ligand.

1 Experimental

1.1 General procedures

All chemicals were reagent grade and used as received. All solvents were of analytical grade and dried with standard methods and distilled before use. 5-nitro-2-thioxo-1,3-benzenedithiol was prepared according to the literature method^[19,20]. Elemental analyses for C, H and N were performed on a Perkin-Elmer 240C analyzer. The ESR spectra were measured using a Bruker ER 200-D-SRC spectrometer at room temperature. The IR spectra were taken on a Vector22 Bruker Spectrophotometer ($400\sim 4\,000\text{ cm}^{-1}$) with KBr pellets. The UV-Vis spectra were recorded on a Shimadzu UV-3100 spectrometer. NMR spectra were measured on a Bruker AM 500 spectrometer. Cyclic voltammetry data were recorded by an EG&G PAR Model 273 electrochemical analytical instrument. The magnetic susceptibility was measured using a Quantum Design MPMS-XL7 SQUID magnetometer at temperatures ranging from 1.8 to 300 K. The complexes were synthesized as shown in Scheme 1.



Scheme 1

1.2 Synthesis of complex 1

Under a nitrogen atmosphere, sodium (92 mg, 4 mmol) was added to 10 mL of methanol. After sodium was dissolved, 5-nitro-2-thioxo-1,3-benzenedithiol (458 mg, 2 mmol) was added to the solution and the reaction mixture was left to stir at 0 °C for 1 hour, then $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (237 mg, 1 mmol) in 5 mL of methanol was added. The color of the solution immediately changed into black-blue. $(\text{C}_4\text{H}_9)_4\text{NBr}$ (645 mg, 2 mmol) in 5 mL of methanol was added to the above solution and black-blue precipitate was observed immediately. The reaction mixture was left to stir for 1 hour. The precipitate was filtered off, washed with methanol and ether, and dried in vacuo. Yield: 750 mg (82%). Anal. Calc. for $\text{C}_{44}\text{H}_{78}\text{N}_4\text{O}_4\text{S}_4\text{Ni}$ (%): C, 57.76; H, 8.53; N, 6.13. Found (%): C, 57.68; H, 8.57; N, 6.20. Air-stable black-blue needle-shaped crystals of $(\text{Bu}_4\text{N})_2[\text{Ni}(\text{nbdt})_2]$ were obtained by slow diffusion of diethyl ether into a solution of the product in acetonitrile.

1.3 Synthesis of complex 2

Iodine (127 mg, 0.5 mmol) in 5 mL of acetonitrile was added to **1** (458 mg, 0.5 mmol) in 10 mL of acetonitrile. The color of the solution changed into brown-black. The brown-black precipitate was obtained by slow evaporation of the resulting solution. Air-stable brown-black needle-shaped crystals of $(\text{Bu}_4\text{N})[\text{Ni}(\text{nbdt})_2]$ were obtained by slow diffusion of diethyl ether into a solution of the product in dichloromethane. Yield: 289 mg (86%). Anal. Calc. for $\text{C}_{28}\text{H}_{42}\text{N}_3\text{O}_4\text{S}_4\text{Ni}$ (%): C, 50.03; H, 6.25; N, 6.25. Found (%): C, 50.11; H, 6.20; N, 6.23.

1.4 X-ray structure determination of complexes 1 and 2

The crystal diffraction data of complexes **1** and **2** were collected on a Siemens (Bruker) SMART CCD diffractometer using graphite monochromatized Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). Cell parameters were retrieved using SMART software and refined using SAINT on all observed reflections. Data collection was carried out by using the following strategy: 606 frames of 0.3° in ω with $\phi=0^\circ$, 435 frames of 0.3° in ω with $\phi=90^\circ$, and 235 frames of 0.3° in ω with $\phi=180^\circ$. An additional 50 frames of 0.3° in ω with $\phi=0^\circ$ were collected to allow for decay correction. The highly redundant data sets were reduced using SAINT and cor-

rected for Lorentz and polarization effects. Absorption corrections were applied using SADABS supplied by Bruker. Structures were solved by direct methods using the program SHELXTL. The positions of metal atoms and their first coordination spheres were located from direct methods E-maps; other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles and, during the final cycles, refined anisotropically. Hydrogen atoms were placed in calculated position and refined as riding atoms with a uniform value of U_{iso} . A summary of crystallographic data and refinement parameters is given in Table 1.

CCDC: 287714; 287715.

Table 1 A summary of crystallographic data for complexes 1 and 2

	1	2
Formula	C ₄₄ H ₇₈ N ₄ O ₄ S ₄ Ni	C ₂₈ H ₄₂ N ₃ O ₄ S ₄ Ni
Formula weight	914.05	671.60
Temperature / K	293(2)	293(2)
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pca2_1$
a / nm	0.967 8(10)	3.310 6(7)
b / nm	1.980 9(2)	1.302 4(3)
c / nm	1.514 7(17)	1.529 6(3)
α / (°)	90	90
β / (°)	119.522(3)	90
γ / (°)	90	90
Z	2	8
V / nm ³	2.5242(5)	6.595(2)
$D_{calc.}$ / (g·cm ⁻³)	1.203	1.353
λ / nm	0.071 073	0.071 073
Absorption coefficient / mm ⁻¹	0.591	0.878
F(000)	988	2 840
θ range / (°)	1.86~26.00	1.56~26.29
Index range (h, k, l)	$-10 \leq h \leq 11, -24 \leq k \leq 17, -17 \leq l \leq 18$	$-41 \leq h \leq 42, -16 \leq k \leq 15, -19 \leq l \leq 14$
Reflection collected	13 453	33 288
Independent reflections	4 958 [$R(int)=0.160$ 9]	12 506 [$R(int)=0.041$ 3]
Data / restraints / parameters	4 958 / 0 / 263	12 506 / 1 / 729
Goodness-of-fit on F^2	0.806	1.024
Final R indices [$I > 2\sigma(I)$]	$R_1=0.0686, wR_2=0.0793$	$R_1=0.0472, wR_2=0.1181$
Largest diff. peak and hole / (e·nm ⁻³)	343 and -251	452 and -306

2 Results and discussion

2.1 Preparation of complexes 1 and 2

The complex **1** was prepared similar to the liter-

ature method^[11]. The synthetic procedures were shown in Scheme 1. Under a nitrogen atmosphere, 4-nitro-1, 2-dithiolate was prepared by the reaction of CH₃ONa and 5-nitro-2-thioxo-1,3-benzenedithiol. Oxidation of **1**

with I₂ as oxidant led to the formation of complex **2**, accompanied with color changes from black-blue to brown. The dried sample of complex **1** is stable in air.

2.2 Crystal structure

Selected bond lengths and angles for complexes **1** and **2** are listed in Table 2. The molecular structure of complex **1** is shown in Fig.1a, the Ni atom is in an inversion center and the four sulfurs surrounding the nickel atom yield an square-planar coordination environment with the bond angles being 90.32(7)° for S(2)-Ni(1)-S(1) and 89.68(7)° for S(2)-Ni(1)-S(1)#1. The Ni-S bond lengths are 0.223 8(19) nm (Ni(1)-S(2)) and 0.227 2(18) nm (Ni(1)-S(1)), respectively. The molecular structure of complex **2** is shown in Fig.1b. Two kinds of independent molecules with slightly different bond lengths and angles exist in the same asymmetric unit of crystal structure of complex **2**. The molecular structure of complex **2** is similar to complex **1**, but the Ni atom is in a slightly distorted square-planar coordination environment with the bond angles being 92.30(6)° for S(2)-Ni(1)-S(1) and 87.58(7)° for S(4)-Ni(1)-S(2). The average bond length of Ni-S is 0.214 8(17) nm, which is shorter than the corresponding value in complex **1**. The bond angles of S(4)-Ni(1)-S(1), S(3)-Ni(1)-S(2) are

176.67(7)°, 179.14(6)°, respectively, which deviate slightly from 180°. The packing diagram of complex **2**

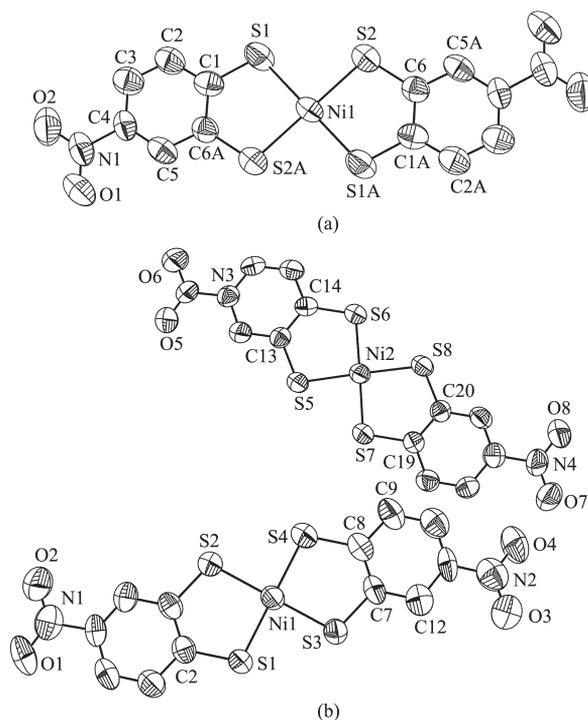


Fig.1 ORTEP diagrams and atomic numbering scheme of complexes: (a) [Ni(nbd)₂]²⁻ in **1** and (b) [Ni(nbd)₂]⁻ in **2**, with thermal ellipsoids at 50% probability level

Table 2 Selected bond distances (nm) and bond angles (°) for complexes **1** and **2**

Complex 1					
Ni(1)-S(2)	0.223 8(19)	S(1)-C(1)	0.168 9(7)	C(3)-C(4)	0.136 8(7)
Ni(1)-S(2)#1	0.223 8(19)	S(2)-C(6)	0.173 7(7)	C(4)-C(5)	0.139 1(8)
Ni(1)-S(1)	0.227 2(18)	C(1)-C(2)	0.139 9(8)	C(5)-C(6)#1	0.140 8(8)
Ni(1)-S(1)#1	0.227 2(18)	C(2)-C(3)	0.139 0(8)	C(1)#1-C(6)	0.139 8(7)
S(1)#1-Ni(1)-S(2)#1	90.32 (7)	S(2)#1-Ni(1)-S(2)	180.00(1)	S(1)-Ni(1)-S(2)	90.32(7)
S(1)#1-Ni(1)-S(2)	89.68(7)	C(1)-S(2)-Ni(1)	103.9(3)	S(1)-Ni(1)-S(2)#1	89.68(7)
S(1)-Ni(1)-S(1)#1	180.00(10)	C(2)-S(3)-Ni(1)	103.6(3)		
Complex 2					
Ni(1)-S(1)	0.214 5(16)	S(1)-C(2)	0.173 2(5)	C(1)-C(2)	0.139 8(7)
Ni(1)-S(2)	0.215 0(17)	S(2)-C(1)	0.174 2(6)	C(2)-C(3)	0.139 8(8)
Ni(1)-S(3)	0.214 7(15)	S(3)-C(7)	0.175 0(6)	C(7)-C(8)	0.138 5(9)
Ni(1)-S(4)	0.215 0(18)	S(4)-C(8)	0.174 0(6)	C(1)-C(6)	0.138 5(7)
S(1)-Ni(1)-S(2)	92.30(6)	S(2)-Ni(1)-S(4)	87.58(7)	C(7)-S(3)-Ni(1)	104.3(2)
S(1)-Ni(1)-S(3)	88.08(6)	S(1)-Ni(1)-S(4)	176.67(7)	C(2)-S(1)-Ni(1)	104.7(2)
S(3)-Ni(1)-S(4)	92.08(7)	S(2)-Ni(1)-S(3)	179.14(6)		

#1: -x+1, -y+1, -z+1.

shows that $[\text{Ni}(\text{nbd})_2]^-$ layers are separated by cation layers preventing any short anion-anion interaction (Fig.2). The two nitro groups of ligands are in *trans*-position in both complexes **1** and **2**.

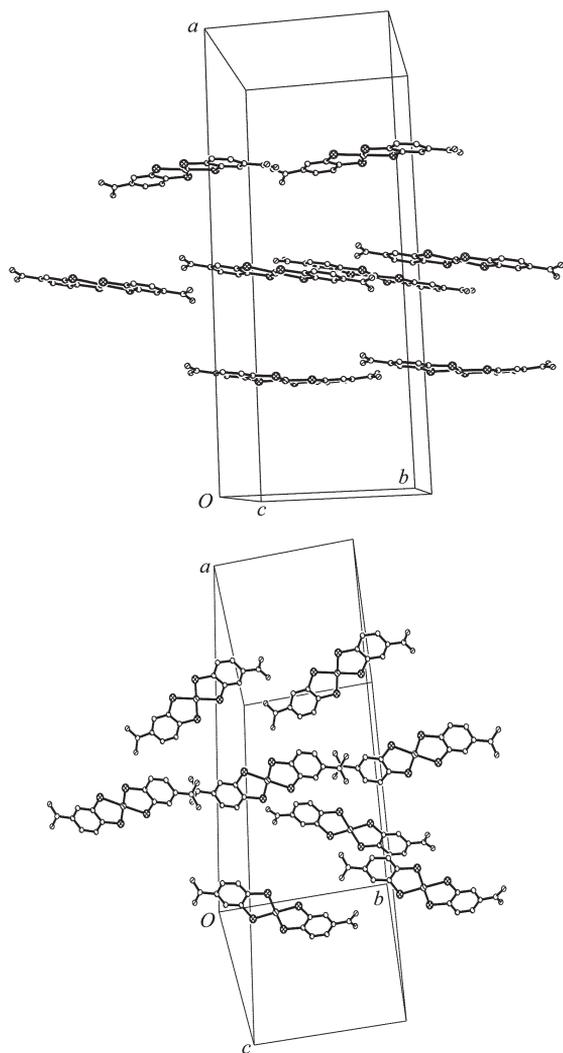


Fig.2 Packing diagram for complex **2** along the *c*-axis
The cations are omitted for clarity.

2.3 Spectroscopic studies

The UV-Vis absorption spectra of complex **1** and **2**, recorded in acetonitrile, are shown in Fig.3. Three absorption peaks at 260 nm, 315 nm and 380 nm were observed for complex **1**, and three absorption bands at 310 nm, 375 nm and 850 nm for complex **2**. The strong absorption at 850 nm for complex **2** is assigned to the $\pi \rightarrow \pi^*$ transition. The EPR spectrum for **2** recorded at room temperature shows the broad feature centered at $g=2.113$ (Fig.4), indicating that

there is an unpaired electron in complex **2**.

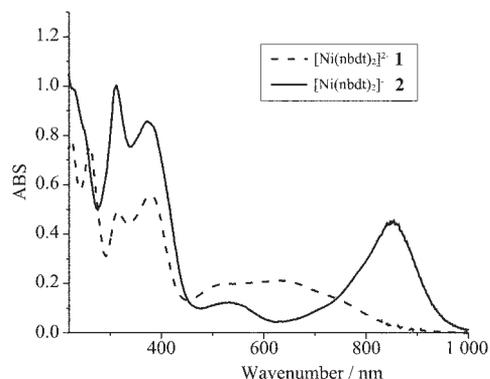


Fig.3 UV-Vis absorption spectrum of the complexes **1** and **2** in acetonitrile

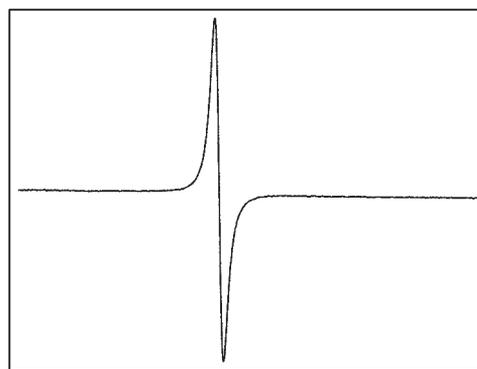


Fig.4 ESR spectrum of complex $[\text{Ni}(\text{nbd})_2]^-$ (**2**) at room temperature

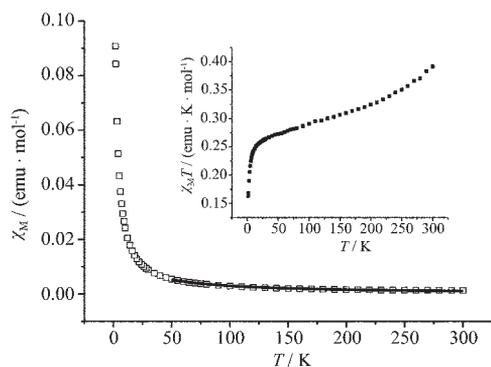
2.4 Cyclic voltammetry

Cyclic voltammetry of complexes **1** and **2** were carried out on a Macroscopic platinum-disc electrode in an acetonitrile solution, and the reference electrode was Ag/AgCl (using $0.1 \text{ mol} \cdot \text{dm}^{-3}$ $(\text{Bu}_4\text{N})\text{ClO}_4$ as supporting electrolyte, scan speed: $100 \text{ mV} \cdot \text{s}^{-1}$). The complex **1** shows two oxidation peaks at 0.15 and 0.85 V, and the complex **2** does an oxidation peak at 0.85 V. They are ascribed to the couple $[\text{Ni}(\text{nbd})_2]^{2-} / [\text{Ni}(\text{nbd})_2]^-$ and $[\text{Ni}(\text{nbd})_2]^- / [\text{Ni}(\text{nbd})_2]$. The first ox-red value is apparently higher than the related values for similar compounds with unsubstituted benzodithiolate (bdt) and toluenedithiolate (tdt) ligands, $[\text{Ni}(\text{bdt})_2]^{2-} / [\text{Ni}(\text{bdt})_2]^-$ (-1.05 V) and $[\text{Ni}(\text{tdt})_2]^{2-} / [\text{Ni}(\text{tdt})_2]^-$ (-1.07 V)^[7], suggesting that the strong electron-withdrawing ability of the substituted nitro group stabilizes the dianionic state of complex **1**. In fact, the monoanionic complexes, $[\text{Ni}(\text{bdt})_2]^-$ and $[\text{Ni}(\text{tdt})_2]^-$, can be easily obtained by oxidation of the dianion $[\text{Ni}(\text{bdt})_2]^{2-}$ or $[\text{Ni}(\text{tdt})_2]^{2-}$ in

air. However, to obtain $[\text{Ni}(\text{nbd})_2]^-$ from the dianion, the stronger oxidizing agent, such as iodine, has to be used.

2.5 Magnetic properties

Magnetic susceptibility measurements for complex **2** were performed on a Quantum Design MPMS-XL7 SQUID magnetometer at temperatures ranging from 1.8 to 300 K. For complex **2** at the room temperature, $\chi_M T$ is $0.41 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$, which is almost equal to the value ($0.375 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$) of an unpaired electron in a molecular sheet. As the temperature lowers, the $\chi_M T$ value decreases slowly to reach $0.25 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ at 15 K, then, the value rapidly decreases to $0.16 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$ at 1.8 K (Fig.5), implying that an antiferromagnetic interaction dominates the magnetic properties of this complex over the whole temperature range. The weak antiferromagnetic exchange results from intermolecular spin coupling. Variable temperature magnetic susceptibility studies in the temperature range 50~300 K show that **2** obeys the Curie-Weiss's law, $\chi_M = C/(T-\theta)$, with value of $\theta = -15.6 \text{ K}$, $C = 0.35 \text{ emu} \cdot \text{K} \cdot \text{mol}^{-1}$.



The solid line is the fitting from 300 K to 50 K

Fig.5 Temperature dependence of the χ_M and $\chi_M T$ (inset) for complex $[\text{Ni}(\text{nbd})_2]^-$ (**2**)

In conclusion, two new nickel complexes with a new 1,2-dithiolate ligand have been synthesized and characterized by X-ray single-crystal structure determination, cyclic voltammetry, ESR, UV-Vis spectra

and magnetic susceptibility measurements. The structures and properties of two nickel complexes are obviously different because of the difference of the valence states of the central Ni atoms.

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