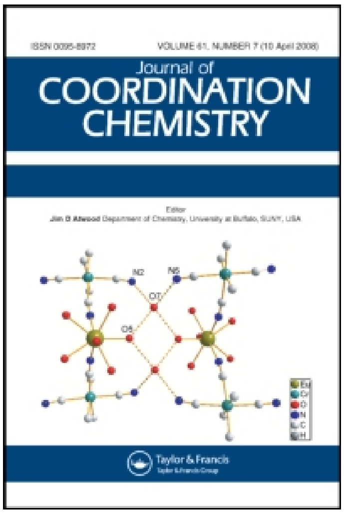

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Synthesis, crystal structure and magnetism of a two-dimensional Ni(II) coordination polymer with thiocyanate anion and dehydrogen-1,10-phenanthrolin-2-ol as bridging ligands

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A two-dimensional coordination polymer $[Ni(\mu_{1,3}\text{-SCN})(\mu\text{-Pheno})(CH_3OH)]_n$ (where Pheno = dehydrogen-1,10-phenanthrolin-2-ol) has been synthesized and its crystal structure determined by X-ray crystallography. Adjacent Ni(II) ions are coordinated by $\mu_{1,3}$-SCN^- and μ-Pheno alternately forming a two-dimensional sheet structure. The fitting of the variable-temperature magnetic susceptibilities with a binuclear nickel(II) formula reveals that there is an anti-ferromagnetic interaction between the bridging Ni(II) ions with the magnetic coupling constant $2J = -0.67\,\text{cm}^{-1}$.

Keywords: Crystal structure; Magnetism; Coordination polymer; Nickel complex

1. Introduction

Molecular magnetism has made major advances in theoretical description and application as new molecular-based materials [1–3]. Thiocyanate is a very useful bridging ligand and some of the complexes play an important role [4–9] in understanding the relation between structure and magnetic coupling, whereas the magnetic interaction for complexes with Pheno as a bridging ligand has not been reported, although Pheno displays electrical conducting behavior [10] and photoluminescence [11]. Interest in the magneto-structural studies of the complexes with mixed bridging ligands [12–15] resulted in our selecting thiocyanate and Pheno as bridging ligands, designing, synthesizing and studying the two-dimensional complex. Here we report the synthesis, the structure, and the magnetic coupling of a two-dimensional Ni(II) coordination polymer.

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2. Experimental

2.1. *Preparation*

PhenoH (1H-[1,10]phenanthrolin-2-one) was synthesized according to the literature method [15]. All other chemicals are of analytical grade and used without purification. $Ni(ClO_4)_2 \cdot 6H_2O$ (0.2190 g, 5.99×10^{-4} mol) and PhenoH (0.1176 g, 5.99×10^{-4} mol) were dissolved in 10 mL methanol and NaSCN (0.0972 g, 1.20×10^{-3} mol) was dissolved in 4 mL H_2O. After the three solutions were mixed and stirred for a few minutes, NaOH (0.024 g, 6.0×10^{-4} mol) was added to the solution and it was further stirred for a few minutes; then the mixture was placed in a teflon-lined autoclave and heated for 144 h at 160°C at an autogenous pressure. The reaction mixture was filtered after it was cooled to room temperature, and single green crystals were obtained after the mother liquor was allowed to stand at room temperature for 2 weeks. Yield: 53% (Found: C, 49.12; H, 3.52; N, 12.62; Ni, 17.75%. $C_{14}H_{11}NiN_3O_2S$ Calcd: C, 48.87; H, 3.22; N, 12.21; Ni, 17.06%). IR(cm^{-1}): 2121 s, 1622 m, 1593 s, 1513 s, 1458 s, 1381 s.

2.2. *Physical measurements*

Infrared spectra were recorded with a Bruker Tensor 27 infrared spectrometer in the $4000-500\,cm^{-1}$ region using KBr discs. C, H, and N elemental analyses were carried out on a Perkin–Elmer 240 instrument. Variable-temperature magnetic susceptibilities of microcrystalline powder samples were measured in magnetic fields of two KOe in the temperature range 2.5−300 K on a MPMS-7SQUID magnetometer. The data were corrected for magnetization of the sample holder and for diamagnetic contributions which were estimated from Pascal's constants.

2.3. *X-ray crystallographic analysis of the complex*

A single crystal of dimensions $0.50 \times 0.40 \times 0.38$ mm was selected and subsequently glued to the tip of a glass fiber. The determination of the crystal structure at 25°C was carried out on a Bruker Smart-1000 CCD X-ray diffractometer using graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). Corrections for *Lp* factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. The programs for structure solution and refinement were SHELXTL (Bruker, 2001). The crystal belongs to monoclinic, space group $P2_1/n$ with $a = 10.8710(17)$ Å, $b = 7.6412(12)$ Å, $c = 17.004(3)$ Å, $\beta = 104.650(2)°$, $V = 1366.6(4)$ Å^3, empirical formula $C_{14}H_{11}NiN_3O_2S$, molecular weight 344.03, $D_c = 1.672\,g/cm^3$, $F(000) = 704$, θ range 2.02–26.00°, index ranges $-13 \leq h \leq 5$, $-9 \leq k \leq 9$, $-20 \leq l \leq 20$. A total of 7198 reflections were collected and 2679 were independent ($R_{int} = 0.026$), of which 2424 observed reflections with $I > 2\sigma(I)$ were used in the succeeding refinement. The final refinement including hydrogen atoms converged to $R = 0.0266$, $wR = 0.0707$, $(\Delta\rho)_{max} = 0.334$ e/Å^3, $(\Delta\rho)_{min} = -0.260$ e/Å^3. The deposition number of the crystal at the CCDC is 643,327.

3. Results and discussion

3.1. *Crystal structure*

Figure 1 shows the coordination diagram with atom numbering scheme. Ni1 is coordinated by N1A, N2, N3, O1A, O2, and S2, in which N1A and S2 come from two $\mu_{1,3}$-SCN$^-$ bridges, O2 from methanol, N2 and N3 from a μ-Pheno bridge, and O1A from another μ-Pheno bridge. The data of table 1 indicate that Ni1 is distorted

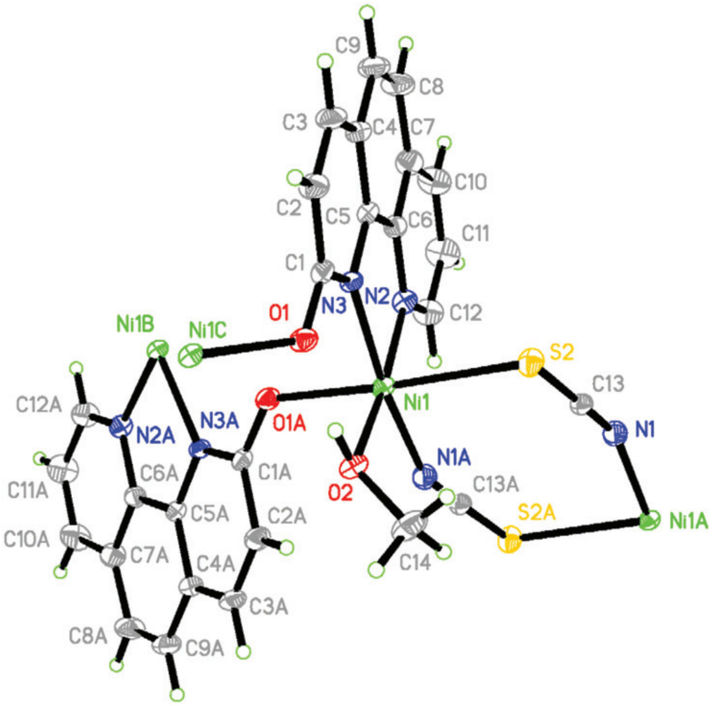

Figure 1. Coordination diagram of the complex with atom numbering scheme.

Table 1. Selected bond lengths (Å) and angles (°).

Bond length					
Ni1–N1A	2.0402(17)	Ni1–N2	2.0693(16)	Ni1–N3	2.0895(15)
Ni1–O1A	2.0840(13)	Ni1–O2	2.0780(13)	Ni1–S2	2.5642(6)
Bond angle					
N1A–Ni1–N2	94.20(7)	N1A–Ni1–O2	93.46(6)		
N2–Ni1–O2	172.34(6)	N1A–Ni1–O1A	92.31(6)		
N2–Ni1–O1A	89.16(6)	O2–Ni1–O1A	90.27(5)		
N1A–Ni1–N3	172.93(6)	N2–Ni1–N3	80.54(6)		
O2–Ni1–N3	91.86(6)	O1A–Ni1–N3	92.33(5)		
N1A–Ni1–S2	90.02(5)	N2–Ni1–S2	88.29(5)		
O2–Ni1–S2	91.97(4)	O1A–Ni1–S2	176.67(4)		
N3–Ni1–S2	85.13(4)				

Notes: Symmetry code: N1A: $-x+1$, $-y+1$, $-z+2$; O1A: $-x+1/2$, $y+1/2$, $-z+3/2$.

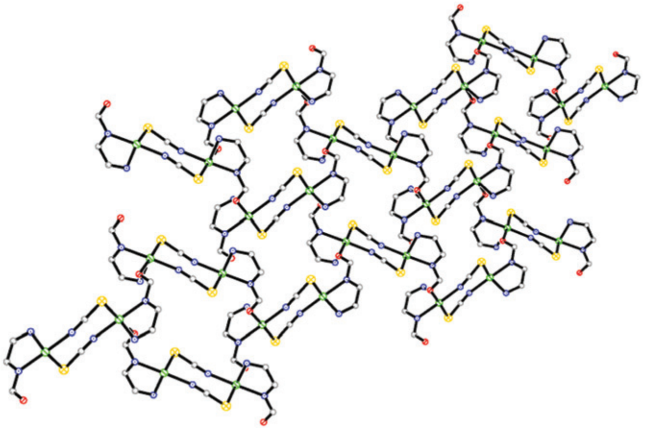

Figure 2. Two-dimensional sheet structure (methanol molecule as terminal ligand has been omitted for clarity; Pheno bridge ligand has been abbreviated into O–C–N–C–C–N chain for clarity).

octahedral coordination geometry. There are two bridging ligands, $\mu_{1,3}$-SCN$^-$ and μ-Pheno, and two Ni(II) ions with Ni$\cdots$Ni separation of 5.6302(8) Å bridged by two $\mu i_{1,3}$-SCN$^-$ ligands leading a binuclear eight-membered unit. Two adjacent eight-membered units with Ni$\cdots$Ni separation of 5.1904(6) Å were joined by μ-Pheno. Figure 2 shows the two-dimensional sheet structure, revealing a unit consisting of four thiocyanates, four μ-Pheno anions, and six Ni(II) cations. The two-dimensional sheet was fabricated by piecing together the units.

3.2. *Magnetism*

With different bridging models in this crystal it seems reasonable that there are two different magnetic coupling pathways, and one may be stronger than the other. Therefore, we used a binuclear fitting formula. The experimental data of variable-temperature (2.5–300 K) magnetic susceptibilities are shown in figure 3, where χ_M is the molar magnetic susceptibility per binuclear Ni(II) unit, μ_{eff} is the magnetic moment per binuclear Ni(II). The μ_{eff} value at 300 K is 4.10 BM, which is a little larger than that of binuclear Ni(II) ion (4.00 BM for $g_{av} = 2$) at room temperature, and the μ_{eff} values decrease very slowly with temperature until 20 K and then decrease more rapidly, reaching a minimum of 3.51 BM at 2.50 K. This implies a very weak anti-ferromagnetic exchange between the bridged Ni(II) ions. A binuclear equation (2) was used to fit for the experimental susceptibility data, which was obtained based on an isotropic Hamiltonian operator as presented in equation (1).

$$\widehat{H} = -2J\widehat{S}_1\widehat{S}_2, \quad S_1 = S_2 = 1 \tag{1}$$

$$\chi_M = \frac{2N\beta^2 g^2}{kT}\frac{A}{B} \tag{2}$$

$$A = 5 + \exp\left(\frac{-4J}{kT}\right); \quad B = 5 + 3\exp\left(\frac{-4J}{kT}\right) + \exp\left(\frac{-6J}{kT}\right)$$

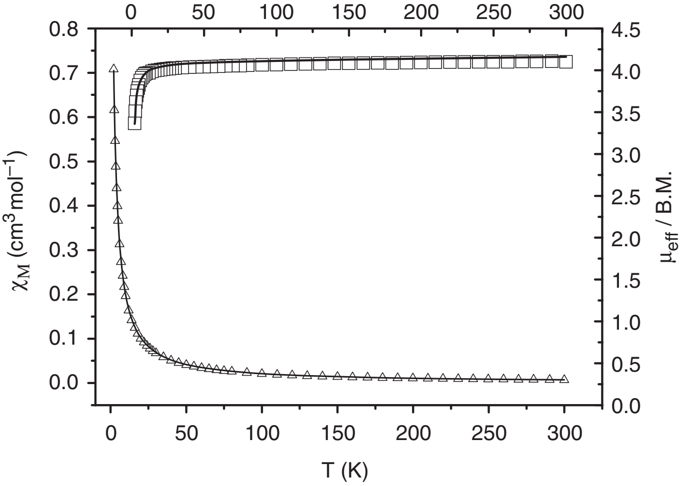

Figure 3. Plots of χ_M (triangle for experimental data, line for theoretical value) and μ_{eff} (open squares for experimental data, line for theoretical value) *versus* T for the complex.

The theoretical model gave good fitting for the experimental results, with agreement factors of $R = 1.44 \times 10^{-5}$ $[R = \sum(\chi_{obsd} - \chi_{calcd})^2/(\chi_{obsd})^2]$, $g = 2.05$, $2J = -0.67\,\text{cm}^{-1}$. The value of $2J = -0.67\,\text{cm}^{-1}$ indicates that there is a very weak anti-ferromagnetic interaction between the bridged Ni(II) ions. Generally the magnetic couplings between bridging Ni(II) ions with thiocyanate as end–end bridge show weak ferromagnetic interactions with coupling constants from $J = 2.4\,\text{cm}^{-1}$ to $J = 6.3\,\text{cm}^{-1}$ [9, 16–19]. The fact that the present complex exhibits a weak anti-ferromagnetic interaction may indicate that the magnetic interaction between μ-Pheno bridging Ni(II) ions is a weak anti-ferromagnetic interaction, but its coupling intensity is stronger than that of thiocyanate bridging Ni(II), offsetting the ferromagnetic interaction, making the present complex exhibit a weak anti-ferromagnetic interaction. We have tried to study the magnetic coupling mechanism by using DFT theoretical calculations and binuclear models [12–15], but we have not obtained the information yet.

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