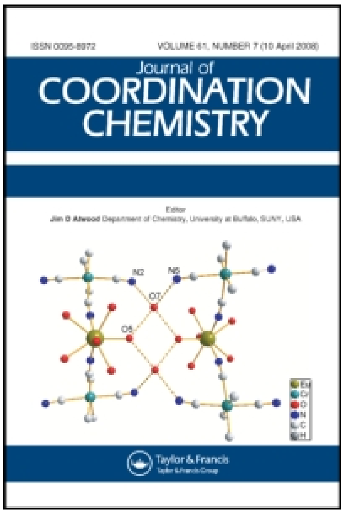

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Synthesis, crystal structure and magnetism of 1D cobalt(II) coordination polymer with thiocyanate as bridging ligand

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Synthesis, crystal structure and magnetism of 1D cobalt(II) coordination polymer with thiocyanate as bridging ligand

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A one-dimensional coordination polymer $[Co(\mu_{1,3}\text{-}NCS)_2(npdo)_2]_n$ (npdo = 4-nitropyridine N-oxide) has been synthesized and structurally determined by X-ray crystallography. The complex crystallizes in the orthorhombic space group of Pbcn with $a = 22.688(5)$ Å, $b = 7.2636(17)$ Å, $c = 10.299(2)$ Å. Adjacent Co(II) ions are coordinated by two $\mu_{1,3}$-SCN$^-$ bridging ligands, forming a one-dimensional chain along the *c* axis and the npdo coordinates to Co(II) ion as a terminal ligand. The thermal variation of the magnetic moments of the complex reflects the antiferromagnetic interaction between the bridged Co(II) ions above 20 K and the ferromagnetic transition or the strong short-range spin interaction below 20 K.

Keywords: Crystal structure; Cobalt(II) complex; Magnetism

1. Introduction

Molecular magnetism has attracted considerable attention, and major advances have been made in both theoretical description and application as new molecular-based materials [1]. In particular, special attention has been paid to design and construction of homo- and hetero-metallic coordination polymers in order to undertake theoretical studies of their magnetic properties and develop high T_c molecular-based magnets [2]. Thiocyanate anion, with ambidentate character of end-to-end or end-on coordination modes [3, 4], is expected to play a key role in the design of polymetallic coupling systems. A number of polynuclear complexes have been synthesized with discrete, one-, two- and three-dimensional, crystal structures [5–11]; most deal with homo-copper(II) [12–15] and homo-nickel(II) [16–18] multinuclear complexes with only one homo-cobalt(II) complex [19] to date. In these thiocyanate-bridged multi-nuclear complexes most of them exhibit weak magnetic interaction and only a limited number of complexes display strong magnetic interaction [19–22].

In order to obtain strong magnetic coupling judicious choice of coordinated atoms with large electron densities is crucial. Theoretical calculations have confirmed that the O atom electron densities of pyridine N-oxide and its derivatives are larger than that of N atom of pyridine and its derivatives [23]. The one-dimensional Cu(II) complex [22] with thiocyanate as brdging ligand and 4-methylpyridine N-oxide as terminal ligand

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exhibits strong magnetic coupling between the bridged Cu(II) ions. Other complexes containing aromatic N-oxide as ligands also display strong magnetic interactions [24].

Interest in understanding the magneto-structure relationship of complexes with thiocyanato and aromatic N-oxide as ligands resulted in the synthesis, characterization and study of the title complex. In this article, we present the crystal structure and magnetic study.

2. Experimental

2.1. *Preparation*

4-Nitropyridine N-oxide was prepared as described in the literature [25]; other chemicals are analytical grade and used without further purification.

A 10 mL acetonitrile solution containing $Co(ClO_4)_2 \cdot 6H_2O$ (0.2762 g, 7.55×10^{-4} mol) and NaNCS (0.1285 g, 1.58×10^{-3} mol) was added to a chloroform solution of 4-nitropyridine N-oxide (0.2231 g, 1.59×10^{-3} mol), and the mixed solution was stirred for a few minutes. Deep red single crystals were obtained after the mixed solution was allowed to stand for 2 weeks at room temperature. Yield 85% (based on npdo). Anal. Calcd for $C_{12}H_8CoN_6O_6S_2$: C, 31.65; H, 1.77; N, 18.46; Co, 12.94. Found: C, 31.90; H, 2.06; N, 18.05, Co, 13.48.

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 a magnetic field of 3K Oe in the temperature range of 4–300 K on a SQUID magnetometer. The data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from Pascal's constants.

2.3. *Crystal structure determination*

A single crystal of dimensions $0.23 \times 0.13 \times 0.03$ mm was selected and subsequently glued to the tip of a glass fiber. The crystal structure at 25°C was determined on an X-ray diffractometer, Model Bruker Smart-1000 CCD using graphite-monochromatic Mo-Kα radiation ($\lambda = 0.71073$ Å). Corrections for *Lp* factor was applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions and included in the final cycles of refinement using a riding model. The programs for structure solution and refinement were SHELXTL (Bruker, 2001). The deposition number at the CCDC is 290793. The relevant structure parameters were given in table 1.

Table 1. Crystal data and details of the refinement for the complex.

Empirical formula	$C_{12}H_8CoN_6O_6S_2$
CCDC deposit no.	290793
Formula weight	455.29
Temperature (K)	298
Crystal size (mm^3)	0.23 × 0.13 × 0.03
Crystal system	Orthorhombic
Space group (Å)	*Pbcn*
a	22.688(5)
b	7.2636(17)
c	10.299(2)
Volume ($Å^3$)	1697.3(7)
Z	4
D_{Calcd} ($Mg\,m^{-3}$)	1.782
Absorption coefficient (mm^{-1})	1.303
F(000)	916
Completeness	0.999 ($\theta = 25.03^\circ$)
Goodness-of-fit on F^2	0.993
Final *R* indices [$I > 2\sigma(I)$]	0.0741
R indices (all data)	0.1745
Largest differential peak and hole ($e\,Å^{-3}$)	1.717, −0.994

Table 2. Selected bond distances (Å) and angles (°).

Co1–N3A	2.0545(54)		
Co1–O1	2.1139(41)		
Co1–S1	2.6339(17)		
S1–Co1–S1B	175.37(9)	O1–Co1–S1B	92.50(12)
O1–Co1–S1	83.99(11)	O1A–Co1–O1	81.74(22)
N3B–Co1–S1B	89.44(14)	N3B–Co1–S1	93.61(14)
N3B–Co1–O1	90.70(18)	N3B–Co1–O1A	169.73(18)
N3A–Co1–N3B	97.60(29)		

Symmetry codes for: N3A: $-x, -y, -z+1$; N3B: $x, -y, z-1/2$; O1A and S1B: $-x, y, -z+1/2$.

3. Results and discussion

3.1. *Crystal structure*

3.1.1. Crystal data. $C_{12}H_8CoN_6O_6S_2$, $M = 455.29$, Orthorhombic, space group *Pbcn*, $a = 22.688(5)$ Å, $b = 7.2636(17)$ Å, $c = 10.299(2)$ Å, $Z = 4$, $V = 1697.3(7)\,Å^3$, $D_c = 1.782\,g\,cm^{-3}$, $F(000) = 916$, $\mu(\text{Mo-K}\alpha) = 1.303\,mm^{-1}$. Selected bond distances and the associated angles are listed in table 2.

3.1.2. Crystal structure. Figure 1 shows the coordination diagram for the complex with atom numbering scheme. Co1 is coordinated by N3A, N3B, O1, O1A, S1 and S1B atoms, N3A, N3B, S1 and S1B atoms come from four $\mu_{1,3}$-NCS^- bridging ligands, and O1 and O1A atoms are from two npdo terminal ligands. Table 1 indicates that Co1 is located in a distorted octahedral geometry. Adjacent Co(II) ions with separation of 5.7983(15) Å are connected by two $\mu_{1,3}$-NCS^- bridging ligands, forming a binuclear unit of the eight-membered ring; the binuclear unit atoms define a plane within 0.0674 Å with a maximum deviation of 0.0972 Å for atom N3. The connected binuclear units led

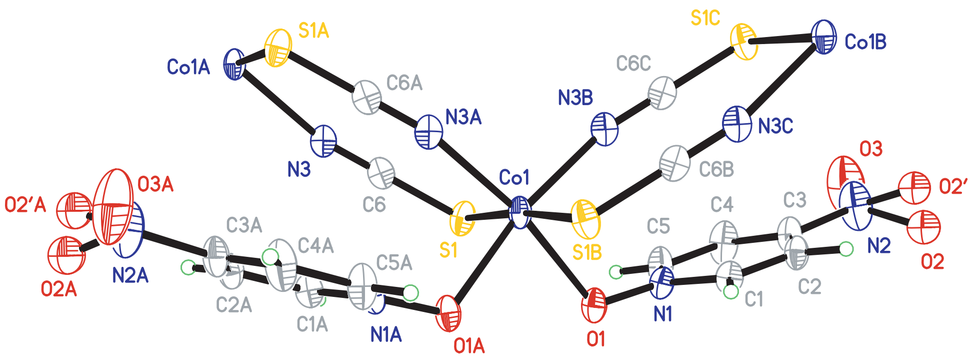

Figure 1. Coordination diagram of the complex with atom numbering scheme.

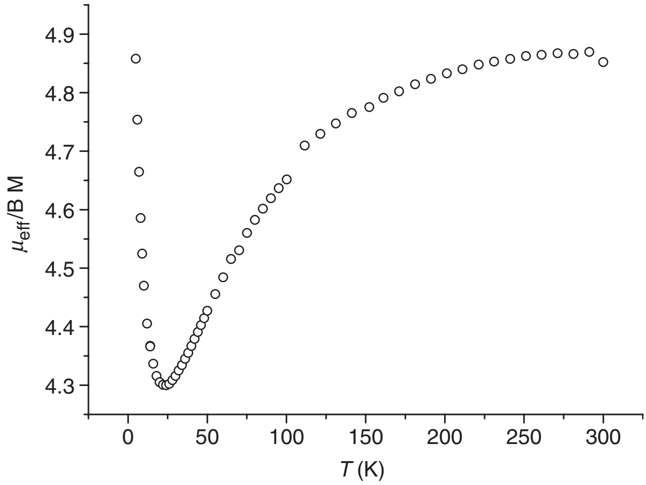

Figure 2. Thermal dependence of μ_{eff} for the complex.

to the formation of a zigzag one-dimensional chain along the *c* axis. The dihedral angle between the neighboring planes of the binuclear units is 73.7°.

3.2. *Infrared spectrum*

The characteristic peak of NCS^- appears at 2099 cm^{-1}, and the peaks at 1634, 1525 and 1471 cm^{-1} obviously are attributed to vibrations of pyridine.

3.3. *Magnetic property*

Figure 2 shows the thermal dependence of magnetic moment with temperature T, where μ_{eff} is the magnetic moment per Co(II). The magnetic moment value at 300 K is 4.85 μ_B, larger than that of uncoupled mononuclear Co(II) ion at room temperature (3.87 μ_B). The magnetic moment decreases with a drop in temperature and reaches a minimum of 4.30 μ_B at 24.06 (0.08) K, which indicates that there is strong spin–orbit coupling due to the $^4T_{1g}$ ground state for octahedral Co(II) complex [26–29] and also indicates an antiferromagnetic interaction between the $\mu_{1,3}$-NCS^- bridged Co(II) ions in this temperature range. Below 20.06 K, the value of the magnetic moment increases upon cooling and reaches a maximum of 4.86 μ_B at 4.94 K, which suggests a ferromagnetic transition or development of strong short-range conversion among spins [30].

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