

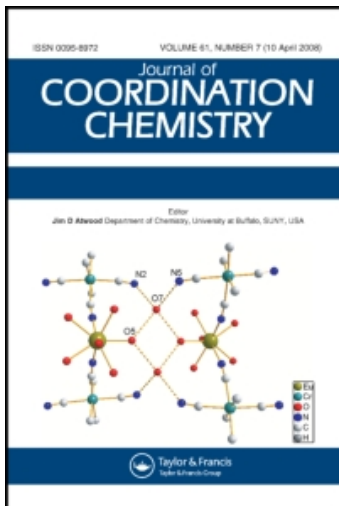
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Synthesis, crystal structure, and magnetic properties of a new end-to-end thiocyanato-bridged dicobalt(II) complex $\text{Co}^{\text{II}}(\text{dien})(\text{H}_2\text{O})(\text{NCS})(\mu_{1,3}\text{-NCS})\text{Co}^{\text{II}}(\text{dien})(\text{NCS})_2$ (dien = diethylenetriamine)

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Synthesis, crystal structure, and magnetic properties of a new end-to-end thiocyanato-bridged dicobalt(II) complex $\text{Co}^{\text{II}}(\text{dien})(\text{H}_2\text{O})(\text{NCS})(\mu_{1,3}\text{-NCS})\text{Co}^{\text{II}}(\text{dien})(\text{NCS})_2$ (dien = diethylenetriamine)

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Synthesis, characterization, crystal structure, and magnetic properties of the first single $\mu_{1,3}$ -thiocyanato-bridged dicobalt(II) compound, $[\text{Co}^{\text{II}}(\text{dien})(\text{H}_2\text{O})(\text{NCS})(\mu_{1,3}\text{-NCS})\text{Co}^{\text{II}}(\text{dien})(\text{NCS})_2]$ (**1**; dien = diethylenetriamine), are described. In **1**, cobalt(II) is six coordinate with distorted-octahedral geometry. The Co(1)⋯Co(2) distance is 5.99 Å. The magnetic properties of **1** have been investigated by variable-temperature magnetic susceptibility measurements. The metal centers are coupled by weak ferromagnetic interaction ($J = 1.14 \text{ cm}^{-1}$). The structure and magnetic properties are compared with related thiocyanate-bridged compounds.

Keywords: Dinuclear complex; Single thiocyanato-bridged; Crystal structure; Magnetic property

1. Introduction

Polynuclear metal complexes and ligands facilitating their formation have been extensively investigated due to potential applications in many fields of chemistry [1, 2]. One fascinating target is molecular-based magnets that exhibit spontaneous magnetization [3–7], which make them promising candidates for future applications in high-density information storage and computing [8]. In this research area, coordination chemistry of transition-metal complexes containing thiocyanate is interesting, because of end-to-end or end-on coordination [9, 10]. To clarify the magneto-structural correlation of thiocyanato-bridged compounds, thiocyanato-bridged polynuclear complexes were introduced and the structures as well as magnetic properties of the complexes have been systematically investigated [11–13]. Although there are two dicobalt(II) complexes in which the metal centers are bridged by double end-to-end NCS^- ligands [6, 14], there is no example of dicobalt(II) compounds bridged by a single thiocyanate connector. Herein, we report the synthesis, characterization, crystal

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structure, and magnetic properties of a dicobalt(II) compound $[\text{Co}^{\text{II}}(\text{dien})(\text{H}_2\text{O})(\text{NCS})(\mu_{1,3}\text{-NCS})\text{Co}^{\text{II}}(\text{dien})(\text{NCS})_2]$ (**1**; dien = diethylenetriamine), in which the metal ions are bridged by a single end-to-end thiocyanate ligand.

2. Experimental

2.1. Materials

All reagents and solvents were commercially available and used as received. FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer as a dry KBr pellet from 400 to 4000 cm^{-1} . Elemental analyses were carried out on an Elementar Vario ELIII microanalyzer. Magnetic measurements were carried out with a Quantum Design (SQUID) magnetometer MPMS-XL-5.

2.2. Synthesis of **1**

A solution (20 mL) of ammonium thiocyanate (NH_4SCN) (0.46 g, 6 mmol) was added to an aqueous solution of cobalt(II) chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) (0.71 g, 3 mmol). Then diethylenetriamine (0.28 mL, 4 mmol) was added with mild heating. Well-shaped pink crystals were obtained from the solution by slow evaporation at room temperature after 2 weeks. Elemental Anal. Calcd (%) for $\text{C}_{12}\text{H}_{28}\text{Co}_2\text{N}_{10}\text{OS}_4$: C, 25.80; H, 5.05; N, 25.08. Found (%): C, 25.83; H, 5.01; N, 25.06.

2.3. X-ray crystallography

Crystallographic data of **1** were collected at room temperature with a Bruker Smart 1000 CCD area-detector diffractometer with Mo-K α radiation ($\lambda = 0.71073\text{ \AA}$) by using an ω -scan mode. An empirical absorption correction was applied using SADABS [15]. All non-hydrogen atoms were located by direct methods and subsequent difference Fourier syntheses. Hydrogens bonded to carbon were located by calculations and their positions and thermal parameters were fixed during structure refinement. All non-hydrogen atoms were refined by full-matrix least-squares. All calculations were performed by SHELXTL-97 [16]. Crystallographic data and experimental details for structural analysis are summarized in table 1, and bond lengths and angles in table 2.

3. Results and discussion

3.1. Descriptions of the structure

The X-ray crystal structure analysis reveals the chiral $P2_12_12_1$ space group with Flack factor of $-0.059(17)$ and the overall structure of $\text{Co}^{\text{II}}(\text{dien})(\text{H}_2\text{O})(\text{NCS})(\mu_{1,3}\text{-NCS})\text{Co}^{\text{II}}(\text{dien})(\text{NCS})_2$, as shown in figure 1. Co(1) and its asymmetry-related counterpart Co(2) are bridged by a single thiocyanate ligand in an end-to-end fashion; the other three thiocyanates are terminal ligands. The coordination polyhedron around Co(1) is

Table 1. Crystal data and structure refinement for **1**.

Empirical formula	C ₁₂ H ₂₈ Co ₂ N ₁₀ OS ₄
Formula weight	574.54
Crystal system	Orthorhombic
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Unit cell dimensions (Å)	
<i>a</i>	10.8495(15)
<i>b</i>	14.0477(19)
<i>c</i>	15.517(2)
Volume (Å ³), <i>Z</i>	2365.0(6), 4
Calculated density (mg m ⁻³)	1.614
Absorption coefficient (mm ⁻¹)	1.781
Crystal size (mm ³)	0.20 × 0.14 × 0.10
θ range (°)	2.29 < θ < 26.39
Reflections measured	3523
Independent reflections	262[<i>R</i> _{int}] = 0.0542]
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0370, <i>wR</i> ₂ = 0.0630
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0711, <i>wR</i> ₂ = 0.0728
Goodness-of-fit on <i>F</i> ²	0.994

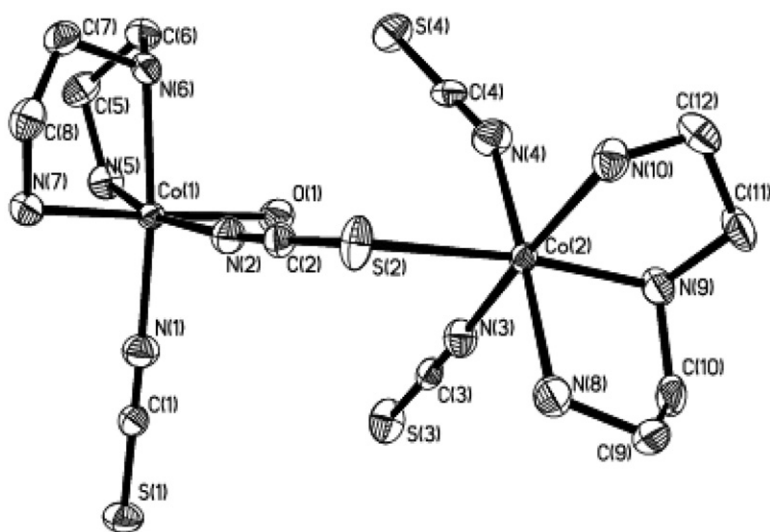
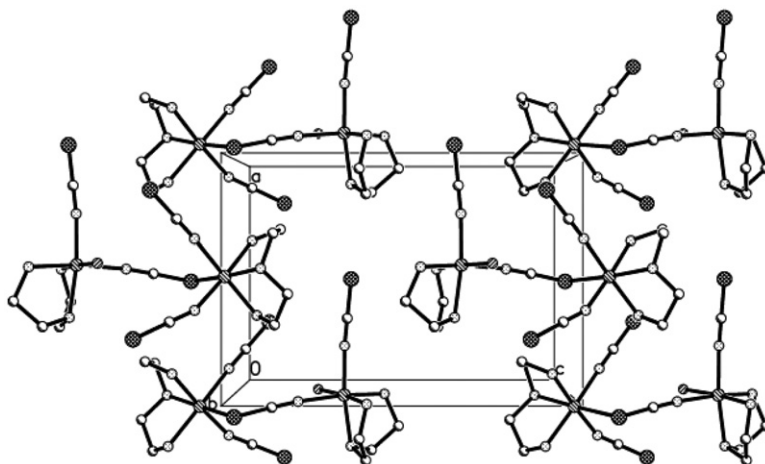
$$R_1 = \frac{\sum(\|F_o| - |F_c||)}{\sum|F_o|}; wR_2 = \frac{[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}}$$

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

Co(1)–N(1)	2.048(4)	Co(1)–N(7)	2.074(3)
Co(1)–N(2)	2.086(4)	Co(1)–N(5)	2.097(3)
Co(1)–N(6)	2.137(3)	Co(1)–O(1)	2.172(3)
Co(2)–N(4)	2.054(4)	Co(2)–N(3)	2.055(4)
Co(2)–N(9)	2.080(3)	Co(2)–N(8)	2.087(4)
Co(2)–N(10)	2.096(3)	Co(2)–S(2)	2.5729(12)
N(1)–Co(1)–N(7)	94.87(14)	N(1)–Co(1)–N(2)	95.18(15)
N(7)–Co(1)–N(2)	90.74(14)	N(1)–Co(1)–N(5)	91.63(15)
N(7)–Co(1)–N(5)	99.43(15)	N(2)–Co(1)–N(5)	167.25(15)
N(1)–Co(1)–N(6)	171.82(14)	N(7)–Co(1)–N(6)	82.23(13)
N(2)–Co(1)–N(6)	92.52(13)	N(5)–Co(1)–N(6)	81.35(14)
N(1)–Co(1)–O(1)	88.57(14)	N(7)–Co(1)–O(1)	174.57(13)
N(2)–Co(1)–O(1)	84.77(12)	N(5)–Co(1)–O(1)	84.64(14)
N(6)–Co(1)–O(1)	94.91(13)	N(4)–Co(2)–N(3)	87.73(15)
N(4)–Co(2)–N(9)	98.14(15)	N(3)–Co(2)–N(9)	91.37(14)
N(4)–Co(2)–N(8)	176.47(16)	N(3)–Co(2)–N(8)	88.82(15)
N(9)–Co(2)–N(8)	82.65(15)	N(4)–Co(2)–N(10)	88.45(15)
N(3)–Co(2)–N(10)	171.64(14)	N(9)–Co(2)–N(10)	81.81(14)
N(8)–Co(2)–N(10)	95.07(15)	N(4)–Co(2)–S(2)	92.49(11)
N(3)–Co(2)–S(2)	92.40(10)	N(9)–Co(2)–S(2)	168.85(11)
N(8)–Co(2)–S(2)	86.94(11)	N(10)–Co(2)–S(2)	95.19(10)

best described as a distorted octahedron with two amido nitrogens from dien, one water, and one nitrogen from NCS in the equatorial plane, and the other amido nitrogen from dien and one nitrogen of NCS at axial positions. The Co–N distances are slightly different: 2.048(4)–2.137(3) Å for Co(1)–N and 2.172(3) Å for Co(1)–O(1). Co(2) coordination is the same as Co(1) with one thiocyanate sulfur substitute for water. The Co(2)–N distances are different: 2.054(4)–2.096(3) Å for Co(2)–N and 2.5729(12) Å for Co(2)–S(2).

The Co(2)–S–C angle is 103.1° and Co(1)–N–C is 173.1°. In comparison, the Co–N–C angles for terminal SCN⁻ are 173.7° for Co(1), 174.9°, and 156.9° for Co(2).

Figure 1. Molecular structure for **1** with atom labeling scheme.Figure 2. Packing diagrams of **1** along the *a*-axis.

The intramolecular Co(1)–Co(2) distance is 5.9991 Å for **1**. The S(2)–C(2) and C(2)–N(2) distances from thiocyanato-bridge are longer than that of all other from non-bridging NCS. In the crystal, each dinuclear complex is stacked alternately in a $\{-AA'-AA'-AA'\}_n$ fashion along the *a*-axis (figure 2), and between A and A' there is a two-fold rotation axis parallel to the *a*-axis. The intermolecular Co(2)⋯Co(2'), Co(1)⋯Co(1), and Co(1)⋯Co(1') distances are 5.880, 10.849, and 12.182 Å, respectively. Between binuclear molecules, there are no intermolecular hydrogen bond or π – π stacking interactions. The shortest S(1)⋯C(10) and S(1)⋯S(4) distances

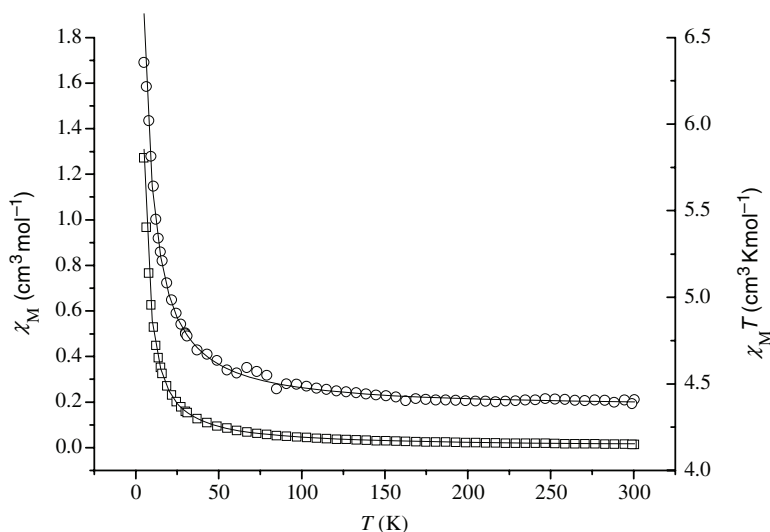


Figure 3. Plots of χ_M (open squares for experimental data, line for theoretical value) and $\chi_M T$ (circles for experimental data, line for theoretical value) vs. T .

between adjacent binuclear molecules are 3.856 and 5.834 Å, larger than the sum of van der Waals radii.

3.2. IR spectrum

The $\nu(\text{CN})$ of a bridging thiocyanate is usually found above 2100 cm^{-1} [17]. For **1**, the $\nu(\text{CN})$ occurs at 2121.99 and 2109.79 cm^{-1} , consistent with those reported earlier [18, 19]. The compound shows two bands with medium intensity at $\nu=3287.44$, 3339.16 cm^{-1} corresponding to $\nu(\text{N-H})$ and at $\nu=2886.29$, 2974.36 cm^{-1} assigned to $\nu(\text{C-H})$ of diethylenetriamine.

3.3. Magnetic properties

The variable-temperature (5–300 K) magnetic susceptibilities of **1** have been measured on a crystalline sample in a 500 Oe field. A plot of $\chi_M T$ versus T is shown in figure 3 (where χ_M is the magnetic susceptibility per mole of metal atoms). The $\chi_M T$ value of $4.40\text{ cm}^3\text{ K mol}^{-1}$ at room temperature is bigger than the expected value of $3.75\text{ cm}^3\text{ K mol}^{-1}$ for two magnetically isolated Co(II) ions ($S=3/2$, $g=2.0$), due to spin-orbit coupling that is common for high-spin octahedral Co(II). At 300–40 K $\chi_M T$ value increases gradually, then sharply increases without a maximum value until 5 K ($6.37\text{ cm}^3\text{ K mol}^{-1}$), indicating the onset of ferromagnetic interaction within the dinuclear complex.

A dinuclear cobalt, with the consideration of other factors (such as intermolecular interactions, ZFS-zero field splitting), is used to simulate $\chi_M T$ versus T and χ_M versus T plots, leading to $g=2.15$, $J=+1.14\text{ cm}^{-1}$, $\theta=+0.35\text{ K}$, $\text{TIP}=300 \times 10^{-6}\text{ cm}^3\text{ mol}^{-1}$, where J , g , θ , and TIP are intramolecular magnetic coupling parameter, Zeeman factor,

other factors, and temperature-independent paramagnetism, respectively [20]. It is clear that this simulation gives evidence for ferromagnetic interactions between Co1 and Co2.

Most nickel compounds connected by double or single end-to-end SCN^- bridges have weak ferromagnetic interactions derived from the orthogonality of the magnetic orbitals [6, 21]. Two Co(II) compounds linked by double end-to-end SCN^- bridges were also found to display weak ferromagnetic interactions [6, 14]. In contrast, the present ferromagnetic interaction is weaker, perhaps due to the single end-to-end SCN^- bridge.

4. Conclusions

We synthesized a new thiocyanate-bridged Co(II) compound with a single end-to-end NCS^- bridge. The magnetic studies suggest weak ferromagnetic behavior. Compound **1** is the first Co(II) bridged by a single end-to-end NCS^- connector. This work enriches thiocyanate-bridging coordination compounds, especially for thiocyanate-bridging Co(II) coordination compounds, and provides structural and magnetic information for the follow-up design and preparation of thiocyanate-bridging Co(II) coordination compounds, as well as magneto-structural studies.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC reference no. 282611.

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