

Nickel(II) and copper(II) coordination polymers with 1,2-bis(tetrazol-1-yl)ethane and thiocyanate: Structure, supramolecular isomerism and magnetism

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ABSTRACT

Two heteroleptic coordination polymers with the flexible 1,2-bis(tetrazol-1-yl)ethane (btze) ligand, $[\text{Ni}(\text{btze})_2(\text{SCN})_2]_n$ (**1**) and $[\text{Cu}(\text{btze})(\text{SCN})_2]_n$ (**2**), have been synthesized in presence of thiocyanate. Compound **1** is composed of 1D chains with double btze bridges in the V-shaped *gauche* conformation, while **2** exhibits 2D coordination networks in which 1D chains with double *N,S*-thiocyanate bridges are cross-linked by btze bridges in the Z-shaped *transoid* conformation. In both compounds, the coordination motifs are stacked into 3D architectures through S...S and C–H...N interactions. The structures of **1** and a previously reported compound illustrate an interesting type of supramolecular isomerism. The two isomers exhibit almost identical 1D coordination structure and 2D hydrogen bonded superstructure, and the difference lies only in the interlayer packing associated with S...S contacts. Compound **2** exhibits weak antiferromagnetic interactions with $J = 0.29 \text{ cm}^{-1}$, consistent with the structural observation that the thiocyanate bridge adopts an equatorial–axial disposition between Cu(II) ions.

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1. Introduction

The study of coordination polymers has evoked considerable attention not only for their diverse and intriguing structures but also for their potential applications such as gas absorption, magnetism, and luminescence [1–3]. The final structures of coordination polymers are not only dependent upon the geometrical and electronic properties of the metal ions and ligands, but also can be strongly influenced by other factors such as the counterion, the solvent system and the metal-to-ligand ratio. Although some coordination networks with specific topologies can be “designed” by the judicious selection of metal ions and organic ligands [2], crystal engineering is still a great challenge for most systems. This is especially true for systems with flexible bridging ligands that can assume different conformations upon coordination [3,4]. Nevertheless, these ligands can lead to interesting phenomena such as dynamic structures [3] and supramolecular isomerism [4]. Bis(tetrazol-1-yl)alkanes, such as 1,2-bis(tetrazol-1-yl)ethane (btze) and 1,4-bis(tetrazol-1-yl)butane (btzb), are a good choice of flexible ligands. Previous studies on such ligands are mainly focused on the Fe(II) spin-transition compounds with non-coordinative ClO_4^- , BF_4^- or PF_6^- as guest anions [5,6]. The conformational flexibility of the alkyl spacers between tetrazole rings makes the ligands adaptable to various coordination networks with one- (1D) [5a–c], two- (2D) [5d], and three-dimensional (3D) [6] topologies. Recently, the assembly of such ligands with other divalent metal

ions (Co, Ni, Cu, Cd) in the presence of coordinative (pseudo)halide ions ($\text{X}^- = \text{Cl}^-$, Br^- , N_3^- , or NCS^-) has been investigated by us and others [7,8]. The assembly has led to various coordination networks with bis(tetrazole) and/or X^- bridges, reflecting the versatile coordination of X^- and the flexible conformation of the bis(tetrazole) ligands. In our work, we have shown that the $\text{M}(\text{II})\text{-N}_3\text{-L}$ ($\text{M} = \text{Cu}$ or Co , $\text{L} = \text{btze}$ or btzb) systems exhibit interesting magnetic properties [7]. In fact, the (pseudo)halide ions are well-known short bridges that mediate magnetic exchange between paramagnetic metal centers and have been used to construct molecular magnetic materials [9,10], the most extensively used being N_3^- [9]. For Cu(II)–NCS systems, some bi- and tetranuclear complexes [11], 1D [12–13] and 2D [14] coordination polymers with single or double thiocyanate bridges have been magnetically characterized. In this paper, we report the synthesis and structures of two Ni(II) and Cu(II) coordination polymers with btze and NCS^- , $[\text{Ni}(\text{btze})_2(\text{NCS})_2]_n$ (**1**) and $[\text{Cu}(\text{btze})(\mu_2\text{-NCS})_2]_n$ (**2**). Compound **1** and a previously reported Ni(II) compound illustrate an interesting kind of supramolecular isomerism associated with S...S contacts, while **2** represents a rare example of 2D hybrid networks in which NCS-bridged 1D Cu(II) chains are interlinked by organic ligands. The magnetic properties of **2** are investigated.

2. Experimental

2.1. Materials and measurements

All chemicals were obtained from commercial sources and used without further purification. The organic ligand btze was prepared

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according to the literature [5b]. Elemental analyses (C, H, N) were determined on an Elementar Vario ELIII analyzer. IR spectra were measured as KBr pellets on a Nicolet Magna 750 FT IR spectrometer in the range of 400–4000 cm^{-1} . Temperature- and field-dependent magnetic measurements were carried out on a Quantum Design SQUID MPMS-5 magnetometer. Diamagnetic corrections were made with Pascal's constants.

2.2. Synthesis

2.2.1. $[\text{Ni}(\text{btze})_2(\text{SCN})_2]_n$ (**1**)

A mixture of nickel(II) nitrate hexahydrate (0.10 mmol, 0.029 g), btze (0.2 mmol, 0.033 g), and ammonium thiocyanate (0.20 mmol, 0.015 g) in H_2O (10 mL) was stirred for 10 min at room temperature. Slow evaporation of the solution at room temperature yielded blue plate-like crystals of **1** within three months. Yield: 63%. Elemental analysis calcd (%) for $\text{C}_{10}\text{H}_{12}\text{N}_{18}\text{S}_2\text{Ni}$: C, 23.68; H, 2.39; N, 49.71. Found (%): C, 23.88; H, 2.71; N, 50.02. IR (KBr, cm^{-1}): 3147 m, 2087 s, 1500 m, 1440 w, 1178 m, 1139 w, 1099 s, 1005 m, 877 w, 650 m.

2.2.2. $[\text{Cu}(\text{btze})(\text{SCN})_2]_n$ (**2**)

Aqueous solution (10 mL) containing ammonium thiocyanate (0.40 mmol, 0.030 g) and btze (0.2 mmol, 0.332 g) in a tube was successively layered by a mixture of H_2O (5 mL) and ethanol (5 mL) and an ethanol solution (5 mL) of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.20 mmol, 0.034 g). Slow diffusion at room temperature yielded dark green crystals of **3** in two weeks. Yield: 50%. Elemental analysis calcd (%) for $\text{C}_6\text{H}_6\text{N}_{10}\text{S}_2\text{Cu}$: C, 20.84; H, 1.75; N, 40.50. Found: C, 20.79; H, 1.80; N, 40.59. IR (cm^{-1} , KBr): 3124 m, 2108 s, 1499 m, 1445 m, 1172 m, 1130 m, 1087 m, 999 m, 883 m, 687 m, 660 m.

2.3. X-ray crystallography

Diffraction intensity data were collected at 293 K on a Bruker APEX II diffractometer equipped with a CCD area detector and graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). Empirical absorption corrections were applied using the SADABS program [15a]. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 , with all non-hydrogen atoms refined with anisotropic displacement parameters [15b]. All the hydrogen atoms attached to carbon atoms were placed in calculated positions and refined using the riding model. Crystallographic data are summarized in Table 1.

Table 1
Crystal data and structure refinement for complexes **1** and **2**.

Complexes	1	2
Empirical formula	$\text{C}_{10}\text{H}_{12}\text{N}_{18}\text{S}_2\text{Ni}$	$\text{C}_6\text{H}_6\text{N}_{10}\text{S}_2\text{Cu}$
F_w	507.21	345.87
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
$a/\text{\AA}$	6.5358(13)	19.970(4)
$b/\text{\AA}$	8.5888(17)	5.5067(10)
$c/\text{\AA}$	10.449(2)	12.672(2)
α/deg	110.46	90
β/deg	101.50	120.357(2)
γ/deg	100.54(3)	90
$V/\text{\AA}^3$	517.73	1202.5(4)
Z	1	4
$D/\text{g cm}^{-3}$	1.627	1.910
μ/mm^{-1}	1.180	2.166
Unique reflections	2215	1372
R_{int}	0.0201	0.0390
$R_1 [I > 2\sigma(I)]$	0.0454	0.0373
wR_2 (all data)	0.1340	0.0854

3. Results and discussion

3.1. Synthesis and IR spectra

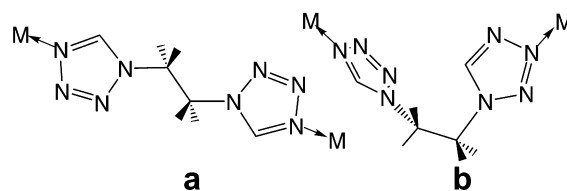
Compound **1** was synthesized by room-temperature evaporation of the aqueous solution containing $\text{Ni}(\text{NO}_3)_2$, NH_4SCN and btze. It was found that the reactions with the starting metal-to-btze molar ratio varying from 1:1 to 1:3 always yield compound **1**, suggesting the metal-to-ligand ratio is not an important factor determining the final product in this system. Compound **2** was synthesized by slow diffusion between the ethanol solution of CuCl_2 and the aqueous solution of NH_4SCN and btze. The infrared spectra of compounds **1** and **2** exhibit very strong absorption at 2086 and 2107 cm^{-1} , respectively, due to the $\nu(\text{C}\equiv\text{N})$ vibration of the thiocyanate ion. The higher frequency of $\nu(\text{C}\equiv\text{N})$ in **2** with respect to that in **1** is consistent with the N,S -bridging coordination mode in **2** and the N-terminal mode in **1**, as revealed by X-ray analysis (vide infra). Both compounds show the sharp C–H vibration band (3147 cm^{-1} for **1** and 3124 cm^{-1} for **2**) characteristic of 1-substituted tetrazole rings [5b,8]. The $\nu(\text{C}-\text{H})$ band for **2** is similar to that for the free btze ligand (3121 cm^{-1}), indicating a Z-shaped *transoid* conformation in **2** (Scheme 1a), while the large shift of this band toward high frequency in **1** implies that the ligand in **1** adopts a V-shaped *gauche* conformation (Scheme 1b) [8b]. These are also in good agreement with X-ray analysis (vide infra).

3.2. Crystal structures

3.2.1. Compound **1**

The structure of **1** comprises 1D chains in which Ni(II) ions are bridged by double btze ligands (Fig. 1). Selected bond distances and angles are given in Table 2. Each Ni(II) ion resides at an inversion center of the $P\bar{1}$ space group, and assumes the axially compressed *trans*-octahedral coordination geometry. The equatorial plane is defined by four tetrazole nitrogen atoms (N1, N1A, N8B, N8C) from different ligands with the Ni–N distances being 2.097(2) and 2.129(2) \AA , and the axial positions are occupied by two thiocyanate nitrogen atoms (N9, N9A) with Ni–N = 2.034(3) \AA . The N–C–N torsion angle of 65.88(3)° defines a *gauche* conformation for the $(\text{CH}_2)_2$ spacer between tetrazole rings, and hence the btze ligand adopts a twisted V shape. Two such ligands set up a double bridge between neighboring Ni(II) atoms to generate a 18-membered centrosymmetric bimetallic cycle of $[\text{Ni}_2(\text{btze})_2]$, with a Ni...Ni separation of 8.589(2) \AA , and the interconnection of such metallacycles by sharing metal centers leads to an infinite chain of loops.

All the chains are parallel to the (010) direction, and two types of weak interchain interactions are operative along the (100) and (101) direction, respectively. Along the (100) direction, each btze from one chain interacts with a neighboring btze from another chain through two equivalent C–H...N hydrogen bonds, each involving a C1–H1A group and a N7 atom from the non-equivalent tetrazole rings of two ligands. The relevant geometric parameters are C–H...N = 145.4°, H...N = 2.36 \AA , and C...N = 3.170(4) \AA . Through such hydrogen bonds, the chains are aligned into 2D supramolecu-



Scheme 1. The Z-shaped *transoid* (a) and V-shaped *gauche* (b) conformations of the btze ligand.

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