Synthesis and Crystal Structure of a Polymeric Cobalt (II) Complex with 1,1’-(1,4-Butanediyl)bis(imidazole)

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Abstract

The title complex [Co(bbi)2(NCS)2]n (bbi = 1,1’-(1,4-butane1,1’-diyl)bis(imidazole)) (1), was synthesized under hydrothermal conditions, and characterized by elemental analysis, IR spectroscopy and single-crystal X-ray diffraction crystallography. Single crystal X-ray analysis reveals that the complex crystallizes in the monoclinic space group of P21/c with a = 8.9697(7) Å, b = 9.6720(10) Å, c = 14.4880(13) Å, and β = 90.9280(10)°. The Co(II) atom is coordinated by six N atoms from four different bbi ligands and two SCN- anions, in a slightly distorted octahedral geometry. Adjacent Co(II) atom are linked by pairs of bbi molecules, resulting in a one-dimensional polymeric structure with a double-strand chain.

Keywords: Cobalt(II); Polymeric complex; Crystal structure; TGA.

Introduction

The construction of metal-organic coordination polymers has gained much interest as materials with potentially new electrical, optical, magnetic and porous properties in recent years[1-2]. Among the synthetic strategies to achieve these coordination polymers in the context of coordination chemistry, is the utilization of neutral organic groups which can act as bridging ligands towards metal ions. Rigid N,N'-bidentate spacers like 4,4'-bipyridine are frequently employed in the construction of metal-organic polymers and has adopted numerous interesting supramolecular architectures[3]. Recently, a new class of flexible ligands, bis(azole), containing nitrogen atoms have been well-studied in the construction of metal-organic coordination polymers for their N-coordinated sites apt to coordinating to transition metals[4]. The five-member-ring heterocyclic ligands of azoles, such as imidazoles, triazoles and tetrazoles ligands, in which N-donor azole rings are separated by alkyl, (CH2)n, spacers, are good choices for flexible bridging ligands[5-6]. An increasing number of interesting frameworks integrating metal ions and flexible chain linkers have been reported[7-8]. In this paper, we introduce 1,1’-(1,4-butane1,1’-diyl)bis(imidazole) (bbi) ligand together with SCN- in order to assemble cobalt(II) coordination polymer under hydrothermal conditions. In addition, thermal stability of 1 was measured and discussed.

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Experimental

All reagents used in the synthesis were analytical grade. The ligand bbi was prepared following the literature method\cite{9}. Elemental analyses for C, H, N and S were performed on a Vario EL III elemental analyzer. The infrared spectra (4000-400 cm\(^{-1}\)) were recorded as a KBr pellet on a Nicolet 170SX FT-IR spectrometer. Thermogravimetric analysis was recorded on a NETZSCH TG 209 instrument under nitrogen by heating the sample from 20 to 900 °C. The crystal structure determination was performed on a Bruker Smart Apex CCD area-detector diffractometer equipped with graphite-monochromatized Mo K\(\alpha\) radiation (\(\lambda = 0.71073 \text{ Å}\)).

Synthesis of \([\text{Co(bbi)}_2(\text{NCS})_2]_n\) (1)

A mixture of CoCl\(_2\)-6H\(_2\)O (0.10 mmol, 0.024 g), bbi (0.1 mmol, 0.019 g), KSCN (0.2 mmol, 0.019 g) and H\(_2\)O (10 mL) was stirred for 10 min in air. Then the mixture was transferred to a Teflon-lined autoclave (20 mL) and kept at 100 °C for 24 hrs. After slow cooling to room temperature, pale red block crystals were obtained, which were suitable for single-crystal X-ray structure analysis. Anal. Calcd for C\(_{22}\)H\(_{28}\)CoN\(_{10}\)S\(_2\): C, 47.52; H, 5.04; N, 25.20; S, 11.52. Found: C, 47.50; H, 5.07; N, 25.17; S, 11.55.

X-Ray Data Collection and Structure Refinement

Single-crystal data were collected at 298(2) K. The structure was solved by direct methods and successive Fourier difference synthesis (SHELXS-97), and refined using the full-matrix least-squares method on \(F^2\) with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97)\cite{10-11}. The final agreement factor values are \(R_1 = 0.0358, wR_2 = 0.0813\). Crystallographic data (cif) have been deposited with the Cambridge Structural Data Centre (CCDC) with reference number 851458. See http://www.ccdc.cam.ac.uk/conts/retrieving.html for crystallographic data in cif or other electronic format. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: 44(0)-1223–336033 or E-mail: deposit@ccdc.cam.ac.uk]. A summary of the crystallographic data is given in table 1. Selected bond distances and angles are given in table 2.

Table 1: Crystal data and structure refinement details for 1

| formula | C\(_{22}\)H\(_{28}\)CoN\(_{10}\)S\(_2\) |
| formula weight | 555.59 |
| Crystal size (mm\(^3\)) | 0.40 x 0.32 x 0.03 |
| Temperature (K) | 298(2) |
| crystal system | Monoclinic |
| space group | \(P2_1/c\) |
| \(a(\text{Å})\) | 8.9697(7) |
Table 2: Selected bond lengths (Å) and bond angles (º) for 1

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<th>Bond</th>
<th>Length (Å)</th>
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<td>2.135(2)</td>
<td>Co1-N4</td>
<td>2.1501(18)</td>
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<td>Co1-N4A</td>
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<td></td>
<td>N2-Co1-N2A</td>
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</table>
Results and discussion

Infrared Spectrum

The IR spectrum of 1 clearly shows both the presence of SCN⁻ and coordinated bbi. The IR spectrum of 1 exhibits two peaks at 3126 and 2942 cm⁻¹, which are assigned to the νC-H stretching mode and indicate the presence of the methylene unit of bbi ligand. The peaks at 1581 and 1520 cm⁻¹ are assigned to the νC=C of the imidazole ring. Furthermore, the band at 1095 cm⁻¹ is attributed to the νC-N of the imidazole ring, and reveals the coordination of the N-atoms of the imidazole ring. The strong absorptions at 2080 cm⁻¹ indicate the C = N stretching vibration of the thiocyanate group, which is consistent with the occurrence of thiocyanate-N coordination[12-14]. The IR spectrum of 1 is in agreement with the crystal structure.

Crystal Structural Description

The coordination polyhedra of the Cobalt(II) atoms in 1 are distorted octahedral, in which the equatorial plane is formed by four nitrogen atoms of four different bbi ligands and the axial position are occupied by two trans thiocyanate ligands (Figure 1). The Co-N{sub NCS distances of 2.135(2) Å are slightly shorter than the Co-N{sub bbi distances of 2.1501(18) and 2.176(2) Å. The N2-Co1-N2A, N4-Co1-N4A and N5-Co1-N5A angles are 180º. The other N-Co-N angles around Co(II) atoms range from 89.10(8)º to 90.90(8)º. The NCS groups in 1 are almost linear with a S1-C11-N5 angle of 178.8(2)º. The Co-N-C linkage are bent with a Co1-N5-C11 angle of 157.5(2)º, which deviate from 180º expected for the sp hybrid orbital of the N atom. The C-N distance of 1.165(3) Å and C-S distance of 1.639(3) Å in the SCN⁻ moiety show the normal structure of the thiocyanate in the complex. It is noteworthy that, in 1, only the N atoms of the SCN⁻ anions coordinate to the metal centre, while in the related compound [Co(SCN)₂(bim)] [bim = 1,2-bis(imidazol-1-yl)ethane], the S atoms are also connected to the central metal atom[15].

As shown in Figure 2, Each Co(II) is connected to other Co(II) ions by two bbi ligands, resulting in the 22-member Co₂(bbi)₂ metallocycle. Two strands for bbi ligands which are wrapped around each other and held together by metal atoms, forming a double chain structure along the a axis. The Co-Co separation bridged by bbi is 8.970 Å, which is similar to that observed in [Ni(NCS)₂(C₁₀H₄N₄)₂]₂ₙ (Ni-Ni distance of 8.9269(4) Å)[16], while significantly shorter than the corresponding Cu-Cu distances of 13.410 and 12.782 Å in [Cu₂(bbi)₂Cl₂]₁⁷. The bbi ligands exhibit the gauche-anti-gauche conformation in 1. The dihedral angle between two imidazole planes is 78.6º. The plane of the N(CH₂)₄N chain is steeply inclined, by 49.9º and 87.5º to the two imidazole ring planes.
Figure 1: Perspective view of the coordination environment of Co(II) in 1 with thermal ellipsoids at 30% probability (hydrogen atoms have been left out for clarity)

Figure 2: View of the 1D linear chain in complex 1 bridged by bbi ligands

**Thermal Analysis**

Compound 1 is stable at ambient conditions. The thermal stability was measured by thermogravimetric analysis (TGA) in a nitrogen atmosphere heated to 900 °C at a rate of 10 °C min⁻¹, as illustrated in Figure 3. For 1, the framework is thermally stable until around 262 °C, and then decomposition begins. The final residue may be CoS (found 17.1%, calcd. 16.4%).
Figure 3: TG curve of complex 1 under N2 atmosphere

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References