

Syntheses and Structural Analytical Studies of Two Co(II) Complexes Based on 1,4-Di(benzimidazole-1-yl)benzene

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Abstract Two new Co(II) complexes of 1,4-di(benzimidazole-1-yl)benzene ligand (**L**) with the formulas $[(\text{CoLCl}_2)(\text{CHCl}_3)(\text{DMF})]_\infty$ (**1**) and $[\text{CoL}(\text{NO}_3)_2]_\infty$ (**2**) have been synthesized by anion-directed self-assembly. Both complexes have been characterized by elemental analyses, IR, and X-ray single crystal diffraction. Complexes **1** and **2** exhibit 1D chain structures. In **1**, Co(II) ions possess a distorted tetrahedral coordination environment composed of N_2Cl_2 donors from two **L** ligands and two chloride ions, while the Co(II) ions in **2** reveal a distorted octahedral structure defined by the N_2O_4 donors from two **L** ligands and two nitrate anions. These results illustrate that the anions play an important role in the self-assembly of metal–organic materials.

Keywords Anion-directed assembly · Benzimidazole-based ligand · Co(II) complexes · Coordination modes

1 Introduction

The rational design and construction of transition metal complexes containing nitrogen heterocycles has been an increasing area of research field in view of their potential catalytic activity [1], magnetic properties [2–5], optical properties [6–9], and use as membranes or biosensors [10–12], and sorption devices

[13–17]. Benzimidazole, as a typical nitrogen heterocyclic ligand, is also an important pharmacophore in drug discovery [18]. Its derivatives have a broad spectrum of biological and pharmaceutical properties; e.g., bactericide, antiparasite and anticarcinogen. In addition, benzimidazole is important in metallo-supramolecular chemistry [19]. Benzimidazole and its derivatives are also appealing for the design of medicinal organic–inorganic hybrid materials [20–24]. Co(II) complexes incorporating benzimidazoles have attracted considerable attention because of their magnetic properties and biological activity [18, 19, 25, 26]. For instance, Xia et al. [25] studied the magnetic properties of Co(II) complexes based on 2-(*n*-pyridyl)benzimidazole. A DNA binding study of a dinuclear macrocyclic Co(II) complex based on 2,2,2',2'-*S,S*[bis(bis-*N,N*-2-thiobenzimidazolyl)oxalato-1,2-ethane] was carried out by Arjmand and Aziz [18]. In addition, Sandoval et al. [26] reported the biological activities of Co(II) complexes with 2-benzimidazole derivatives.

Herein, we report the synthesis of two new Co(II) complexes based on the 1,4-di(benzimidazole-1-yl)benzene (**L**) ligand (Chart 1), $[(\text{CoLCl}_2)(\text{CHCl}_3)(\text{DMF})]_\infty$ (**1**) and $[\text{CoL}(\text{NO}_3)_2]_\infty$ (**2**). The analysis of their crystal structures was carried out to give valuable insight into the construction of organic–inorganic hybrid materials. Complexes **1** and **2** were also characterized by IR, elemental analysis and single crystal X-ray diffraction. Both materials possess a 1D chain structure.

2 Experimental

2.1 Materials and General Methods

All reagents and solvents for the syntheses were commercially available (Alfa Aesar Company) and used as supplied.

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Ligand **L** was synthesized from the reaction of 1*H*-benzimidazole with 1,4-dibromobenzene according to the literatures [27–29]. The IR spectra were obtained with a TENSOR 27 OPUS (Bruker) FT-IR spectrometer from 4000–400 cm⁻¹ using dispersed sample powders on KBr disks. Elemental analyses of C, H, and N were performed with a Perkin-Elmer 240C analyzer. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were obtained with a Perkin-Elmer Diamond Thermogravimetric Analyzer from room temperature to 800 °C at a heating rate of 10 °C/min under a N₂ stream.

2.2 Synthesis of the Complexes

2.2.1 [(CoLCl₂)(CHCl₃)(DMF)]_∞ (**1**)

A transition layer (5 mL) of methanol/chloroform (v/v 1:1) was carefully layered over a chloroform solution (4 mL + 2-drops *N,N*-dimethylformamide (DMF)) of **L** (0.05 mmol). A solution of CoCl₂·6H₂O (0.1 mmol) in methanol (4 mL) was carefully layered over the transition layer. The tube was covered and left undisturbed. Blue block crystals stable in air were harvested after 4 weeks. Yield: ~40% (based on **L**). Anal. Calcd. (%) for (C₂₄H₂₂CoON₅Cl₅): C 45.56, H 3.51, N 11.07. Found (%): C 45.71, H 3.59, N 11.23. IR (cm⁻¹): 1663s, 1587w, 1556w, 1497w, 1440wm, 1415w, 1391s, 1255m, 1158w, 1104s, 1063w, 1025w, 865w, 729m, 689w, 665s, 566w.

2.2.2 [CoL(NO₃)₂]_∞ (**2**)

Species **2** was prepared in a similar procedure of **1** using Co(NO₃)₂·6H₂O instead of CoCl₂·6H₂O. Yield: ~50% (based on **L**). Anal. Calcd. (%) for (C₂₀H₁₄CoO₆N₆): C 48.70, H 2.86, N 17.04%. Found (%): C 48.55, H 2.77, N 17.15%. IR (cm⁻¹): 1726w, 1612 m, 1529w, 1500s, 1462w, 1396w, 1301w, 1275s, 1240s, 1163w, 1151w, 1119w, 1010m, 993m, 939w, 913m, 874w, 844m, 806m, 778w, 751s, 627m, 594m, 540m, 432w.

2.3 X-Ray Crystallographic Studies

X-ray single-crystal diffraction data for **1** was collected on a Rigaku Raxis Rapid IP diffractometer at 293(2) K. The data for **2** was collected on a Bruker Smart 1000 CCD diffractometer at 293(2) K. The program SAINT [30] was used for integration of the diffraction profiles. All the structures were solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares methods with SHELXL [31]. Metal atoms in each complex were located from the *E*-maps. The other non-hydrogen atoms were located in successive difference Fourier syntheses and refined with

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

	1	2
Empirical formula	C ₂₄ H ₂₂ CoON ₅ Cl ₅	C ₂₀ H ₁₄ CoO ₆ N ₆
Formula weight	632.65	493.30
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	12.948(3)	15.376(3)
<i>b</i> (Å)	13.681(3)	8.9859(2)
<i>c</i> (Å)	16.034(3)	14.724(3)
β/°	97.63(3)	91.620(3)
Volume (Å ³)	2815.1(1)	2033.6(6)
<i>Z</i>	4	4
<i>D</i> _{calcd} (g/cm ³)	1.493	1.611
μ (mm ⁻¹)	1.111	0.897
GOF	1.106	1.049
<i>T</i> /K	293(2)	293(2)
<i>R</i> ^a / <i>wR</i> ^b [<i>I</i> > 2σ(<i>I</i>)]	0.0743/0.1825	0.0506/0.1096

$$^a R = \frac{\sum(|F_o| - |F_c|)}{\sum|F_o|}$$

$$^b wR = \left[\frac{\sum w(|F_o|^2 - |F_c|^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$$

anisotropic thermal parameters on *F*². All hydrogen atoms were placed geometrically. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

3 Results and Discussion

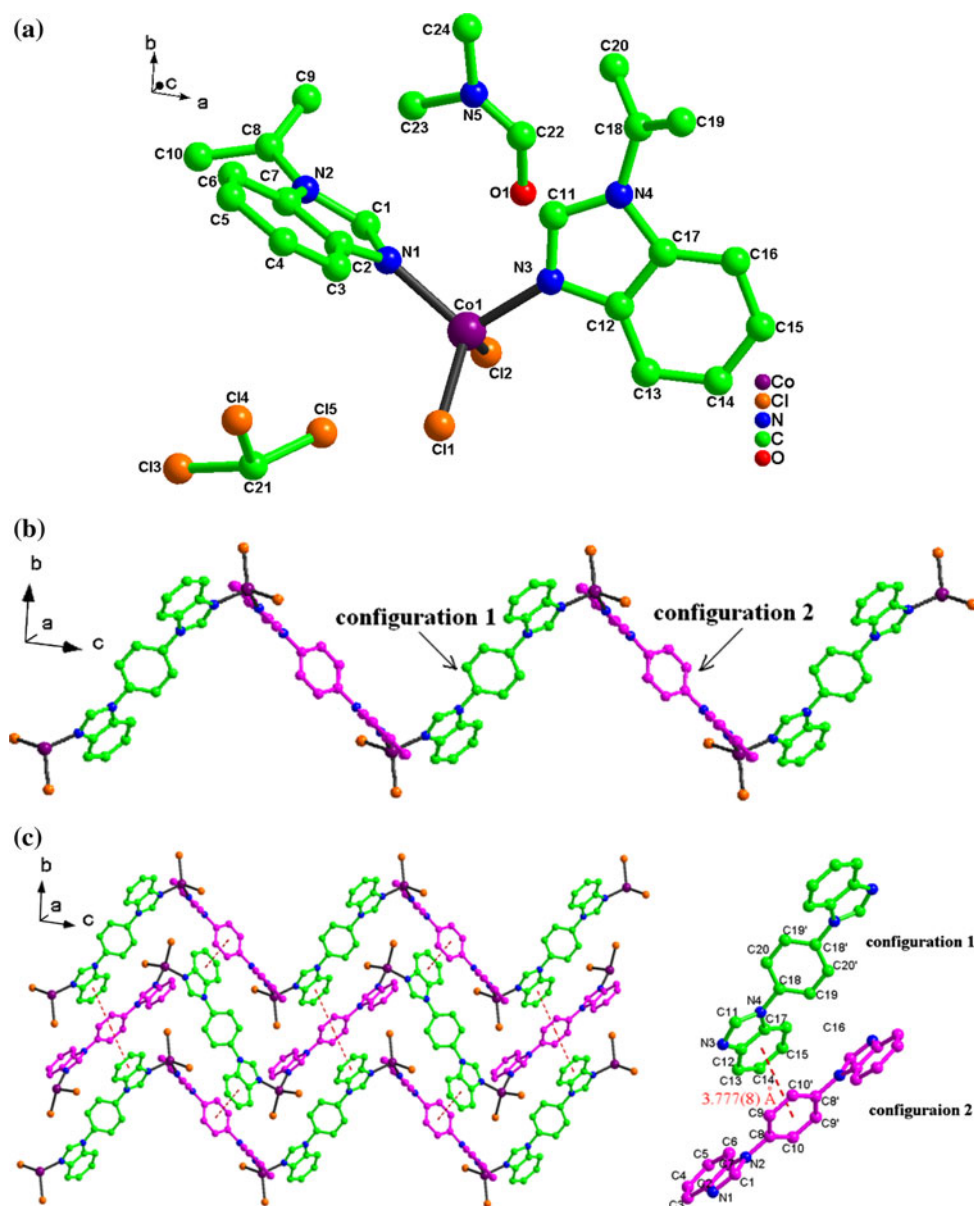
3.1 Synthesis and General Characterizations of Complexes **1** and **2**

Two different reactions of 1,4-di(benzimidazole-1-yl)benzene with cobalt(II) salts led to different crystalline materials. The reaction of 1,4-di(benzimidazole-1-yl)benzene with CoCl₂·6H₂O in methanol/chloroform produced crystallographically characterizable [(CoLCl₂)(CHCl₃)(DMF)]_∞ (Fig. 1), whereas Co(NO₃)₂·6H₂O yielded [CoL(NO₃)₂]_∞ (Fig. 2). The results of elemental analyses for the two complexes were in good agreement with the theoretical compositions.

3.2 Crystal Structures of **1** and **2**

Complex **1** crystallizes in a monoclinic system with the *P*2(1)/*n* space group (Table 1). The basic structural unit consists of one Co(II) ion, one **L** ligand, two chlorine anions, one chloroform and one DMF molecule (Fig. 1a). The Co(II) ion adopts a tetrahedral geometry involving two chlorine anions and two N-atoms from two **L** ligands. The Co–Cl bond [2.2397(2) and 2.2527(2) Å] and Co–N bond

Fig. 1 **a** Coordination environment of Co(II) in **1**; **b** the 1D zigzag structure of **1** (all solvent molecules omitted for clarity); **c** 2D supramolecular framework linked by $\pi\cdots\pi$ interactions

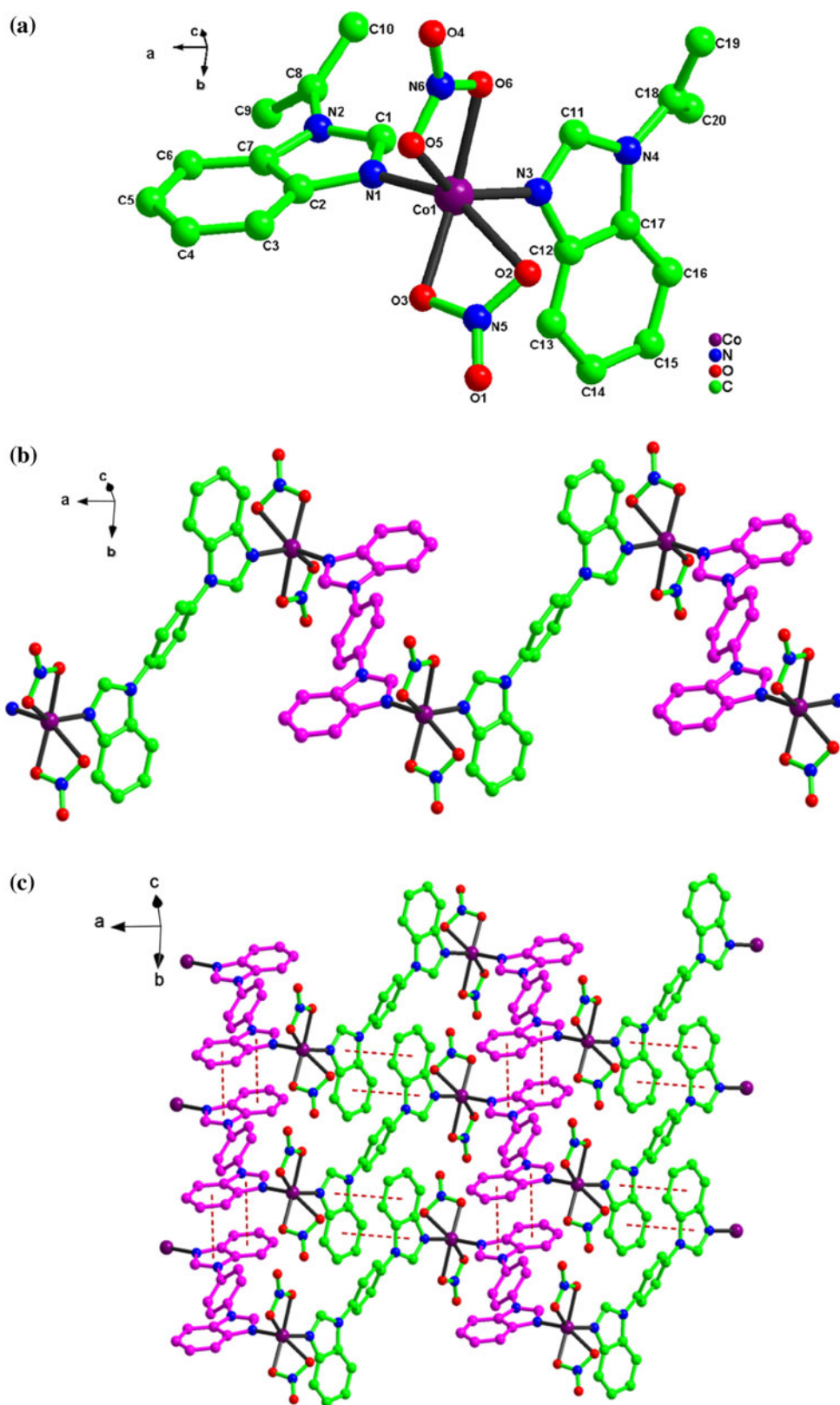


[2.024(4) and 2.010(4) Å] distances are consistent with the similar structures reported earlier [32]. The **L** ligands have two types of configuration in **1**; i.e., configuration 1 and configuration 2, which bridge two Co(II) ions by turns to a linear zigzag chain (Fig. 1b). The two benzimidazole rings of each **L** configuration are in the same plane. The dihedral angle between the benzene ring (C19–C18–C20–C19′–C18′–C20′) and the benzimidazole ring (N3–C11–N4–C12–C13–C14–C15–C16–C17) in configuration 1 is 47.5°, and the dihedral angle between the benzene ring (C9–C8–C10–C9′–C8′–C10′) and the benzimidazole ring (N1–C1–N2–C2–C3–C4–C5–C6–C7) in configuration 2 is 59.7°. The benzimidazole rings of configuration 1 in each chain are parallel to the benzene rings of configuration 2 of the adjacent chains with a centroid-to-centroid distance of

3.777(8) Å and interplanar distance of 3.719 Å, which indicates that there are $\pi\cdots\pi$ interactions between the adjacent chains. Such $\pi\cdots\pi$ interactions link the 1D chains into 2D framework structures (Fig. 1c). Chloroform and DMF act as solvent molecules filling in the interspaces of the 2D sheets.

The single-crystal X-ray diffraction analysis of **2** indicates that it crystallizes in the triclinic space group of *P*-1 (Table 1). The asymmetric unit of **2** contains one Co(II) ion, one **L** ligand and two NO_3^- anions (Fig. 2a). The Co(II) ions possess a distorted octahedral coordination environment composed of O4N2 donor atoms from the two **L** ligands and two NO_3^- anions. All the Co–O bond [2.042(4)–2.348(2) Å] and Co–N bond [2.043(4)–2.045(4) Å] distances are in the normal range [33] (Table 2). Similar to complex **1**, **L** ligands

Fig. 2 Perspective view of **a** the coordination environment around the Co(II) ions in **2**; **b** 1D chain of **2**; **c** 2D supramolecular framework linked by $\pi\cdots\pi$ interactions in **2**



adopt two kinds of trans-configurations to connect Co(II) ions by turns forming a zigzag chain (Fig. 2b). The dihedral angles between the benzene ring and the benzimidazole ring

in two configurations are 40.3° and 40.6° , respectively. The NO_3^- ions coordinate to the Co(II) ion in a bidentate chelate coordination mode. Furthermore, the two benzimidazole

Table 2 Selected bond lengths [Å] and angles [°] for **1** and **2**

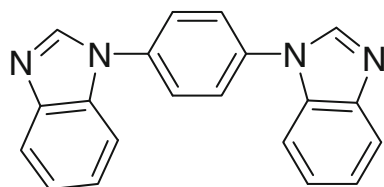
Complex 1			
Co(1)–N(1)	2.024(4)	Co(1)–N(3)	2.010(4)
Co(1)–Cl(1)	2.2397(2)	Co(1)–Cl(2)	2.2527(2)
N(3)–Co(1)–N(1)	105.61(2)	N(3)–Co(1)–Cl(1)	110.92(1)
N(1)–Co(1)–Cl(1)	111.11(1)	N(3)–Co(1)–Cl(2)	109.09(1)
N(1)–Co(1)–Cl(2)	104.27(1)	Cl(1)–Co(1)–Cl(2)	115.23(6)
Complex 2			
Co(1)–N(1)	2.043(4)	Co(1)–N(3)	2.045(4)
Co(1)–O(2)	2.348(4)	Co(1)–O(3)	2.042(4)
Co(1)–O(5)	2.142(5)	Co(1)–O(6)	2.187(5)
O(3)–Co(1)–N(1)	97.50(2)	O(3)–Co(1)–N(3)	113.83(2)
N(1)–Co(1)–N(3)	96.93(2)	O(3)–Co(1)–O(5)	95.26(2)
N(1)–Co(1)–O(5)	100.8(2)	N(3)–Co(1)–O(5)	143.4(2)
O(3)–Co(1)–O(6)	149.36(2)	N(1)–Co(1)–O(6)	99.18(2)
N(3)–Co(1)–O(6)	89.42(2)	O(5)–Co(1)–O(6)	56.43(2)
O(3)–Co(1)–O(2)	57.35(1)	N(1)–Co(1)–O(2)	153.09(2)
N(3)–Co(1)–O(2)	86.44(1)	O(5)–Co(1)–O(2)	91.67(2)
O(6)–Co(1)–O(2)	107.56(2)		

rings from two adjacent chains are parallel to each other with a centroid-to-centroid distance of 3.833 Å. Here too $\pi \cdots \pi$ interactions link the 1D chains into 2D sheets (Fig. 1c).

The reaction of 1,4-di(benzimidazole-1-yl)benzene with $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ produced crystallographically characterizable $\{[\text{Co}(\text{L})_2](\text{ClO}_4)_2\}_\infty$ (**3**), which has been recently reported [34]. In contrast to **1** and **2**, **3** consists of a 3D three-fold interpenetrating diamondoid network, which crystallizes in the monoclinic space group of $C2/c$.

3.3 Analysis of Structure

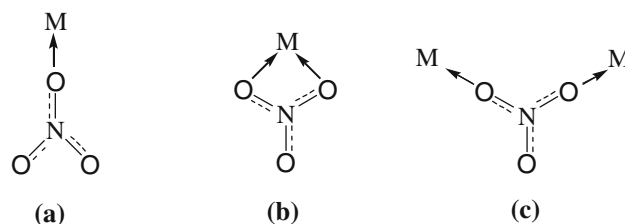
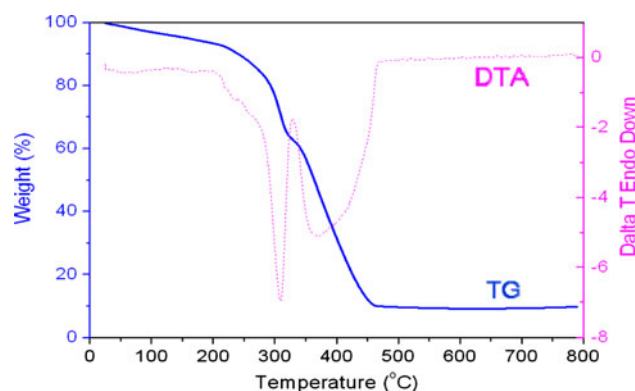
Comparing the structures of **1**, **2**, and **3**, we find that the different coordination abilities, coordination modes and spatial structures of the three anions, Cl^- , NO_3^- and ClO_4^- , determine the final structural features of the three Co(II) complexes. Due to its relatively small volume and strong coordination ability, Cl^- is a normal monodentate and terminal ligand [26, 32, 35]. In **1**, two Cl^- anions occupy two coordination sites of the Co(II) ions and limit the dimension of **1** to a 1D chain. NO_3^- often adopts multiple coordination modes; e.g., a monodentate terminal ligand [6, 36] (Chart 2a), a bidentate chelate ligand [6, 37]

**Chart 1** The ligand **L** used in this work

(Chart 2b) and a bidentate bridging ligand [38] (Chart 2c). Therefore, the monodentate terminal and bidentate chelate coordination modes are able to limit the dimensions of the complexes; and, the bidentate bridging coordination mode does just the opposite. In **2**, the NO_3^- ion has an intermediate volume and serves as a bidentate chelate ligand. Its strong coordination ability limits the complex to low dimensional topology. The ClO_4^- with its large volume but weak coordination ability is a good choice for the design of high dimensional polymers [34]; and, complex **3** is a good example.

3.4 Thermal Analysis

The thermal stabilities of the complexes were studied. The structures of **1** and **2** have a similar 1D chain structure. Therefore, the TGA and DTA of **2** were examined. The result is given in Fig. 3. The TGA curve of **2** exhibits three stages of weight loss. The first weight loss of 6% occurs between 25 and 200 °C and corresponding to the loss of solvent molecules (H_2O , DMF, CHCl_3) attached to the sample surfaces. The second weight loss of 29% occurs between 200 and 315 °C and results from the loss of two NO_3^- . The third weight loss of 55% occurs between 315 and 465 °C and results from the loss of one **L** ligand. Two obvious endothermic peaks are observed at 308 and 370 °C (DTA curve), and are related to the heat-absorbing process

**Chart 2** a Terminal ligand; b Chelate ligand; c Bridging ligand**Fig. 3** TG–DTA curves of the complex **2**

of the loss of NO_3^- and **L** ligand, respectively. Thus, **2** decomposes at ca. 200 °C.

4 Conclusions

Two new Co(II) complexes of the 1,4-di(benzimidazole-1-yl)benzene ligand were synthesized and characterized by elemental analyses, IR, and X-ray single crystal diffraction. **1** and **2** exhibit different 1D chain structures. These results illustrate that the anions can play an important role in the self-assembly of metal–organic materials.

5 Supplementary Data

Crystallographic data (excluding structure factors) for the structures in this article have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 796416 and 796417 (for **1** and **2**). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223336033 or E-mail: deposit@ccdc.cam.ac.uk).

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