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A polymeric cobalt compound $[Co(DCNT)(H_2O)]_n$ with novel topology: Synthesis, structure, luminescence, and magnetic property

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Abstract

The hydrothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ and a new designed ligand H_2DCNT yields a three-dimensional polymer $[Co(DCNT)(H_2O)]_n$ (**1**), H_2DCNT = 2,4-bis(4-carboxyphenylamino)-6-diethylamino-1,3,5-triazine. In the structure of **1**, each $DCNT^{2-}$ has three coordination sites, one nitrogen atom in the triazine ring coordinating to Co(II) and two carboxylates adopting μ_2-bridging mode, which make the infinite Co(II) chains array uniformly and evenly toward crystallographic *c*-axis. Luminescent and magnetic properties of **1** were also studied.

Keywords: Hydrothermal method; Coordination polymer; Luminescence; Magnetic property

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The rational design and construction of new polymeric compounds based upon assembly of metal ions and multifunctional organic ligands are an increasingly interesting research field due to their intriguing structural diversities and potential applications in functional materials [1]. In particular, the hydrothermal route is currently being developed in solid-state and coordination chemistry, for the design of novel polymeric architectures. In this method, structural motifs of these organic–inorganic hybrid systems are closely related to the geometry and the number of coordination sites provided by the ligand. Many works focused on the use of N– or O– donor organic molecules to act as exo-bidentate ligands to bridge metal ions, generating polymeric metal compounds with infinite chain structure and two or three-dimensional network [2].

It is well known that chlorine atoms in cyanuric chloride are easily replaced by other organic groups [3]. Using cyanuric chloride as reactant and controlling react ratio and temperature, we have synthesized a new dicarboxylate ligand, 2,4-bis(4-carboxyphenylamino)-6-diethylamino-1,3,5-triazine (H_2DCNT) [4]. The carboxyphenylamino has been introduced into triazine ring, so that the versatile coordination modes of carboxylate and triazine ring could be utilized to provide new polymeric organic–inorganic hybrid materials. There are some reported carboxylate triazine-based ligands with three symmetrically substituted sites used for construction of novel polymeric coordination compounds, such as 1,3,5-triazine-2,4,6-triaminehexaacetic acid [5], 2,4,6-tricarboxylato-1,3,5-triazine [6], 2,4,6-triyltribenzoato-1,3,5-triazine [7], and 2,4,6-tri(4-carboxyphenylamino)-1,3,5-triazine [8]. But polymeric compound including carboxylate triazine-based ligand with two substituted sites is rarely reported. We demonstrate in this communication construction of a three-dimensional polymer $[Co(DCNT)(H_2O)]_n$ (**1**) with novel topology Scheme 1.

The hydrothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ and H_2DCNT yields purple crystals of $[Co(DCNT)(H_2O)]_n$ (**1**) [9]. All major peaks of experimental powder X-ray pattern (XRPD) of compound **1** match quite well with that of the simulated XRPD, indicating reasonable crystalline phase purity. The antisymmetric and symmetric C=O stretches in free ligand H_2DCNT appear at 1549 cm^{-1} and 1421 cm^{-1}, while the antisymmetric and symmetric

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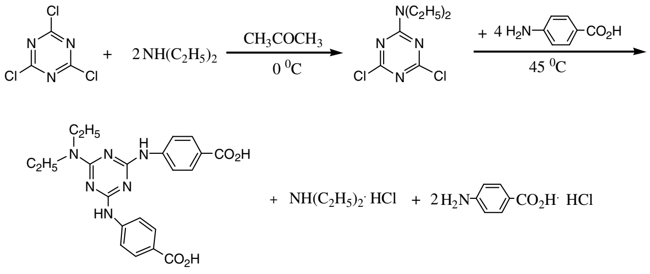

Scheme 1. The structure and synthetic route of H_2DCNT.

C=O stretching frequencies (1517 cm^{-1} and 1434 cm^{-1}, respectively) for **1** suggests μ_2-bridging mode of the carboxylate group. Thermal gravimetric analysis (TGA) of **1** under N_2 atmosphere demonstrates that the first weight loss corresponds to the loss of H_2O (at the range of 174–252 °C, 3.58% the weight loss observed; 3.62% theoretical). $DCNT^{2-}$ begins to decompose at 420 °C. The thermal stability of **1** is comparable to that of high-thermal-stability (up to 400 °C) coordination polymers with ligand 2,4,6-triyltribenzoato-1,3,5-triazine in the literature [7a].

Compound **1** possesses three-dimensional polymeric structure. Fig. 1 shows coordination environment of Co(II) and bonding mode of $DCNT^{2-}$ in compound **1**. The coordination geometry of Co(II) is a distorted octahedron completed by four carboxylato–oxygen atoms, one triazine nitrogen atom and one water oxygen atom. Each $DCNT^{2-}$ has three coordination sites, one triazine nitrogen atom coordinating to Co(II) and two carboxylates adopting μ_2-bridging mode which connect Co(II) centers to form infinite wavy cobalt–carboxylate chains. Fig. 2 shows three-dimensional polymeric network of compound **1**. The infinite wavy cobalt–carboxylate chains are linked through coordination by two carboxylates and one triazine nitrogen donor in $DCNT^{2-}$, making compound **1** a three-dimensional polymer. Interestingly the infinite wavy cobalt–carboxylate chains array uniformly and evenly toward crystallographic *c*-axis. As shown in geometric topology (Fig. 3), distance of the neighboring cobalt–carboxylate chains is 11.22 Å. The ligands $DCNT^{2-}$ arrange

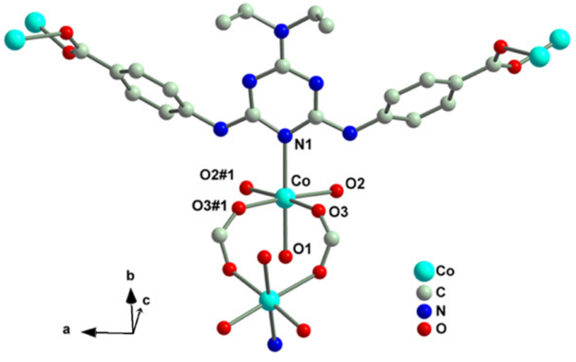

Fig. 1. Coordination environment of Co(II) and coordination mode of $DCNT^{2-}$ (hydrogen atoms were omitted for clarity). Color scheme: cyan sphere, Co; light green sphere, C; blue sphere, N; red sphere, O. Selected bond lengths (Å) and angles (°): Co–O1 2.136(6); Co–O2 2.176(3); Co–O3 2.074(3); Co–N1 2.249(4); O2–Co–O3 88.19(13); O2–Co–O3#1 174.61(15); N1–Co–O1 178.7(2). Symmetry code: #1 1−*x*, *y*, *z*. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

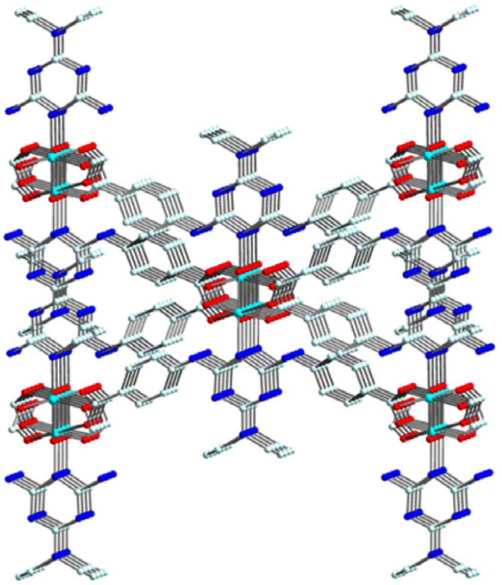

Fig. 2. Three-dimensional network structure of **1**, viewed down the crystallographic *c*-axis (hydrogen atoms were omitted for clarity).

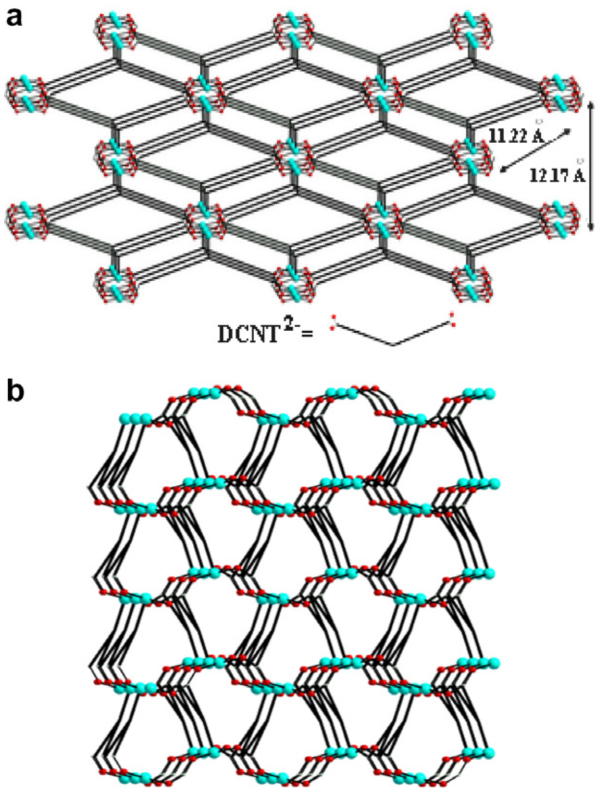

Fig. 3. The geometric topology of **1** building on Co(II) and ligand $DCNT^{2-}$. (a) Viewed down the crystallographic *c*-axis, (b) viewed down the crystallographic *a*-axis.

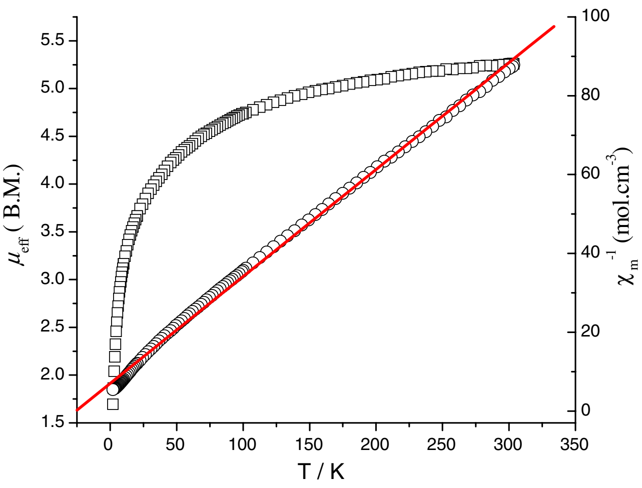

Fig. 4. Temperature-dependence of μ_{eff} (□) and χ_{m}^{-1} (○) for **1**.

along crystallographic *c*-axis in perfect face-to-face mode with separation of 8.71 Å. Although there are many reported polymeric compounds with cobalt–carboxylate chains [10], it is very rare that cobalt–carboxylate chains array uniformly and evenly toward one direction in three-dimensional polymeric network.

Compound **1** exhibits shoulder peak (374 nm) and maximum peak (410 nm) in the emission spectrum. The first emission peak is assigned to ILCT (intra-ligand charge-transfer) excitation, because the similar emission peak (370 nm) was also observed in emission spectrum of free ligand H_2DCNT. The second emission peak probably origins from LMCT (ligand-to-metal charge-transfer). One nitrogen atom in the triazine ring coordinates to Co(II), which favors charge-transfer from the donor group diethylamino along aromatic triazine ring to Co(II).

The temperature-dependent magnetic susceptibility of **1** was measured in the 2–300 K region at 5KG applied field. The μ_{eff} and χ_{m}^{-1} vs. T curves are shown in Fig. 4. The μ_{eff} value at 300 K is 5.26 B.M. which is larger than the uncoupling spin-only value of 3.87 B.M., indicating contribution to the susceptibility from orbital angular momentum at high temperature. The data in χ_{m}^{-1} vs. T plots can be fitted to the Curie–Weiss law, $\chi_{\mathrm{m}} = C_{\mathrm{m}}/(T - \theta)$, closely with $C_{\mathrm{m}} = 3.76\ \mathrm{cm}^3\ \mathrm{K}\ \mathrm{mol}^{-1}$ and $\theta = -28.1$ K. Upon cooling to 2 K, the μ_{eff} values decrease gradually to 1.69 B.M. The drop of μ_{eff} with T can be attributed largely to the single-ion behavior of Co(II). These results indicate very weak antiferromagnetic interactions between cobalt(II) centers, which is consistent with crystal structure of compound **1**, where the exchange pathways between neighboring magnetic centers (Co···Co distance: 4.69 Å) involve μ_2-carboxylate which actually serves as weak mediator of magnetic exchange.

In summary, compound **1** represents a polymer based upon the assembly of Co(II) and a new multifunctional ligand H_2DCNT and a rare case where infinite Co(II) chains linked by carboxylate array conformably toward one direction in the three-dimensional network.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.inoche.2007.04.023.

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[4] Diethylamine (3.66 g, 0.05 mol) in 20 ml acetone was added slowly with stirring to a solution of cynanuric chloride (4.61 g, 0.025 mol) in 100 ml acetone at 0 °C, over a period of 45 min. The solution of *p*-aminobenzoic acid (13.71 g, 0.1 mol) in 200 ml acetone was then added, which created more white deposit. The mixture was heated to 45 °C and reacted with stirring for 12 h. After cooling, the white product was filtered from the reaction mixture, washed free of hydrochloric acid salt of diethylamine and *p*-aminobenzoic acid with water, oven-dried at 60 °C in 76% yield. mp: 360–362 °C. Anal. Calc. for $H_2DCNT \cdot 2H_2O$: C 55.02, H 5.72, N 18.33, O 20.94. Found: C 55.13, H 5.75, N 18.24, O 20.86. ^{1}H NMR (DMSO): N–H 10.128, phen 7.902 7.781, H_2O 3.650, $-CH_2$ 1.220, $-CH_3$ 1.194. IR (KBr pellet, cm^{-1}): 2974 b, 1687 s, 1631 s, 1583 s, 1549 s, 1421 m, 1313 s, 1288 m, 1258 s, 1171 s, 1091 w, 855 m, 769 m, 648 w.

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[9] *Solution of* $Co(NO_3)_2 \cdot 6H_2O$ (0.09 g, 0.3 mmol), $N(C_2H_5)_3$ (0.06 g, 0.6 mmol), $H_2DCNT \cdot 2H_2O$ (0.14 g, 0.3 mmol) and H_2O (27.0 g, 1.5 mol) in the mole ratio of 1:2:1:5000 was heated in an autoclave at 160 °C for 3 days and then cooled to room temperature for 2 days. Purple crystals of $[Co(DCNT)(H_2O)]_n$ (**1**) were collected in 80% yield. Anal. Calc. for $Co_1C_{21}H_{22}N_6O_5$: Co 12.02, C 50.61, H 4.45, N 16.86, O 16.05. Found: Co 12.11, C 50.38, H 4.56, N 16.66, O 16.23. IR (KBr pellet, cm^{-1}): 3285 b, 1597 s, 1546 s, 1517 s, 1434 s, 1360 s, 1301 s, 1244 s, 1173 m, 1090 m, 856 w, 802 m, 777 m, 726 m, 646 m.
Crystal data for compound **1**: fw 497.38, orthorhombic, $Cmc2_1$, $a = 18.856(2)$, $b = 12.1727(15)$, $c = 8.7140(9)$, $V = 2000.1(4)$, $Z = 4$, $\rho_{calc.} = 1.652\ g\ cm^{-1}$; $R1/wR2 = 0.0519/0.1541$ ($I > 2\sigma$) and 0.0553/0.1587 (all data); GOF = 1.035.

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