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Hydrothermal Synthesis, Crystal Structure, and Luminescent Property of a Cobalt(II) Complex Based on Carbazole Derivative[1]

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Abstract—A new cobalt(II) mononuclear complex, formulated as $[Co(HL)_2(H_2O)_2]$ (**I**), has been successfully synthesized by self-assembly of cobalt nitrate with 9-ethylcarbazole-3,6-dicarboxylic acid (H_2L) under hydrothermal condition. The structure of complex **I** was determined by single-crystal X-ray diffraction analysis (CIF file CCDC no. 648810). The result shows that the central cobalt ion is six-coordinated and the crystal extends into a 2D supramolecular framework by hydrogen bonding and p···p stacking interactions. The luminescent properties were investigated.

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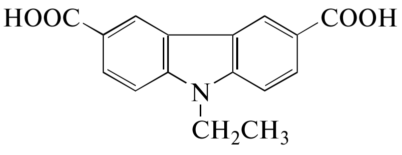
INTRODUCTION

Supramolecular complexes built from metal ions and organic ligands have been rapidly developed over the past decades because of their fascinating structural diversities and excellent properties such as catalysis, luminescence, magnetism, electrical conductivity, molecular recognition and gas storage [1–10]. The structural topologies of the resulting supramolecular complexes are affected by many factors such as organic ligands, metal ions, synthetic methods, and so on [11–13]. Among these, organic ligands have significant influences on the desirable supramolecular coordination complexes. Multidentate π-conjugated ligands containing N- or O-donors often bring intriguing topologies due to their strong coordination ability, diverse coordination modes, potential hydrogen bonding and p···p stacking interactions [14–16]. In this context, large numbers of aromatic multicarboxylate ligands have been extensively explored for the preparation of supramolecular complexes [17–20]. Because of the existence of aromatic rings as well as abundant hydrogen bonding acceptor and donor atoms, extended high-dimensional supramolecular networks can be formed by the self-assembly of zero-dimensional or low-dimensional entities through weak intermolecular interactions, leading to interesting supramolecular architectures [21–23]. In this work, we used a functional organic ligand containing carbazole and dicarboxylate groups, 9-ethylcarbazole-3,6-dicarboxylic acid (H_2L), as a basic building block. Schematic drawing of the ligand is shown below:



(H_2L)

On the other hand, metal ions play vital roles in the formation of both molecular structures and packing structures of complexes. It is well-known that different metal ions possess different properties and coordination modes [24, 25]. Plenty of studies have shown that Co^{2+} ion is a good candidate for construction of metal-organic materials because it exhibits flexible coordination environment and preference according to different donors [26]. In addition, synthetic methods have been found to exert influence on the structural construction of complexes. A wide variety of synthetic methods to obtain metal-organic complexes have been reported, including diffusion method, hydro(solvo)thermal method, microwave reaction and ultrasonic methods [27]. Among them, hydrothermal synthesis is a typical, simple and environment-friendly technique to produce crystals by self-assembly process in which the synthesis of materials occurs automatically under mild conditions and often results in various structural topologies.

In this paper, we synthesized a new cobalt(II) complex $[Co(HL)_2(H_2O)_2]$ (**I**) under hydrothermal condition. The crystal structure and solid state luminescent properties were investigated in detail.

EXPERIMENTAL

General methods. All reagents were purchased commercially and used directly without further purifi-

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[1] The article is published in the original.

Table 1. Crystallographic data and structure refinement for complex **I**

Parameter	Value
Formula weight	659.49
Crystal system	Monoclinic
Space group	$C2/c$
a, Å	31.410(6)
b, Å	5.0260(9)
c, Å	20.900(4)
β, deg	120.402(3)
V, Å^3	2845.8(9)
Z	4
ρ_{calcd}, g cm^{-3}	1.539
μ, mm^{-1}	0.669
$F(000)$	1364
Color	Red
Crystal size, mm	0.35 × 0.32 × 0.20
θ Range, deg	1.50–25.00
Limiting indices	$-36 \le h \le 17, -5 \le k \le 5,$ $-22 \le l \le 24$
Reflections collected	5061
Reflections unique (R_{int})	2458 (0.0223)
Parameters refined	205
Goodness-of-fit on F^2	1.051
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0521$, $wR_2 = 0.0964$
R indices (all data)	$R_1 = 0.0714$, $wR_2 = 0.1359$
Largest diff. peak and hole, e Å^{-3}	0.511 and –0.518

cation. Elemental analyses were performed on an Elmentar Vario EL-III analyzer. Infrared (IR) spectra were recorded on a Nicolet MAGNA-IR 750 infrared spectrophotometer with KBr pellets in the 4000–400 cm^{-1} regions. Powder X-ray diffraction (PXRD) data were measured on a MAC Science Co. Ltd. MXP 18 AHF X-ray diffractometer with monochromatized CuK_b radiation ($\lambda = 1.54178$ Å) in the 2θ range of 5°–65°. The thermogravimetric analysis (TGA) was determined on a PerkinElmer Diamond TG/DTA in N_2 at a heating rate of 10°C min^{-1} in the temperature range 20–600°C. The fluorescence spectra were carried out on a steady-state spectrofluometer (Fluorolog-3-TAU, JOBIN YVOU, light source: Xe lamp) at room temperature.

Synthesis of H_2L was carried out as described in [28].

Synthesis of complex I was carried out by the hydrothermal method under autogenous pressure. The mixture of $Co(NO_3)_2 \cdot 6H_2O$ (0.1451 g, 0.5 mmol), H_2L (0.0286 g, 0.2 mmol) and NaN_3 (0.0325 g, 0.5 mmol) in 10 mL of distilled water was sealed in a 13 mL Teflon-lined autoclave and heated to 170°C for 4 days, followed by cooling to room temperature naturally. Red prism crystals were collected and air-dried after washed by distilled water and ethanol. The yield was 0.018 g (30% based on H_2L).

For $C_{32}H_{28}N_2O_{10}Co$

anal. calcd., %:	C, 58.28;	H, 4.28;	N, 4.25.
Found, %:	C, 57.76;	H, 4.87;	N, 3.81.

IR bands (ν, cm^{-1}): 3218 s, 1887 w, 1674 v.s, 1596 v.s, 1533 m, 1466 m, 1380 v.s, 1300 m, 1234 v.s, 1145 s, 1126 s, 1023 m, 773 v.s, 726 m, 652 s, 528 m, 422 m.

Caution! Sodium azide is potentially explosive. Only a small amount should be handled with care.

X-ray crystallography. Single-crystal X-ray diffraction data were collected on a Bruker-AXS SMART CCD area detector diffractometer with graphite monochromatized MoK_α radiation ($\lambda = 0.71073$ Å) at 293 K. The structure was solved by direct methods and refined by full-matrix least-squares techniques based on F^2 using SHELXTL program package [29]. Anisotropic thermal parameters were applied to all non-hydrogen atoms. The hydrogen atoms were added theoretically and refined isotropically using a riding model. The crystal data and structure refinement parameters are summarized in Table 1. Selected bond lengths and angles are listed in Table 2.

Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 648810; deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk/conts/retrieving.html).

RESULTS AND DISCUSSION

Crystals of complex **I** were synthesized by the hydrothermal reaction of $Co(NO_3)_2 \cdot 6H_2O$ and H_2L in the presence of sodium azide. In the search of single crystal of complex **I**, it was found that sodium azide played a vital role. We tried to employ inorganic or organic base, such as NaOH or Et_3N instead of NaN_3, to deprotonate the carboxylic group of the ligand, but failed to obtain crystal product. Moreover, single crystal of complex **I** cannot be formed when H_2L was directly treated with cobalt nitrate without sodium azide. From the experimental result, we can safely conclude that sodium azide not only acts as a base to deprotonate the H_2L ligand but also has a structure-directing effect for the formation of cobalt-containing complex cystal.

Single-crystal X-ray analysis reveals that complex **I** consists of one cobalt cation, two HL^- groups and two H_2O molecules. As shown in Fig. 1a, the central cobalt ion is hexacoordinated by four O atoms of two different carboxylic groups from two ligands HL^- and two coordinated water molecules to form a highly distorted octahedral geometry. The OCoO bond angles around the Co^{2+} ion are in the range of 58.27°–100.13° and the Co–O bond lengths are ranging from 1.99 to 2.38 Å. For HL^- ligand, only one carboxylic group was deprotonated to chelate with cobalt ion. The OCO angle of deprotonated carboxylic group is 118.5(5)°, which is slightly smaller than that of the non-deprotonated carboxylic group (123.3(5)°).

The most interesting feature of the complex is that the neighboring molecules are linked into 1D chains along the y axis by intermolecular O(6)–H(6*A*)···O(1) hydrogen bonding interactions between coordinated water molecules and the deprotonated carboxylic groups and p···p stacking interactions between adjacent parallel carbazole rings (Fig. 1b). The distances of H(6*A*)···O(1) and centroid···centroid are 2.19 and 3.47 Å, respectively. The angle of O(6)–H(6*A*)···O(1) is 119°. In addition, the hydrogen bonding interactions along the *xz* plane also play an important role in the formation of 2D structure. Specifically, the O(3)–H(3*A*)···O(2) interactions with 2.60 Å of H(3*A*)···O(2) and 144° of O(3)–H(3*A*)···O(2), the O(3)–H(3*A*)···O(6) interactions with 2.03 Å of H(3*A*)···O(6) and 138° of O(3)–H(3*A*)···O(6), and the O(6)–H(6*B*)···O(3) interactions with 2.07 Å of H(6*B*)···O(3) and 130° of O(6)–H(6*B*)···O(3), extend the 1D chains into 2D supramolecular architecture (Fig. 1c).

To confirm whether the crystal structures are truly representative of the bulk materials, PXRD experiments have been carried out for complex **I**. Although the experimental pattern has a few unindexed diffraction lines in comparison with that simulated from the single-crystal data, it can still be safely considered that the bulk synthesized materials and the as-grown crystals are homogeneous [15, 18]. The differences in intensity may be due to the preferred orientation of the powder samples [21].

Table 2. Selected bond lengths (Å) and angles (deg) for complex **I***

Bond	*d*, Å
Co(1)–O(1)	2.057(3)
Co(1)–O(2)	2.384(3)
Co(1)–O(6)	1.997(3)
Angle	**ω, deg**
O(3)C(13)O(4)	123.3(5)
O(1)C(4)O(2)	118.5(4)
O(1)Co(1)O(2)	58.27(12)
O(1)Co(1)O(6)	100.13(13)
$O(2)Co(1)O(6)^{\#1}$	82.54(12)

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, y, -z + 1/2$.

TGA shows that complex **I** has high thermal stability (Fig. 2). It starts to lose its two coordinated water molecules at 189°C, with the weight loss of 5.81% consistent with the calculated value 5.50%. Upon further heating, complex **I** has two almost identical weight loss steps (~28%) ranging from 300 to 500°C, which are corresponding to the sequential decomposition of two coordinated organic molecules. The result indicates that complex **I** maintains its crystal form from room temperature to 189°C. The high stability may be attributed to intermolecular H-bonding and p···p stacking interactions.

The luminescent properties of the title complex and the free ligand are investigated in the solid state at room temperature. As shown in Fig. 3, the free ligand exhibits an emission at ca. 426 nm (excited at 340 nm), which can be assigned to the typical intraligand π–π* electronic transition [30]. Complex **I** shows luminescent emissions with three maxima at 371, 389 and 448 nm upon the excitation at 290 nm, respectively.

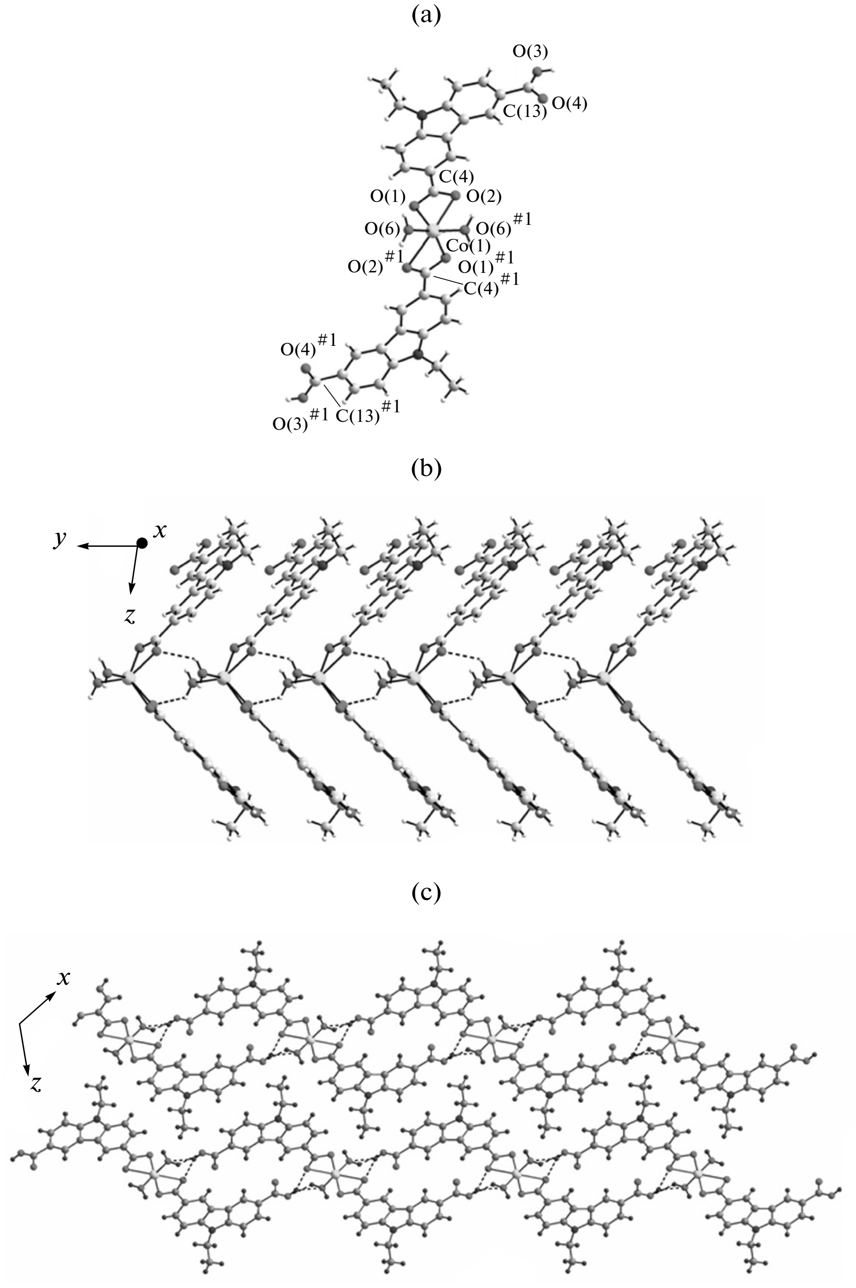

Fig. 1. Crystal structure with atomic numbering scheme of complex **I** (a); 1D chain of complex **I** along the *y* axis linked by H-bonds and $\pi\cdots\pi$ stacking interactions (b); 2D packing diagram of complex **I** with intermolecular hydrogen bonds (dash-lines) viewed along the *xz* plane (c). Symmetry code: $^{\#1}$ $-x, y, -z + 1/2$.

The maximal emission at 371 nm is blue-shifted by 55 nm in comparison with the free ligand, which can be attributed to the ligand-to-ligand charge transfer of the coordinated H_2L ligands [31]. The shoulders at 389 and 448 nm can be ascribed to the excimer emission of the ligand because of the interactions between the molecules [32].

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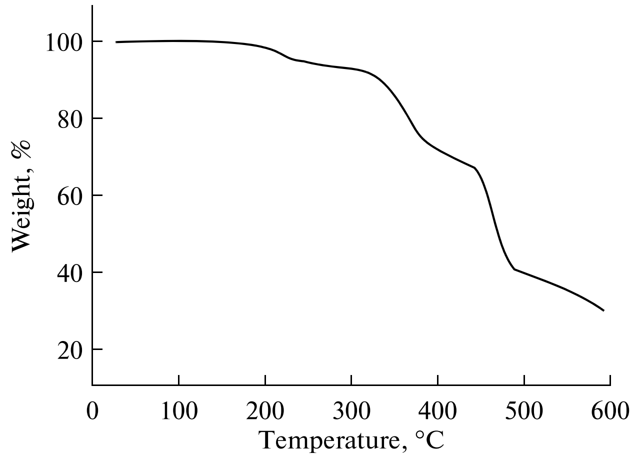

Fig. 2. The thermal decomposition curve of complex **I**.

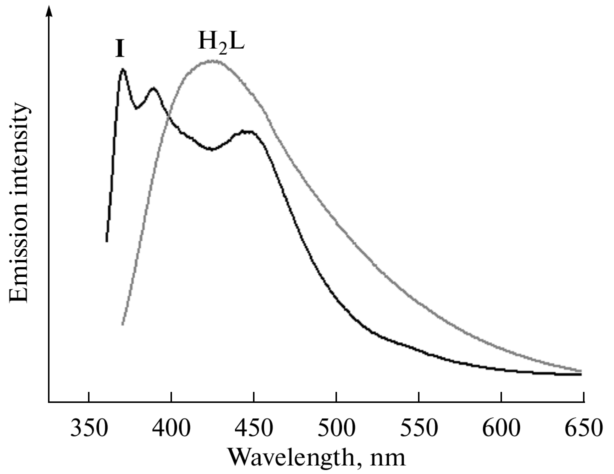

Fig. 3. Solid state emission spectra at room temperature of complex **I** and the ligand H_2L.

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REFERENCES

1. Uemura, T., Uchida, N., Asano, A., et al., *J. Am. Chem. Soc.*, 2012, vol. 134, p. 8360.
2. Jin, F., Zhang, Y., Wang, H.Z., et al., *Cryst. Growth Des.*, 2013, vol. 13, p. 1978.
3. Yoon, M., Srirambalaji, R., and Kim, K., *Chem. Rev.*, 2012, vol. 112, p. 1196.
4. Guo, F.S., Leng, J.D., Liu, J.L., et al., *Inorg. Chem.*, 2012, vol. 51, p. 405.
5. Chen, D.Y., Zou, J.H., Li, W.X., et al., *Inorg. Chem. Commun.*, 2014, vol. 40, p. 35.
6. Meek, S.T., Greathouse, J.A., and Allendorf, M.D., *Adv. Mater.*, 2011, vol. 23, p. 249.
7. Tanabe, K.K. and Cohen, S.M., *Chem. Soc. Rev.*, 2011, vol. 40, p. 498.
8. Bellini, R., Chikkali, S.H., Berthon-Gelloz, G., et al., *Angew. Chem. Int. Ed.*, 2011, vol. 50, p. 7342.
9. Tomar, K., *Inorg. Chem. Commun.*, 2013, vol. 37, p. 132.
10. Yang, L.R., Wu, L.Z., Zhang, H.M., et al., *Dyes Pigments*, 2013, vol. 99, p. 257.
11. Richards, V.J., Argent, S.P., Kewley, A., et al., *Dalton Trans.*, 2012, vol. 41, p. 4020.
12. Yang, M.D., Xi, W.G., Zheng, J., et al., *Russ. J. Coord. Chem.*, 2014, vol. 40, no. 8, p. 588.
13. Luo, L., Chen, K., Liu, Q., et al., *Cryst. Growth Des.*, 2013, vol. 13, p. 2312.
14. Zhao, N.N., Li, W.J., Sun, C.Y., et al., *Solid State Sci.*, 2012, vol. 14, p. 317.
15. Wang, J.J., Yan, L.F., Li, Z.X., et al., *Inorg. Chim. Acta*, 2009, vol. 362, p. 3147.
16. Wang, L., Ni, L., and Yao, J., *Polyhedron*, 2013, vol. 59, p. 115.
17. Wang, X.L., Luan, J., Lu, Q.L., et al., *J. Organomet. Chem.*, 2012, vol. 719, p. 1.
18. Gu, J.Z., Lv, D.Y., Gao, Z.Q., et al., *J. Solid State Chem.*, 2011, vol. 184, p. 675.
19. Liao, S.Y., Gu, W., Yang, L.Y., et al., *Polyhedron*, 2012, vol. 36, p. 38.
20. Tao, B., Cheng, F.R., Jiang, X., et al., *J. Mol. Struct.*, 2012, vol. 1028, p. 176.
21. Bai, Y., Wang, J.L., Dang, D.B., et al., *Synth. Met.*, 2012, vol. 162, p. 2081.
22. Liu, L.L., Huang, J.J., Wang, X.L., et al., *Inorg. Chim. Acta*, 2013, vol. 394, p. 715.
23. Mei, C.Z., Shan, W.W., and Liu, B.T., *Spectrochim. Acta, Part A*, 2011, vol. 81, p. 764.
24. Morrison, C.N., Powell, A.K., and Kostakis, G.E., *Cryst. Growth Des.*, 2011, vol. 11, p. 3653.
25. Hou, S., Liu, Q.K., Ma, J.P., et al., *Inorg. Chem.*, 2013, vol. 52, p. 3225.
26. Zhang, J.Z., Cao, W.R., Pan, J.X., et al., *Inorg. Chem. Commun.*, 2007, vol. 10, p. 1360.
27. Lo, S.H., Liu, H.K., Zhan, J.X., et al., *Inorg. Chem. Commun.*, 2011, vol. 14, p. 1602.
28. Zhou, H.P., Zhu, Y.M., Cui, C.M., et al., *Inorg. Chem. Commun.*, 2006, vol. 9, p. 351.
29. Sheldrick, G.M., *SADABS, a Program for Exploiting the Redundancy of Area-Detector X-ray Data*, Göttingen: Univ. of Göttingen, 1999.
30. Zhang, W.F., Guo, H., Ma, G.H., et al., *Chem. J. Chin. Univ.*, 1998, vol. 19, no. 4, p. 591.
31. Vogler, A. and Kunkely, H., *Coord. Chem. Rev.*, 2006, vol. 250, p. 1622.
32. Grabowski, Z.R. and Rotkiewicz, K., *Chem. Rev.*, 2003, vol. 103, p. 3899.