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Inorganica Chimica Acta 360 (2007) 1819–1824

Inorganica Chimica Acta

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Synthesis, characterization and 1D helical chain crystal structure of $[Cu(DBA)_2(1,10\text{-phen})]_n$ and $[Cd(DBA)_2(1,10\text{-phen})_2]$ (DBA = benzilic acid)

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Received 4 August 2006; received in revised form 24 September 2006; accepted 25 September 2006

Abstract

Two novel complexes $[Cu(DBA)_2(1,10\text{-phen})]_n$ (**1**) and $[Cd(DBA)_2(1,10\text{-phen})_2]$ (**2**) [HDBA = benzilic acid: $(C_6H_5)_2C(OH)COOH$] have been synthesized and characterized by element analysis and fluorescence spectroscopy. The crystal structures of compounds **1**, **2** and HDBA (**3**) were also determined. Complex **1** is a one-dimensional (1D) helical infinite chain, in which $[(1,10)\text{-phen}]Cu^{(II)}$ units were bridged by benzilic acid. Complex **2** is a mononuclear structure, and is self-assembled through π–π stacking interactions to form a 1D helical chain. Compound **3** is self-assembled to form a 1D helical chain through hydrogen bonds interactions. Thermal analyses indicate that complexes **1** and **2** are stable under 200 and 254 °C in solid state, respectively.

Keywords: Coordination polymer; Helical chain; Crystal structure; Fluorescence

1. Introduction

In recent years, extensively attention has been paid to the design and construction of the Metal-Organic Framework (MOF) from building blocks due to their fascinating structural properties and potential applications in catalysis, host–guest chemistry, enantioselective separation, electrical conductivity, and magnetism [1–5]. It has been thought that many novel properties and potential applications would emerge from unusual MOF [6,7]. Therefore, the rational designed synthesis of novel MOF is still a challenge for chemists.

Molecular structures with helical morphology have practical implication due to their structure similarities with DNA [8,9]. van Koten et al. reported a binuclear $[Ag_2(N_4)_2]^{2+}$ dication with helical structure [10]. Hannon et al. described a Schiff base silver(I) double helical complex [11]. Inoue et al. synthesize one dimensional (1D), R-helical chains $[Mn(hfac)_2]$ (hfac = hexafluoroacetylacetonate) [12]. Hong et al. prepared three helical-chain copper(II) complexes with 4,4′-bipy and diphenic acid [13]. Considerable strategies have been developed for the preparation of helical coordination polymers [14–19]. However, to the best of our knowledge, no examples of the polymer structures comprising helical chains from benzilic acid have been reported.

For metal ions, benzilic (DBA) can provide a variety of chelating and/or bridging coordination modes displayed by the carboxylic or hydroxy groups. In particular, two phenyl rings are not coplanar with each other owing to the steric hindrance. Once the metal ions combine with DBA through carboxylic and hydroxy groups from both sides, distortion at both ends of diphenyl spaced by the central C atom endows DBA to link the metal ions to helical chains. Herein, we present the synthesis, X-ray studies and thermo-stability properties of the compounds **1**, **2**, and **3**. It is noted that three crystal structures exhibit 1D helical chain through different actions (covalent bond, hydrogen bond, and π–π stacking interactions).

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0020-1693/$ - see front matter
doi:10.1016/j.ica.2006.09.027

2. Experimental

2.1. Materials and general methods

All the materials and reagents were obtained commercially and used without further purification. Elemental (C, H, N) analyses were performed on a Perkin–Elmer 2400 element analyzer. Thermogravimetric analysis (TGA) experiments were carried out on a Perkin–Elmer TGA 7 thermogravimetric analyzer with the heating rate of 10 °C/min from room temperature to 800 °C under nitrogen atmosphere. The IR spectra were acquired using Nicolet Avatar 360 FT-IR spectrophotometer. Proton NMR spectra were obtained using a Varian Mercury 300 FT-NMR spectrometer. Fluorescence spectra were recorded with an F-2500 FL Spectrophotometer analyzer.

2.2. Synthesis

2.2.1. Synthesis of crystal structure of HDBA

Benzilic acids were dissolved in 50% ethanol solution (15 cm^3) with stirring. The colorless single crystals suitable for X-ray diffraction were obtained by slow evaporation for 7d. *Anal.* Calc. for $C_{14}H_{12}O_3$ (%): C, 73.67; H, 5.30; O, 21.03. Found: C, 73.71; H, 5.27; O, 19.99%.

2.2.2. Synthesis of $[Cu(DBA)_2(1,10\text{-phen})]_n$ (**1**)

A mixture of $CuCl_2 \cdot 2H_2O$ (0.5 mmol), 1,10-Phen (0.5 mmol) and 50% ethanol solution (20 cm^3) was stirred for 30 min at 70 °C, it was then added to benzilic acid (0.5 mmol) and adjusted with an aqueous solution of sodium hydroxide (0.1 mol/L) to pH 7.0. The mixture was continuously stirred for another 30 min and filtered. Blue lamellar single crystals were obtained from the filtrate at room temperature for 5d. (75% yield). *Anal.* Calc. for $C_{40}H_{28}CuN_2O_6$ (%): C, 69.01; H, 4.05; N, 4.02. Found: C, 69.10; H, 4.09; N, 3.95%. (KBr pellet) (cm^{-1}): 3056, 1651, 1630, 1518, 1489, 1445, 1426, 1335, 1222, 1169, 1052, 1033, 963, 873, 852, 765, 737, 724, 699, 604, 526, 495.

2.2.3. Synthesis of$[Cd(DBA)_2(1,10\text{-phen})_2]$ (**2**)

The same synthetic procedure as for complex **2** was employed except that $CuCl_2 \cdot 2H_2O$ was replaced by $CdCl_2 \cdot 6H_2O$, resulting in prism colorless single-crystals suitable for X-ray diffraction in 52% yield. *Anal.* Calc. for $C_{52}H_{38}CdN_4O_6$ (%): C, 67.35; H, 4.13; N, 6.04. Found: C, 67.40; H, 4.10; N, 6.09%. (KBr pellet) (cm^{-1}): 3048, 1614, 1591, 1515, 1492, 1447, 1426, 1386, 1343, 1200, 1171, 1144, 1049(s), 981, 939, 903, 858, 754, 727, 705, 677, 633, 552, 473. ^1H NMR (CD_3SOCD_3, 300 MHz) δ: 9.12–9.15 (m, 4H), 8.94–8.97 (m, 4H), 8.93–8.91 (m, 4H), 8.86–8.89 (m, 4H), 8.27–8.30 (m, 4H), 8.31–8.33 (m, 4H), 8..08 (d, 2H), 8.07 (d, 2H), 8.06 (d, 2H), 8.05 (d, 2H), 7.30 (s, 2H), 7.13–7.17 (m, 4H).

2.3. X-ray crystallography

Single crystal X-ray diffraction data collections of 1–3 were performed on a Bruker Apex II CCD diffractometer operating at 50 kV and 30 mA using Mo Kα radiation

Table 1

Crystallographic data and structure refinement summary for complexes **1**–**3**

Formula	$C_{14}H_{12}O_3$	$C_{40}H_{29}CuN_2O_6$	$C_{52}H_{38}CdN_4O_6$
Mr	228.24	697.19	1173.26
Crystal system	orthorhombic	monoclinic	monoclinic
Crystal size (mm)	0.40 × 0.32 × 0.25	0.30 × 0.25 × 0.18	0.35 × 0.26 × 0.20
Space group	*Pna*2$_1$	*P*2$_1$/*c*	*C*2/*c*
a (Å)	11.2776(11)	27.756(2)	26.2200(3)
b (Å)	8.6554(9)	11.3675(7)	11.46210(10)
c (Å)	24.418(2)	22.7132(15)	17.4611(2)
α (°)			
β (°)		112.999(5)	123.3220(10)
γ (°)			
V ($Å^3$)	383.5(4)	6596.79	4384.95(8)
Z	8	8	4
D_{calc} (g/cm^3)	1.272	1.404	1.405
θ Range (°)	1.67–27.77	1.96–21.30	1.86–25.25
μ (mm^{-1})	0.089	0.714	0.554
$F(000)$	960	2880	1896
Range of h,k,l	−14/14, −11/10, −31/32	−25/28, −11/11, −23/23	−31/31, −13/13, −20/20
Total/independent reflections	15638 /5464	35731/7341	29749/3977
Parameters	311	883	286
Goodness-of-fit	0.995	1.158	1.085
R_1 $[I > 2\sigma(I)]$[a]	0.0698	0.0812	0.0283
wR_2 (all data)[b]	0.1621	0.2130	0.0653

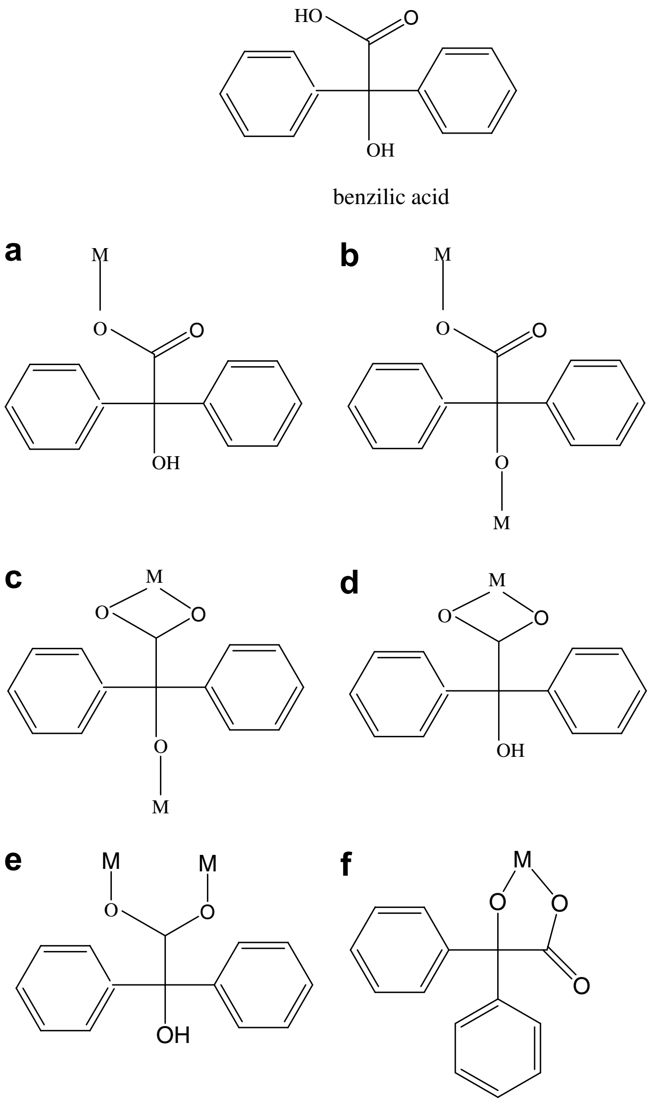
[a] $R_1 = \sum \|\|F_o\| - \|F_c\|\|/\sum \|F_o\|$.

[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum(F_o^2)^2\}^{1/2}$.

$\lambda = 0.71073$ Å) at 293 K. Data collection and reduction were performed using the SMART and SAINT software [20]. A multi-scan absorption correction was applied using the SADABS program [21]. All three structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL program package [22]. Hydrogen atoms were located from difference Fourier maps and a riding mode. Crystal parameters and details of the data collection and refinement are given in Table 1.

3. Results and discussion

The benzilic acid is a multifunctional ligand in that it has the potential to coordinate in a number of different ways (Scheme 1) [23–25]. The X-ray crystal structures of compounds **1**, **2**, and **3** were determined (Fig. 1). The X-ray crystal structures of complexes **1** and **2** show that they are 1D chain polymer and mononuclear structure, respectively.



Scheme 1. Structure of benzilic acid and some of its possible coordination modes.

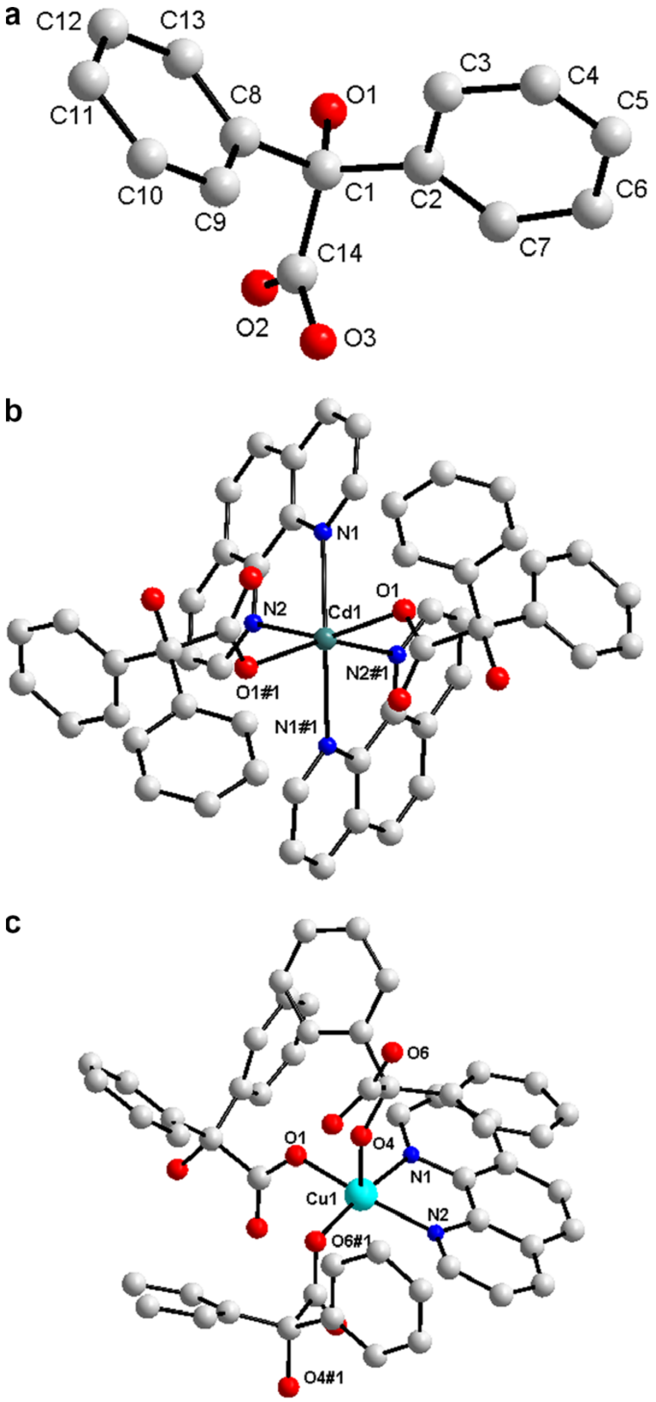


Fig. 1. Benzilic acid structure and the coordination environment of the metal centers in the complexes.

In **3** (HDBA), there is a cone-shaped geometry around a carbon center similar to methane (Table 2), and there are two crossed phenyl rings, with the dihedral angle between them being 81.6°. The carboxylate group and hydroxyl group are non-coplanar. Interestingly, the compound is linked into a 1D helical chain by continuous O–H···O hydrogen bonds rings (see Fig. 2). The hydrogen bonds distances are shown in Table 3.

Table 2
Selected bond distances (Å) and angles (°)

HDBA			
C1–O1	1.411(5)	O1–C1–C2	104.3(3)
C1–C2	1.518(6)	O1–C1–C14	107.9(3)
C1–C14	1.537(5)	C2–C1–C14	111.9(3)
C1–C8	1.540(5)	O1–C1–C8	111.3(3)
C14–O2	1.213(2)	C2–C1–C8	115.1(3)
C14–O3	1.301(1)	O2–C14–O3	124.5(2)
*Complex **1***			
Cu1–O1	1.907(6)	O1–Cu1–O6#1	93.6(2)
Cu1–O6#1	1.929(5)	O1–Cu1–N1	89.7(3)
Cu1–N1	2.010(7)	O6#1–Cu1–N1	172.7(3)
Cu1–N2	2.018(7)	O1–Cu1–N2	170.6(3)
Cu1–O4	2.317(5)	O6#1–Cu1–N2	94.6(3)
N1–Cu1–N2	81.7(3)	O1–Cu1–O4	91.3(2)
O6#1–Cu1–O4	81.1(2)	N1–Cu1–O4	105.4(2)
N2–Cu1–O4	94.5(3)		
*Complex **2***			
Cd1–O1	2.199(2)	O1#2–Cd1–N1#2	85.0(2)
Cd1–N1	2.373 (2)	O1–Cd1–N1#2	114.2(3)
Cd1–N2	2.444(2)	N1–Cd1–N1#2	147.8(3)
O1#2–Cd1–N2	90.1(2)	O1–Cd1–N2	152.5(3)
N1–Cd1–N2	69.0(2)	N1#2–Cd1–N2	86.2(3)
N2–Cd1–N2#2	79.9(3)		

Symmetry code: (#1) $-x$, $y+1/2$, $-z+1/2$; (#2) $-x$, y, $-z+1/2$.

Table 3
Hydrogen-bond geometry (Å, °)

HDBA				
D–H···A	D–H	H···A	D···A	D–H···A
O1–H1···O2	0.82	2.28	2.638(6)	107
O1–H1···O2′#1	0.82	2.06	2.812(5)	152
O1′–H1′···O2#2	0.82	1.95	2.729(6)	159
O3′–H3′1···O1′#3	0.82	1.81	2.632(4)	175
O3–H3A···O1#3	0.82	1.83	2.646(4)	171

Symmetry code: (#1) $1/2+x$, $3/2-y$, $-1+z$; (#2) x, y, $1+z$; (#3) $-1/2+x$, $3/2-y$, z.

In complex **1**, each Cu^{II} center displays a distorted square pyramidal geometry with two carboxylate oxygen donors and a hydroxylate oxygen donor from three benzilic acid ligands, two nitrogen donors from one bidentate chelating 1,10-phen ligand. The distinct different bond lengths are Cu1–O1 [1.907(6) Å] and Cu1–O4 [2.317(5) Å], the Cu–N bond lengths are 2.018(7) Å and 2.010(7) Å (Table 2). The crossed phenyl rings of two BDA ligands with the dihedral angles between them are 78.7° and 70.5°, respectively. The complex is linked with Scheme 1a and b coordination mode and 1,10-phen, mode (b) plays an important role in forming the 1D helical chain (Fig. 3). In the chain, the distance of two adjacent $Cu^{II}$is 7.489 Å, and the distance of three adjacent Cu···Cu···Cu angles is 98.7°. The 1D helical chain presents an attractive structure framework with an unprecedented, very small diameter of approximately 18.5 Å.

In complex **2**, the Cd^{II} center is in a distorted octahedral geometry by coordinating to two carboxylate oxygen atoms from two BDA ligands, four nitrogen atoms from two bidentate ligands chelating two 1,10-phen ligands. The Cd–O distance is 2.199(2) Å, and the two Cd–N distances are 2.010(7) and 2.018(7) Å (Table 2), which are typical values for $Cd–N_{phen}$ and $Cd–O_{coo}$ coordination distances. The dihedral angle between the twisting phenyl rings of BDA ligand is 79.3°, and the dihedral angle between the twisting phens is 62.5°. The combination of these twists and π–π stacking interactions between phens results in the formation of a 1D helical chain as shown in Fig. 4. The centroid to centroid and interplanar distances of the π–π stacking interactions between phen planes are 3.799(1) and 3.496(2) Å, respectively. As stated by Janiak [26], the usual π–π interaction is an offset or slipped stacking, i.e., the rings are parallel displaced, and the ring nor-

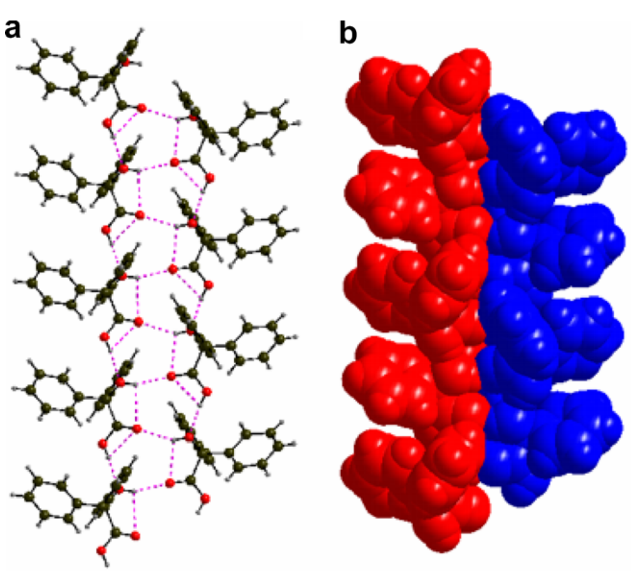


Fig. 2. Hydrogen-bonds network and the helical chain in complex **1**.

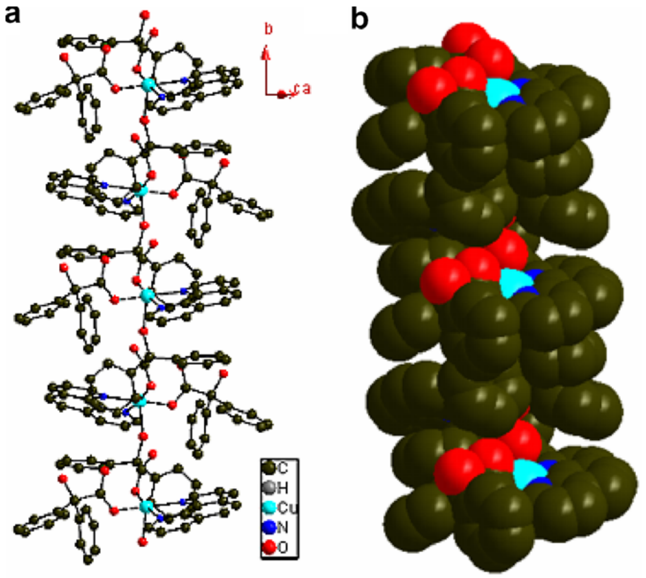


Fig. 3. 1D helical chain of Cu^{II} complex through covalence bond.

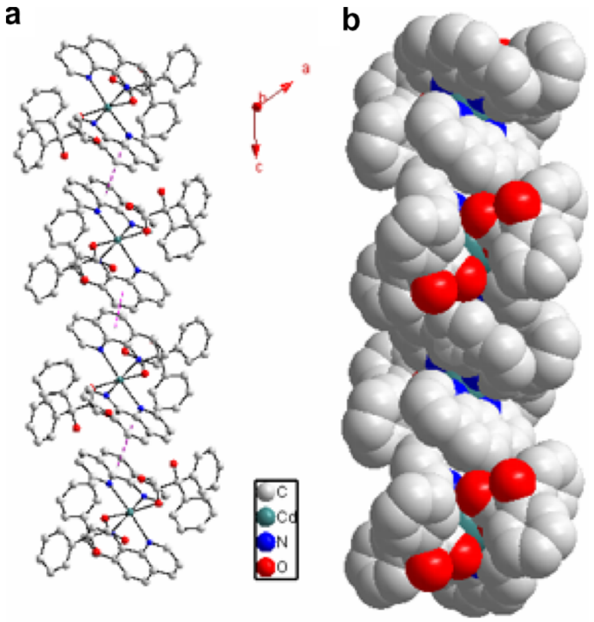


Fig. 4. 1D helical chain of Cd^{II}complex through π–π stacking interactions.

mal and the vector between the ring centroids form an angle of about 20° up to the centroid–centroid distances of 3.8 Å.

Complex **1** forms a 1D helical chain polymer with Scheme 1a and (b) coordination mode, whereas complex **2** with Scheme 1a coordination mode displays another 1D helical chain through π–π stacking interactions between phens. This may originate from the nature of heterometallic atoms employed. Cu(II) favors a square–planar or square–pyramidal geometry, whereas Cd(II) tends to adopt an octahedral geometry owing to the strong Jahn–Teller effect. Meanwhile, the steric effect of phen and DBA ligands appears to play a significant role in the construction of the unique structures of **1** and **2**. The large steric hindrance of phen and L ligands prevents the formation of heterometallic layered structures. And it is well known that metal-involved self-assembly processes can be influenced by many factors used for crystallization. Besides the fundamental and strong metal–ligand coordination driven force (complex **1**) , other relatively weak intramolecular or intermolecular interactions such as hydrogen bonding compound **3** and aromatic stacking (complex **2**) are also useful tools in constructing the supramolecular framework and coordination polymers.

The thermogravimetric analyses (TGA) of complexes were performed in a N_2 atmosphere when it was heated to 900 °C at a rate of 10 °C min^{-1}. For Cu^{II} complexes, TGA studies indicated that the weight loss in the range of 200–480 °C is attributed to the burning DBA group and 1,10-phen ligand, the final residual weight is 12.01% (Calc. 11.49%) corresponding to CuO; for Cd$^{(II)}$ complexes, TGA results show that the crystals were unchanged (0.93 wt%) until 695 °C; whereupon, decomposition occurred (Fig. 5).

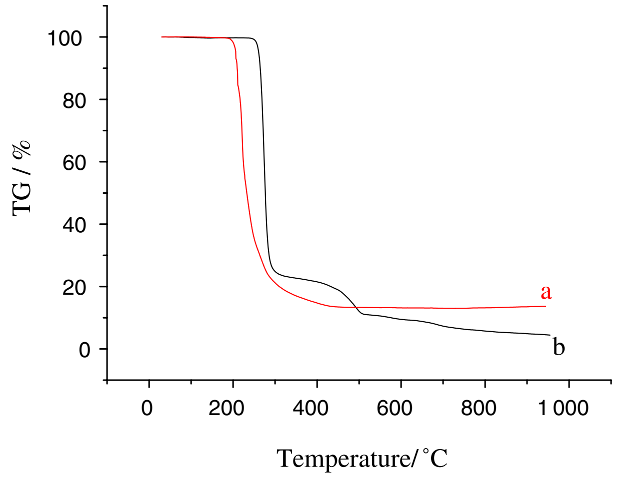


Fig. 5. (a) TG curve of complex **1** and (b) TG curve of complex **2**.

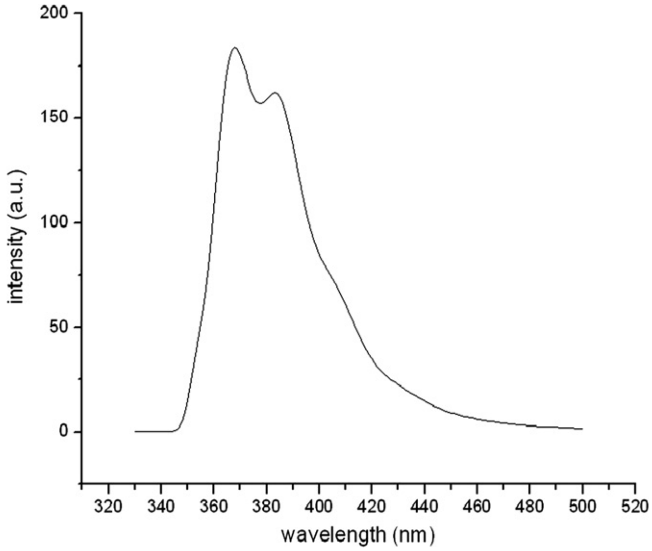


Fig. 6. Liquid solution fluorescent emission spectra of complex **2** at room temperature.

The fluorescent spectral property of the complexes has also been studied. Compounds **1**, **2**, and **3** were dissolved in the ethanol solution and their fluorescent emission spectrum was measured at room temperature, respectively (Fig. 6). Compound **3** does not show any photoluminescence and complex **1** also has no fluorescent emission, which may be due to the quenching effect of Cu ions. Whereas complex **2** exhibits two intense fluorescent emission bands at 368, 383 nm, which may be attributed to intraligand charge transfer of coordinated phen ligands, similar to the emission of free phen · H_2O [27].

4. Summary

In summary, two new complexes [Cu(DBA)$_3$(1,10-phen)]$_n$ and [Cd(DBA)$_2$(1,10-phen)$_2$] have been synthesized. Complex **1** exhibits an attractive rope-like 1D helical-chain structure framework with unprecedented very small diameter approximately of 18.5 Å, which is generated mainly by DBA ligand as an efficient template. In complex **2**, (1,10-phen) Cd^{II}-based show supramolecular architectures assembled through π–π stacking interactions. This work shows that the rational selection of benzilic ligand can yield helical-chain complexes, whereas the different diameters of atoms and coordinate modes can affect the spatial orientation of ligand strands.

Appendix A. Supplementary material

CCDC 615761, 609309 and 609468 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2006.09.027.

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