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Inorganica Chimica Acta 360 (2007) 1819–1824
Inorganica Chimica Acta
www.elsevier.com/locate/ica

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
Available online 12 October 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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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. ^{1}H 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)	$0.40 \times 0.32 \times 0.25$	$0.30 \times 0.25 \times 0.18$	$0.35 \times 0.26 \times 0.20$
Space group	$Pna2_1$	$P2_1/c$	$C2/c$
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] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2] / \sum (F_o^2)^2\}^{1/2}$.