Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of Molecular Structure 738 (2005) 183–187

Journal of
MOLECULAR
STRUCTURE

www.elsevier.com/locate/molstruc

Synthesis, characterization and crystal structures of two discrete Cu(II) complexes with mixed-ligands: [Cu(mal)(**L**)(H_2O)]·H_2O and [Cu(Phmal)(**L**)$_2$] (mal = malonate dianion, phmal = phenylmalonate dianion and **L** = 5,5′-dimethyl-2,2′-bipyridine)

Guang-Hua Cui, Jian-Rong Li, Tong-Liang Hu, Xian-He Bu*

Department of Chemistry, Nankai University, Weijing Road 94, Tianjin 300071, People's Republic of China

Received 30 September 2004; revised 2 December 2004; accepted 3 December 2004
Available online 19 January 2005

Abstract

Two new Cu(II) complexes with mixed ligands, [Cu(mal)(**L**)(H_2O)]·H_2O (**1**) and [Cu(phmal)(**L**)]$_2$ (**2**) (mal = malonate dianion, phmal = phenylmalonate dianion, **L** = 5,5′-dimethyl-2,2′-bipyridine) have been synthesized and characterized by elemental analyses, IR, UV–vis and X-ray single crystal diffraction. In both complexes the Cu(II) ions take five-coordinated square pyramidal geometry. **1** has a mononuclear structure, and assembles into a 2D supramolecular network by hydrogen bonding. **2** is a dinuclear complex, and also forms 2D framework via π–π interactions. The structural differences of the two complexes may be attributed to the variation of the substituted group of malonate dianion.

Keywords: Cu(II) complexes; Hydrogen bonds; Malonate dianion; Mixed-ligand; π–π interactions

1. Introduction

The copper(II)–malonate complexes with suitable N-heterocyclic auxiliary ligands are of interest because the metal-N-heterocyclic chelate ring could influence the Cu–O(carboxyl) bond lengths and exhibits some degree of 'metalloaromaticity' [1–10]. On the other hand, self-assembly process involving metal ions and organic ligands has attracted increasing attention for the development of novel functional materials with desired properties [11–15]. However, in most cases, it is still difficult to predict the exact structures and composition of the assembly products by the mixed ligands [16]. In this report, we describe the preparations, characterizations and structures of two new complexes with mixed-ligands [Cu(mal)(**L**)(H_2O)]·H_2O **1** and [Cu(phmal)(**L**)]$_2$ **2** (mal = malonate dianion, phmal = phenylmalonate dianion, **L** = 5,5′-dimethyl-2,2′-bipyridine), which were further self-assembled into 2D networks through hydrogen bonding and π–π interactions, respectively. The subtle change in the substituted group of malonate dianion may exert influence on the structures and supramolecular assembly of the two complexes.

2. Experimental

2.1. Materials and general methods

All reagents for syntheses and analyses were of analytical grade. FT-IR spectra (KBr pellets) were obtained on a FT-IR 170 SX (Nicolet) spectrometer, and UV–vis spectra on a Hitachi UV-3010 spectrophotometer. Elemental analyses were taken using a Perkin–Elmer 240C analyzer.

---

* Corresponding author. Tel.: +86 22 235 02 809; fax: +86 22 235 02 458.

E-mail address: buxh@nankai.edu.cn (X.-H. Bu).

0022-2860/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.molstruc.2004.12.004

2.2. Synthesis of the complexes

*[Cu(mal)(**L**)(H$_2$O)]·H$_2$O* **1** Basic copper(II) carbonate (221 mg, 1 mmol) was treated with an aqueous solution (10 mL) of malonic acid (208 mg, 2 mmol) in a steam bath until the solid disappeared. The solution was then filtered and diluted to approximately 40 mL with water. An ethanol solution (10 mL) of 5,5′-dimethyl-2,2′-bipyridine (368 mg, 2 mmol) was then added to above solution. The resultant clear-blue solution was warmed on a steam bath for 1 h. The volume was kept constant by periodic addition of water. Then the solution was filtered and allowed to stand at room temperature. Blue single crystals of **1** were obtained after 2 days. They were filtered, washed with water and ethanol and air-dried. Yield: 37% (based on basic copper(II) carbonate). Anal. Found: C, 44.36; H, 4.77; N, 7.20. Calcd. for $C_{15}H_{20}CuN_2O_7$: C, 44.61; H, 4.99; N, 6.94. FT-IR (cm^{-1}): 3490w, 3187m, 1628s, 1481m, 1415s, 1316s, 1055w, 854w, 728w, 422w. UV–vis ($\lambda_{\max}$, nm): 631, 316, 281, 225.

*[Cu(phmal)(**L**)]$_2$* **2**. This compound was prepared by following an analogous procedure to that of **1** except for using phenylmalonic acid instead of malonic acid. The shape and color of the crystals of **2** are nearly the same as those of **1**. Yield: 35% (based on basic copper(II) carbonate). Anal. Found: C, 58.86; H, 4.53; N, 6.25. Calcd. for $C_{21}H_{18}CuN_2O_4$: C, 59.22; H, 4.26; N, 6.58. FT-IR (cm^{-1}): 1644s, 1602s, 1475m, 1396s, 1301m, 1049m, 941w, 839m, 751w, 727w, 422w. UV–vis ($\lambda_{\max}$, nm): 634, 321, 257, 213.

2.3. X-ray crystallographic studies

Single-crystal X-ray diffraction measurements were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam for data collection at room temperature. The determination of unit cell parameters and data collections were performed with Mo Kα radiation (λ=0.71073 Å). Unit cell dimensions were obtained with least-squares refinements and structures were solved by direct methods [17]. Copper atoms in each complex were located from *E*-maps. The other non-hydrogen atoms were located in successive difference Fourier syntheses. The final refinement was performed by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2 [18]. The hydrogen atoms except for those of water molecules in **1** were generated geometrically. Hydrogen atoms of the water molecules were located from difference Fourier maps and refined isotropically with the restrain. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

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

	1	**2**
Empirical formula	$C_{15}H_{20}CuN_2O_7$	$C_{42}H_{36}Cu_2N_4O_8$
Formula weight	403.87	851.85
Crystal system	Orthorhombic	Triclinic
Space group	*Pnma*	*P*-1
Unit cell dimensions (Å, deg)		
a	6.650(3)	8.701(3)
b	13.698(6)	9.953(4)
c	19.573(9)	11.666(4)
α	90	111.304(6)
β	90	93.034(6)
γ	90	102.584(6)
Volume (Å^3)	1783(1)	908.9(6)
Z	4	1
D_{calcd} (g/cm^3)	1.505	1.556
μ (mm^{-1})	1.264	1.233
F (000)	836	438
Range of *h*, *k*, *l*	−8/5, −17/16, −23/24	−10/10, −12/6, −14/14
Reflections collected/unique	9719/1905	5313/3694
Max. and min. transmission	1.0000 and 0.7799	1.0000 and 0.7732
Data/restraints/parameters	1905/3/130	3694/0/253
Goodness-of-fit on F^2	1.082	1.021
R and R_w	0.0399 and 0.1032	0.0545 and 0.1156
Largest diff. peak and hole (e/Å^3)	0.297 and −0.287	0.407 and −0.335

$R=\sum(||F_0|-|(F_C||)/\sum|F_0|$; $wR=[\sum w(|F_0|^2-|F_C|^2)^2/\sum w(F_0^2)]^{1/2}$.

3. Results and discussion

3.1. Synthesis and spectral characterization of 1 and 2

The title complexes **1** and **2** were prepared by the reaction of basic copper(II) carbonate, corresponding malonic acid and 5,5′-dimethyl-2,2′-bipyridine in 1:2:2 molar ratio in water/alcohol system. The results of elemental analyses for the two complexes were in good agreement with the theoretical requirements of their compositions (X-ray analysis results). Both complexes are stable in air. The IR spectra of the title complexes show strong bands at 1628 cm^{-1} for **1** and 1644 cm^{-1} for **2**, which can be attributed to C=O stretching vibration, and the bands at 1415 and 854 cm^{-1} for **1**, 1396 and 839 cm^{-1} for 2 arise from the C=C and C=N stretching vibrations of the coordinated 5,5′-dimethyl-2,2′-bipyridine, respectively. The observed bands in the range of 3600–3200 cm^{-1} in **1** suggest the coordination of water molecules with hydrogen bonds.

The UV–vis spectra of **1** and **2** in methanol were measured at room temperature. The bands of 213–281 nm (281, 225 nm for **1** and 257, 213 nm for **2**) can be ascribed to π–π transitions of the ligands. The shoulder band at ca. 320 nm (316 nm for **1** and 321 nm for **2**) may arise from the ligand-to-ligand or metal-to-ligand charge transfer transition. The broad bands centered at 631 nm for **1** and