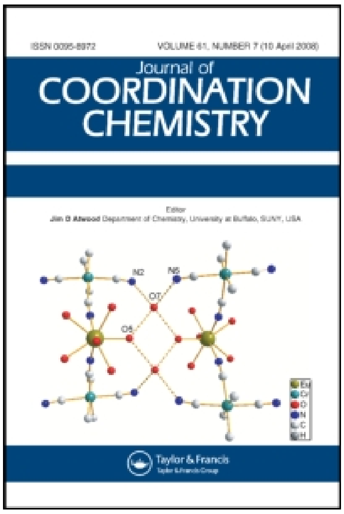

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Synthesis and crystal structure of a Cu(II) complex with mixed malonate/1,10-phenanthroline ligands

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Synthesis and crystal structure of a Cu(II) complex with mixed malonate/1,10-phenanthroline ligands

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A Cu(II) complex with mixed ligands, $[Cu_3(mal)_3(phen)_3(H_2O)_2] \cdot 11H_2O$ (mal = malonate, phen = 1,10-phenanthroline) was synthesized and characterized by elemental analysis, IR, UV, electron paramagnetic resonance (EPR) and luminescence spectra and single-crystal X-ray diffraction. The complex crystallizes in the monoclinic system, space group *Cc* with $a = 13.1631(10)$ Å, $b = 20.1089(10)$ Å, $c = 20.1267(13)$ Å, $\beta = 103.500(3)^\circ$, $V = 5180.2(6)$ Å^3, $Z = 4$, and $R_1 = 0.0476$ for 7993 observed reflections. In the complex, one Cu is coordinated by a mal dianion and a phen molecule, exhibiting N_2O_2 square-planar geometry, while the other two Cu atoms are coordinated, respectively, by a mal dianion, a phen and water molecules, exhibiting N_2O_3 square pyramidal coordination geometry.

Keywords: Copper(II); Malonate; 1,10-Phenanthroline; Crystal structure

1. Introduction

As an important dicarboxylate ligand, malonate has been extensively used for preparation of transition metal complexes. In numerous complexes, the malonate dianion generally exhibits bidentate [1–3], tridentate [4–5] or tetradentate [6–8] coordination modes. Although many complexes containing mixed malonate and nitrogen-donor ligands have been synthesized and characterized, the complexes containing mixed malonate (mal) and 1,10-phenanthroline (phen) ligands have been less reported. To the best of our knowledge, there are only three reports on the structures with malonate/1,10-phenanthroline ligands, namely, $[Cu(mal)(phen)(H_2O)] \cdot 1.5H_2O$ [9], $[Mn(mal)(phen)_2(EtOH)]$ [10] and $[Mn_2(mal)(phen)_3(H_2O)(Cl)]Cl$ [2]. Both $[Cu(mal)(phen)(H_2O)]$ and $[Mn(mal)(phen)_2(EtOH)]$ are mononuclear structures in which the malonate is a chelating ligand, while the third complex $[Mn_2(mal)(phen)_3(H_2O)(Cl)]Cl$ is dinuclear, with the malonate ligand serving as *syn-anti* bridge. We report here the preparation and crystal structure of a Cu(II) complex with

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mixed malonate/1,10-phenanthroline ligands, $[Cu_3(mal)_3(phen)_3(H_2O)_2] \cdot 11H_2O$, in which the malonate is bidentate.

2. Experimental

2.1. *Preparation and analysis of $[Cu_3(mal)_3(phen)_3(H_2O)_2] \cdot 11H_2O$*

An ethanol solution (10 mL) of 1,10-phenanthroline (1 mmol) was added slowly to an aqueous solution (10 mL) of $CuSO_4 \cdot 5H_2O$ (1.5 mmol) with continuous stirring. An aqueous solution (10 mL) of malonic acid (1.1 mmol), adjusted to pH 5 with an aqueous NaOH solution (1 N), was then added slowly to the above reaction mixture with continuous stirring. After half an hour, the reaction mixture was allowed to stand at room temperature undisturbed for 3 weeks, resulting in blue crystals of $[Cu_3(mal)_3(phen)_3(H_2O)_2] \cdot 11H_2O$ and $Na_2[Cu(mal)_2] \cdot 2H_2O$ [11].

Elemental analysis was performed with a Vario EL *III* CHNOS Elemental Analyzer. IR spectra of KBr pellets were recorded in the range 4000–400 cm^{-1} on a FTS-40 spectrophotometer. A UV-visible spectrum was recorded in aqueous solution with a Perkin-Elmer Model L 19 spectrophotometer. Electron paramagnetic resonance (EPR) spectra were recorded on a FD-ESR-I spectrometer. Fluorescence spectra were carried out on an FLS920 spectrometer. Anal. Calcd for $C_{45}H_{66}Cu_3N_6O_{25}$: C, 42.17; H, 5.19; N, 6.56%. Found: C, 42.09; H, 5.11; N, 6.51%. IR (KBr pellet, cm^{-1}): 3519 (s), 3367 (s), 1579 (s), 1518 (w), 1433 (s), 1373 (s), 1346 (w), 1275 (w), 1153 (w), 957 (w), 860 (s), 725 (s), 613 (w). Yield: approximately 17%.

2.2. *X-ray crystallography*

A crystal with dimensions $0.20 \times 0.17 \times 0.11\,mm^3$ was mounted on a computer-controlled RIGAKU MERCURY CCD/AFC diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. The structure was solved by direct methods, successive Fourier difference synthesis and refined by full matrix least-squares based on F^2 using the SHELXTL-97 program package. All non-hydrogen atoms were refined anistropically. Hydrogen atoms were not located. The crystallographic data are listed in table 1.

3. Result and discussion

3.1. *Crystal structure*

Selected bond lengths and angles for $[Cu_3(mal)_3(phen)_3(H_2O)_2] \cdot 11H_2O$ are listed in table 2. An asymmetric unit of $[Cu_3(mal)_3(phen)_3(H_2O)_2] \cdot 11H_2O$ is shown in figure 1.

The complex contains two mononuclear $[Cu(mal)(phen)(H_2O)]$ units and a mononuclear [Cu(mal)(phen)] unit. In each $[Cu(mal)(phen)(H_2O)]$ unit, the geometry around the Cu(II) ion is five-coordinate, distorted square pyramidal, showing similar structural features to those of $[Cu(mal)(phen)(H_2O)] \cdot 1.5\,H_2O$ [9] and $[Cu(mal)(bipy)(H_2O)] \cdot H_2O$ [12]. Around the coordinated Cu center, both 1,10-phenanthroline and malonate are symmetrically coordinated with mean Cu1–N, Cu1–O distances of 2.006, 1.932 Å and Cu3–N, Cu3–O distances of 2.009, and 1.918 Å, respectively. Two N atoms and

Table 1. Crystallographic parameters for $[Cu_3(mal)_3(phen)_3(H_2O)_2] \cdot 11H_2O$.

Empirical formula	$C_{45}H_{66}Cu_3N_6O_{25}$
Molecular weight	1281.66
Crystal system	Monoclinic
Space group	*Cc*
a (Å)	13.1631(10)
b (Å)	20.1089(10)
c (Å)	20.1267(13)
β (°)	103.500(3)
V (Å^3)	5180.2(6)
Z	4
T (K)	293(2)
D_c (g cm^{-3})	1.643
$F(000)$	2660
μ (mm^{-1})	1.315
λ (Å)	0.71073
Goodness of fit on F^2	1.050
Largest diff. peak and hole (e Å^{-3})	0.706 and −0.791
Final R indices $[I > 2\sigma(I)]^a$	$R_1 = 0.0476$, w$R_2 = 0.1191$
R indices (all data)	$R_1 = 0.0531$, w$R_2 = 0.1244$

$^aR_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)2]^{0.5}$.

Table 2. Selected bond lengths (Å) and angles (°) for $[Cu_3(mal)_3(phen)_3(H_2O)_2] \cdot 11H_2O$.

Cu(1)–O(1)	1.926(4)	Cu(2)–N(4)	1.997(4)
Cu(1)–O(4)	1.937(4)	Cu(2)–N(3)	2.005(4)
Cu(1)–N(2)	2.005(4)	Cu(3)–O(10)	1.918(4)
Cu(1)–N(1)	2.008(4)	Cu(3)–O(13)	1.918(4)
Cu(1)–O(5)	2.373(4)	Cu(3)–N(5)	1.995(5)
Cu(2)–O(9)	1.908(4)	Cu(3)–N(6)	2.024(5)
Cu(2)–O(6)	1.916(4)	Cu(3)–O(14)	2.252(4)
O(1)–Cu(1)–O(4)	2.65(16)	O(9)–Cu(2)–N(3)	91.25(17)
O(1)–Cu(1)–N(2)	93.89(16)	O(6)–Cu(2)–N(3)	171.67(16)
O(4)–Cu(1)–N(2)	162.07(16)	N(4)–Cu(2)–N(3)	82.59(18)
O(1)–Cu(1)–N(1)	175.82(19)	O(10)–Cu(3)–O(13)	94.24(16)
O(4)–Cu(1)–N(1)	90.46(16)	O(10)–Cu(3)–N(5)	172.50(18)
N(2)–Cu(1)–N(1)	82.32(18)	O(13)–Cu(3)–N(5)	90.94(18)
O(1)–Cu(1)–O(5)	91.66(15)	O(10)–Cu(3)–N(6)	91.29(17)
O(4)–Cu(1)–O(5)	102.98(15)	O(13)–Cu(3)–N(6)	164.46(18)
N(2)–Cu(1)–O(5)	93.50(16)	N(5)–Cu(3)–N(6)	82.35(18)
N(1)–Cu(1)–O(5)	90.35(15)	O(10)–Cu(3)–O(14)	91.39(16)
O(9)–Cu(2)–O(6)	94.36(16)	O(13)–Cu(3)–O(14)	102.90(16)
O(9)–Cu(2)–N(4)	171.95(19)	N(5)–Cu(3)–O(14)	92.75(17)
O(6)–Cu(2)–N(4)	91.24(17)	N(6)–Cu(3)–O(14)	91.46(17)

two carboxyl O atoms are in the equatorial plane with mean deviation of 0.1219 Å for Cu1 and 0.0819 for Cu3. The Cu1 atom is above the equatorial plane N1, N2, O1, O4 by 0.1613 Å towards the apical oxygen (O5), while the Cu3 atom is above the equatorial plane N5, N6, O10, O13 by 0.1625 Å towards the apical oxygen (O14). In both $[Cu(mal)(phen)(H_2O)]$ units, the water molecules (O5, O14) occupy the fifth coordination site of the Cu atoms with corresponding Cu1–O5 and Cu3–O14 distances of 2.373(4) and 2.252(4) Å, respectively. In the Cu1 unit, the dihedral angle between the planes N1–Cu1–N2 and O1–Cu1–O4 is 16.7°, while in the Cu3 unit the corresponding value is 15.0°.

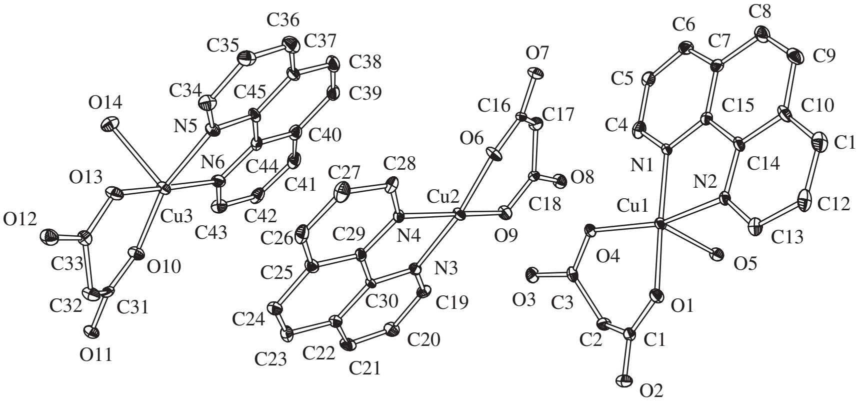

Figure 1. Three Cu-mal-phen units showing the atom-labeling scheme and 30% thermal ellipsoids.

Compared with the analogous complex [Cu(mal)(phen)(H_2O)] · 1.5H_2O [9], the most interesting feature is that there exists an additional [Cu(mal)(phen)] unit (Cu2 unit) between the Cu1 and Cu3 units. In this Cu2 unit, the Cu is coordinated by two O atoms (O6, O9) from different carboxylate groups and two N atoms (N3, N4) from a 1,10-phenanthroline ligand, forming a four-coordinate, square-planar geometry (mean Cu2–N 2.001 and Cu2–O 1.912 Å). Whereas the five-membered chelate ring of 1,10-phenanthroline with Cu2 atom is essentially planar (largest deviation 0.0219 Å), the six-membered chelate ring of malonate with Cu2 assumes a boat conformation. The Cu2 and C17 atoms are displaced by +0.4013 and +0.2497 Å, respectively, from the least-squares plane O6, O9, C18, and C16. The Cu2 ··· Cu1, and Cu2 ··· Cu3 distances are 3.534 and 6.444 Å, respectively. In the Cu2 and Cu3 units the two 1,10-phenanthroline rings are parallel to each other and cause π–π stacking interactions with an inter-ring distance of about 3.54 Å. The molecules are assembled through complex hydrogen bonding (O–H ··· O) to form a three-dimensional structure.

3.2. *IR, UV-visible, luminescence and EPR spectra*

IR spectra of uncoordinated malonate shows a strong ν_{as}(OCO) band at 1700 cm^{-1} and ν_s(OCO) band at 1450 cm^{-1}, as well as two medium intensity bands at 800 and 750 cm^{-1} assigned to the OCO bending frequencies. These frequencies are significantly shifted to lower frequencies in this complex: the ν_{as}(OCO) and ν_s(OCO) appear at 1579 and 1433 cm^{-1}, respectively, which indicates the carboxylate groups are coordinated to metal centers [13–15]. Two strong vibrations at 860 and 725 cm^{-1}, correspond to out-of-plane C–H deformations of 1,10-phenanthroline. The other characteristic bands of 1,10-phenanthroline are visible in the 1518–1153 cm^{-1} regions. A UV-visible spectrum was measured in the 200–800 nm range in aqueous solution. The result shows a very weak absorption at 350 nm from the Cu(II) → LMLCT charge-transfer transition. In addition, a strong, broad absorption at 625 nm may be ascribed to the d–d charge-transfer for a five-coordinated Cu(II) center with square-pyramidal geometry.

Fluorescent analysis was performed at room temperature in the solid state. The results show that the complex exhibits intense photoluminescence at 468 nm (λ_{ex} = 228 nm) (figure 2). The fluorescent emission is not from free 1,10-phenanthroline

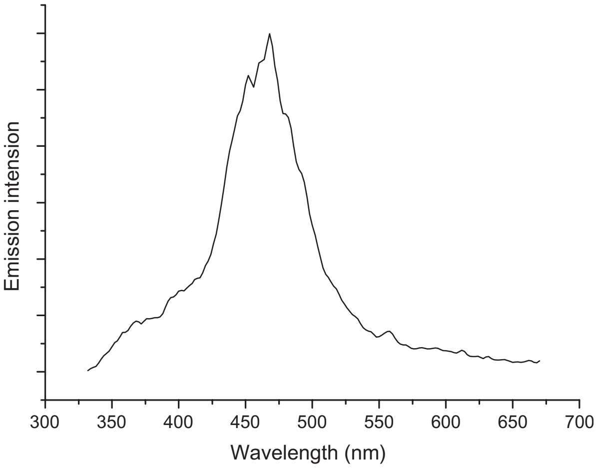

Figure 2. The emission spectrum of the complex.

ligand and the enhancement of fluorescence is due to coordination of 1,10-phenanthroline to Cu(II) increasing the ligand conformational rigidity.

The powder EPR spectrum recorded at room temperature shows an asymmetric broad absorption with a g value of 2.0740. Due to spin–spin interaction, the hyperfine structure cannot be observed. The EPR spectrum in an aqueous solution at room temperature shows the following EPR parameters: $g_{\parallel} = 2.1738$ ($A_{\parallel} = 60\,\mathrm{G}$), $g_{\perp} = 2.0653$. The g values have the relationship: $g_{\parallel} > g_{\perp} > g_{\mathrm{e}}$, indicating that the 3d unpaired electron should occupy the $\mathrm{d}_{x^2-y^2}$ orbital [16].

The complex was separated in about 17% yield with another complex $\mathrm{Na_2[Cu(mal)_2]\cdot 2H_2O}$ [11] from the reaction system. We tried to increase the yield by changing reaction temperature, pH value and so on, but no product could be obtained.

Supplementary material

CCDC-252466 contains the supplementary crystallographic data for this article. Copies of the data can be obtained free of charge on application to the Cambridge Crystallographic Data Center (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (+44) 1223-336-033; Email: deposit@ccdc.cam.ac.uk].

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