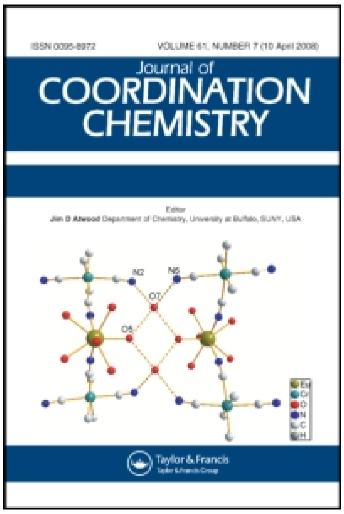

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Synthesis and crystal structure of a binuclear copper complex $[Cu_2(L)_2(Cl)_2]\cdot 2(C_3H_7NO)$, where $L = $ 1H-benzimidazol-2-yl-methanol

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The copper(II) compound, (**1**), $[Cu_2(L)_2(Cl)_2]\cdot 2(C_3H_7NO)$, $C_{22}H_{28}Cl_2Cu_2N_6O_4$ [where $HL = $ 1H-benzimidazol-2-yl-methanol, $C_3H_7NO = $ N,N′-dimethylformamide(DMF)], crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.363(2)$ Å, $b = 8.866(2)$ Å, $c = 9.327(3)$ Å, $\alpha = 91.415(5)$, $\beta = 93.924(5)$, $\gamma = 109.318(4)^\circ$ and $Z = 1$; R_1 for 2280 observed reflections $[I > 2\sigma(I)]$ was 0.0356. The centrosymmetric molecule comprises a pair of copper(II) atoms connected by two 1H-benzimidazol-2-yl-methanol ligands in *syn-syn* bridging mode. Four-coordination of copper(II) is further completed by chloride. The Cu^{II}–Cu^{II} distance and Cu–OR–Cu bond angle in **1** are 3.043(1) Å and 104.3(1)°, respectively.

Keywords: 1H-benzimidazol-2-yl-methanol; Binuclear copper; Crystal structure; Raman; IR spectrum

1. Introduction

Copper(II) complexes with organic acids and other donor ligands in living organisms play an important role in a vast range of chemical and biochemical catalytic systems [1]. Much attention has been paid to their role in structures and reaction mechanisms of metalloenzymes [2]. Numerous articles dealing with copper(II) carboxylate complexes have been published [3–5]; most of these complexes show a binuclear cage structure or a mononuclear square-based pyramidal structure [6, 7]. Binuclear copper(II) complexes are of interest as models for intramolecular magnetic exchange interactions between two metal centers in different structural motifs, *viz*. the ‘‘paddle-wheel’’ dicopper(II) tetracarboxylates, symmetrically dibridged hydroxo or alkoxo species, and asymmetrically dibridged complexes with a (l-hydroxo/alkoxo)(l-carboxylato) dicopper(II) core [8, 9]. Dicopper(II) complexes are also of importance as precursors in the chemistry of supramolecular and discrete high-nuclearity copper(II) complexes [10–12]. Herein, we constructed a binuclear copper complex with 1H-benzimidazol-2-yl-methanol.

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2. Experimental

All reagents were commercial grade materials and used without further purification. Elemental analysis (C, H, N) was performed by a PE 1700 CHN auto elemental analyzer. IR spectra were recorded on a Spectrum One Perkin-Elmer FT-IR spectrophotometer (KBr disc) in the range 4000–400 cm^{-1}. The crystal structure was determined by single-crystal diffraction using the SHELXL crystallographic software. The TG analysis was performed on TG209. Raman spectra were recorded on a Renishaw Plc Wotton under-edge UK (Single crystal sample) in the range 4000–50 cm^{-1}.

2.1. *Preparation of $[Cu_2(L)_2(Cl)_2]\cdot 2(C_3H_7NO)$*

The ligand (1H-benzimidazol-2-yl)-methanol (HL) was prepared according to a literature procedure [13].

A solution of HL (1 mmol, 0.148 g) in ethanol (10 mL) was added slowly to a solution of $CuCl_2 \cdot 2H_2O$ (1 mmol, 0.170 g) in ethanol (15 mL). The mixture was stirred for 30 min at room temperature. The solution was filtered and the precipitate was dissolved in DMF (20 mL) then filtered. The filtrate was left to stand at room temperature. Deep blue block crystals suitable for X-ray diffraction were obtained in a yield of 67% (based on copper). Elemental analysis found: C, 40.87; H, 4.68; N, 13.31%. Calcd: C, 41.38; H, 4.42; N, 13.16%. IR (cm^{-1}): 3273(s), 3057(m), 1663(w), 1639(w), 1529(w), 1445(s), 1309(w), 1082(s), 913(w), 730(s), 605(m), 493(w). Raman (cm^{-1}): 3061(w), 2836(w), 2822(w), 1560(s), 1257(s), 1030(m), 596(w), 423(w), 147(m) (s, strong; m, medium; w, weak).

2.2. *X-ray crystallography*

Intensity data for **1** was collected at 173 K on a Bruker SMART CCD area detector diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the ω–θ scan mode in the range $2.19 \leq \theta \leq 25.05°$. Raw frame data were integrated with the SAINT program [14]. The structure was solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXS-97 [15]. An empirical absorption correction was applied with the program SADABS [16]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined by a riding mode, with a common thermal parameter. All calculations and graphics were performed with SHELXTL [15]. Crystal data and details of the structure determination are given in table 1. Selected bond lengths and angles are given in table 2. Figure 1 illustrates the structure of the title compound.

3. Results and discussion

X-ray single-crystal diffraction reveals that **1** (deep blue blocks) crystallizes in the triclinic space group ($P\bar{1}$). As shown in figure 1, copper(II) is coordinated

Table 1. Crystal data and refinement details for **1**.

Formula	$C_{22}H_{28}Cl_2Cu_2N_6O$
CCDC deposit no.	655075
Formula weight	638.48
Temperature (K)	173(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	8.363(2)
b (Å)	8.866(2)
c (Å)	9.327(3)
a (°)	91.415(5)
β (°)	93.924(5)
γ (°)	109.318(4)
Z	1
Volume (Å^3)	650.3(3)
D_{calcd} (g cm^{-3})	1.630
Absorption coefficient (mm^{-1})	1.88
F(000)	326
Crystal size (mm^3)	$0.18 \times 0.26 \times 0.28$
θ_{min}, θ_{max} (deg)	2.19, 25.05
Index ranges	$-9 \leq h \leq 9$
	$-9 \leq k \leq 10$
	$-11 \leq l \leq 9$
Total data	4737
Total unique data	2280
Completeness $\theta = 25.05°$	99
Absorption correction	None
Max. and min. transmission	0.816, 0.526
Data/restraints/parameters	2280/0/165
Goodness-of-fit on F^2	1.099
Final R indices [$I > 2\sigma$(I)]	0.0356
R indices (all data)	0.0850
Largest diff. peak and hole (e Å^{-3})	0.416, −0.371

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Cu1–O1	1.948(2)	Cu1–O1^a	1.907(2)
Cu1–N1	1.950(3)	Cu1–Cl	2.205(1)
Cu1–Cu1^a	3.044(1)		
O1–Cu1–O1^a	75.7(1)	O1–Cu1–N1^a	156.7(1)
O1–Cu1–N1	82.2(1)	O1–Cu1–Cl^a	98.9(1)
O1–Cu1–Cl	168.9(1)	N1–Cu1–Cl	104.1(1)

Symmetry code, a: $1-x$, $-y$, $1-z$.

by a 1,4-dichelate of L^{-1}; it is also linked to one oxygen of another L^{-1}. The four-coordinate geometry is completed by chloride (Cu1–N1, 1.950(3) Å; Cu1–O1, 1.948(3) Å, Cu1–Cl, 2.205(1) and Cu1–O1^a, 1.907(3) Å, symmetry code: a: $1-x$, $-y$, $1-z$). Each pair of Cu(II) ions is bridged by a pair of *syn-syn* phenolato oxygens of L^{-1} into a dimer with an intramolecular Cu ··· Cu distance of 3.043(1) Å, which is longer than copper ··· copper distances in the dimeric copper(II) carboxylates (2.59–2.747 Å) [17] and shorter than the copper ··· copper distances in a dimeric copper(II) complex (3.472(1) Å) [18]. The dimeric complex further constructed a 1-D supramolecular network through C–H ··· Cu^i (H ··· Cu^i distance is 3.153(1) Å, symmetry code: i, $1+x$, y, z) interaction (figure 2).

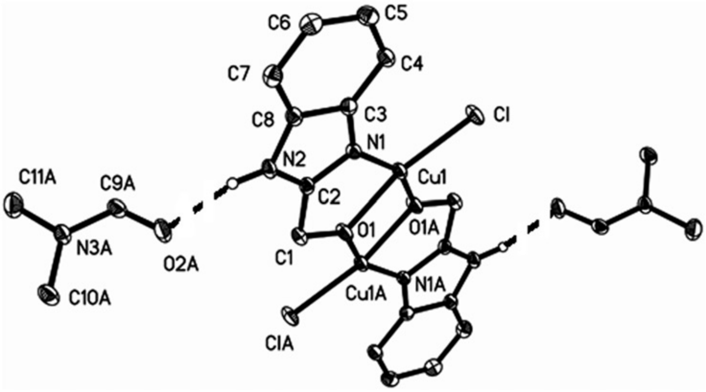

Figure 1. Molecular structure of **1**; non hydrogen bonding hydrogen atoms have been omitted.

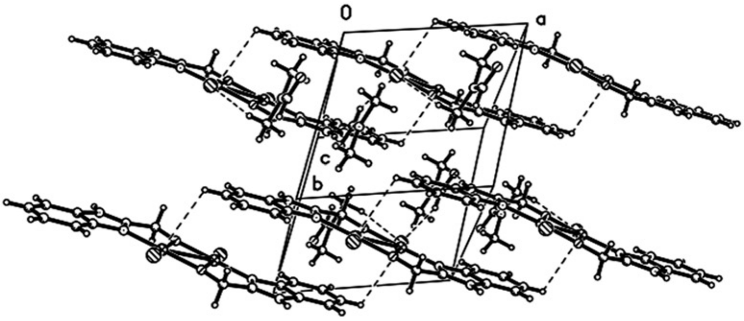

Figure 2. Packing **1**.

3.1. *IR spectrum*

The IR spectrum of **1** (figure 3 supplemental material) shows a medium shoulder at 1663 cm^{-1} assigned to C=O from DMF; the strong band located at 1082 cm^{-1} is assigned to C–O from L^{-1}; the associated NH stretching at 3273 cm^{-1} can be attributed to L^{-1} [19]; the shoulder at 3057 cm^{-1} was assigned to CH aromatic or heterocyclic vibrations. At lower frequencies, four characteristic absorptions at 1529, 1447 cm^{-1} (C=C and C=N vibrations [20]), 913 and 730 (out-of-plane CH in center ring or heterocyclic ring, respectively [21]) were observed. At very low frequencies (500–450 cm^{-1}), a weak band at 493 cm^{-1} is observed from Cu–N [22]; bands from Cu–N and Cu–O stretching vibrations are usually observed around or below 400 cm^{-1} [22].

3.2. *Raman spectrum*

Raman spectrum of **1** (figure 3 supplemental material) shows a medium strong band at 1560 cm^{-1} is assigned to C=O from DMF, the strong band at 1030 cm^{-1} to C–O from L^{-1}, the associated NH stretching at 3061 cm^{-1} to L^{-1}, and the bands at 423 and 596 cm^{-1} to bending and symmetric stretching of the framework Cu–O–Cu species, respectively [22]. The relatively strong υ(Cu–Cl) is observed at 147 cm^{-1} in the

Raman spectrum [23]. Very weak bands at 2822 and 2836 cm^{-1} from C–H bonds are observed in the Raman spectrum [24].

3.3. *Thermal decomposition*

The TG–DTG curve (figure 4 supplemental material) was obtained using a NETZSCH TG209 thermal analyzer. The heating rate was 10°C min^{-1} and the air flow rate was 20 mL min^{-1}. The TG–DTG thermogram of **1** revealed that decomposition takes place in two steps, the first stage mass loss is 23.4% between 78 and 140°C, calculated value (22.87%), for loss of two molecules of DMF from the complex. In the second stage, $Cu_2(L)_2$ began decomposing at 230°C.

Supplementary data

Crystallographic data for the title complex in the CIF format have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 655075. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-366-033; Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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