

# Synthesis and Structural Characterization of the Mixed Ligand Complex $[\text{Cu}(\text{HmL})_2(\text{phen})] \cdot 2 \text{H}_2\text{O}$ ( $\text{H}_2\text{mL} = 2\text{-Methyl-lactic Acid}$ )

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A new mixed-ligand complex of copper(II) with 1,10-phenanthroline and 2-methylactate was prepared.  $[\text{Cu}(\text{HmL})_2(\text{phen})] \cdot 2\text{H}_2\text{O}$  (where  $\text{HmL} = \text{monodeprotonated 2-methyl-lactic acid}$ ) was characterized by elemental analysis, IR, electronic and EPR spectroscopy, magnetic measurements at room temperature, thermogravimetric analysis and X-ray diffractometry. The copper atom is in a tetragonally distorted octahedral environment and the 2-methylactate ligand is bidentately chelating. The presence of lattice water molecules mediates the formation of a three-dimensional network.

**Key words:** Copper(II), 2-Methyl-lactic Acid, Phenanthroline

## Introduction

$\alpha$ -Hydroxycarboxylic acids are ubiquitous in living organisms and play an important role in many biological processes such as vanadium and iron metabolism [1]. Also, mixed-ligand complexes play key roles in some biological processes [2]. With a view to the possible advantages of combining in mixed-ligand complexes a bioactive divalent metal cation such as copper(II), an  $\alpha$ -hydroxycarboxylate anion and an aromatic diamine, we have previously reported on investigations of copper(II) /  $\alpha$ -hydroxycarboxylate / 1,10-phenanthroline systems [3]. So, we have prepared and spectroscopically characterized the compounds of the formula  $[\text{Cu}(\text{HL})_2(\text{phen})] \cdot n\text{H}_2\text{O}$ , where  $\text{HL} = \text{glycolato (Hglyo)}, \text{lactato (Hlaco)}, \text{mandelato (Hmano)} \text{ or } \text{benzylato (Hbeno)}$ . Attempts to obtain single crystals suitable for X-ray diffractometry of these compounds led to the crystallization and diffractometric study of the following pentacoordinated copper(II) complexes:  $[\text{Cu}(\text{laco})(\text{phen})(\text{OH}_2)] \cdot 4 \text{H}_2\text{O}$  and  $[\text{Cu}(\text{beno})(\text{phen})(\text{OH}_2)] \cdot 2\text{H}_2\text{O}$ , where the  $\alpha$ -hydroxycarboxylic acid is a bidentate dianion, as well as  $[\text{Cu}(\text{Hglyo})(\text{phen})_2](\text{Hglyo}) \cdot \text{H}_2\text{glyo} \cdot \text{CH}_3\text{CN}$  and  $[\text{Cu}(\text{Hmano})(\text{phen})_2](\text{Hmano}) \cdot \text{H}_2\text{mano}$ , where there are three different types of  $\alpha$ -hydroxycarboxylic

acid molecules: one acting as a monodentate monoanion, one as a monoanionic counterion, and one as a neutral molecule lying in the outer coordination sphere [3]. In this paper we describe the synthesis, physical properties and crystal structure of a new mixed-ligand complex of copper(II) with 1,10-phenanthroline and the  $\alpha$ -hydroxycarboxylic acid, 2-methyl-lactic acid ( $\text{H}_2\text{mL}$ ). This compound is the first hexacoordinated copper(II) complex in the copper(II) / 1,10-phenanthroline /  $\alpha$ -hydroxycarboxylate system which could be characterized by X-ray diffractometry.

## Experimental Section

Chemicals were obtained from commercial sources and used without further purification. Elemental analysis (C, H, N) was performed with a FISON EA-1108 microanalyser. Melting points (m. p.) were measured in a Gallenkamp MBF-595 apparatus. The FT-IR spectrum of the sample incorporated in KBr discs ( $4000\text{--}400 \text{ cm}^{-1}$ ) was recorded on a Bruker VECTOR 22 spectrometer. A Shimadzu UV-3101PC spectrophotometer was used to obtain the electronic spectrum in the region  $900\text{--}350 \text{ nm}$ . Magnetic susceptibility measurements were made at room temperature using a Johnson Matthey Magnetic Susceptibility Balance. The X-band

(9300 MHz) EPR spectrum was obtained at room temperature with a Bruker ESP 300E spectrometer. The thermogravimetric analysis was performed on a Shimadzu TGA-DGT-50H instrument coupled to a Nicolet Magma 550 FT-IR spectrophotometer.

#### Preparation of [Cu(HmL)<sub>2</sub>(phen)] · 2 H<sub>2</sub>O (**1**)

A mixture of CuCO<sub>3</sub>·Cu(OH)<sub>2</sub> (0.30 mmol), 2-methylactic acid (1.00 mmol) and 1,10-phenanthroline (0.50 mmol) in 20 ml EtOH and 5 ml CH<sub>2</sub>Cl<sub>2</sub> was stirred at room temperature for 5 d. The excess of CuCO<sub>3</sub>·Cu(OH)<sub>2</sub> was filtered and the resulting blue solution was left standing in air. The blue oil obtained was dissolved in a mixture MeOH/<sup>i</sup>PrOH (1:1) and slow evaporation of this solution yielded blue single crystals of **1**. Yield: 70%.

M. p.: 195 °C. – UV/vis (solid state):  $\nu$  = 13300 cm<sup>-1</sup>. – IR (pellet)  $\nu$  = 3418s, 3207m (OH); 1657sh (CC); 1589s (OCO); 1360s (OCO); 1519m, 1428m (CC, CN); ring breathing = 1051w,  $\gamma$  = 726m (CH). – C<sub>20</sub>H<sub>26</sub>O<sub>8</sub>N<sub>2</sub>Cu (485.97): calcd. C 49.4, H 5.4, N 5.8; found C 49.4, H 5.4, N 5.7%.

#### X-ray crystallography

Crystallographic data were collected at 293 K using graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) on a Bruker SMART CCD diffractometer. The data were corrected for absorption using the SADABS program of the SAINT software package [4]. The structure was solved by direct methods using the program SHELXS97 [5]. All non-hydrogen atoms were refined with anisotropic thermal parameters by full matrix least-squares calculations on F<sup>2</sup> using the program SHELXL97 [6]. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters, except those of the hydroxyl groups and water molecules, which were located from a Fourier-difference map and refined with the restrain DFIX 0.9. Drawings were produced with PLATON [7] and SCHAKAL [8]. Crystal data and structure refinement parameters are listed in Table 1. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication CCDC 194820. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax, +44-1223/336-033; E-mail, deposit@ccdc.cam.ac.uk).

## Results and Discussion

Reaction at room temperature between copper(II) hydroxidecarbonate and 2-methylactic acid in the presence of the chelating agent 1,10-phenanthroline resulted in the deprotonation of the acid and the coordination of the diamine.

Table 1. Crystal and structure refinement data.

Empirical formula	C <sub>20</sub> H <sub>26</sub> N <sub>2</sub> O <sub>8</sub> Cu
Formula weight	485.97
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	
<i>a</i> (Å)	29.437(4)
<i>b</i> (Å)	10.2477(14)
<i>c</i> (Å)	24.223(3)
$\beta$ (°)	111.758(3)
<i>V</i> (Å <sup>3</sup> )	6786.5(16)
<i>Z</i>	12
$\rho_{\text{calc}}$ (g·cm <sup>-3</sup> )	1.427
Absorption coeff. (mm <sup>-1</sup> )	1.012
<i>F</i> (000)	3036
Crystal size (mm <sup>3</sup> )	0.40 × 0.10 × 0.06
$\theta$ Range (°)	1.81 – 28.04
Index ranges	–38 ≤ <i>h</i> ≤ 34, –13 ≤ <i>k</i> ≤ 12, –31 ≤ <i>l</i> ≤ 31
Reflections collected	18260
Independent reflections	7590 [ <i>R</i> <sub>int</sub> = 0.0663]
Absorption correction	SADABS
Max/min transmission	1.0000/0.5775
Data/parameters	7590/462
Final <i>R</i> indices [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0464; <i>wR</i> <sub>2</sub> = 0.0933

The IR spectrum of the product **1** shows two bands in the 3000–3500 cm<sup>-1</sup> region corresponding to the OH stretching vibrations of ligands and water of crystallization. The strong band at 1589 cm<sup>-1</sup> is attributable to  $\nu_{\text{asym}}(\text{OCO})$  and the band at 1360 cm<sup>-1</sup> to  $\nu_{\text{sym}}(\text{OCO})$ . The  $\Delta\nu = \nu_{\text{asym}}(\text{OCO}) - \nu_{\text{sym}}(\text{OCO})$  value of 229 cm<sup>-1</sup> is typical of monodentate carboxylato ligands [9] and also very similar to data found for other copper(II)/ $\alpha$ -hydroxycarboxylato/1,10-phenanthroline complexes [3].

The electronic spectrum obtained by diffuse reflectance shows a d-d band centred at 13300 cm<sup>-1</sup> in the range found for octahedral copper(II) complexes with a tetragonal distortion [10]. The EPR spectrum is isotropic with a *g* value of 2.09.

The magnetic moment at room temperature is only 1.52 B.M., suggesting some antiferromagnetic coupling between the metal centres [11], although similar low magnetic moments are also observed in complexes of Cu(II) with 1,10-phenanthroline and glycolic or mandelic acid in which there is no antiferromagnetic coupling [3].

The thermogravimetric analysis shows that weakly bound water is largely lost during stabilization of the balance. Decomposition of the 2-methylactato ligand begins at 120 °C and continues up to 225 °C. The next mass loss (at 225–300 °C) corresponds to the loss of

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

Cu1-O11	1.964(2)	Cu1-N1	2.018(3)
Cu1-O13	2.286(3)		
Cu2-O31	1.956(2)	Cu2-O21	1.982(2)
Cu2-N2	2.011(3)	Cu2-N3	2.024(3)
Cu2-O23	2.246(3)	Cu2-O33	2.259(3)
O11-Cu1-O11 <sup>i</sup>	94.96(15)	O11-Cu1-N1 <sup>i</sup>	169.52(12)
O11-Cu1-N1	92.29(13)	N1-Cu1-N1 <sup>i</sup>	81.6(2)
O11-Cu1-O13	74.70(10)	N1-Cu1-O13	89.08(11)
O11-Cu1-O13 <sup>i</sup>	100.13(10)	N1-Cu1-O13 <sup>i</sup>	96.59(11)
O13-Cu1-O13 <sup>i</sup>	172.53(14)		
O31-Cu2-O21	95.37(10)	O31-Cu2-N2	167.12(12)
O21-Cu2-N2	93.57(12)	O31-Cu2-N3	93.17(12)
O21-Cu2-N3	163.88(12)	N2-Cu2-N3	80.47(13)
O31-Cu2-O23	98.20(11)	O21-Cu2-O23	75.30(10)
N2-Cu2-O23	93.02(11)	N3-Cu2-O23	89.98(11)
O31-Cu2-O33	76.16(10)	O21-Cu2-O33	95.98(10)
N2-Cu2-O33	93.72(11)	N3-Cu2-O33	99.33(11)
O23-Cu2-O33	169.29(10)		

Symmetry transformations: i = -x, y, -z + 1/2.

Table 3. Main hydrogen bonds.

D-H...A	d(D-H) /Å	d(H...A) /Å	d(D...A) /Å	<(DHA) /°
O13-H13...O2w <sup>i</sup>	0.859(18)	1.790(19)	2.645(4)	173(4)
O23-H23...O3w <sup>iii</sup>	0.879(18)	1.81(2)	2.669(4)	166(4)
O33-H33...O1w	0.858(18)	1.84(2)	2.682(4)	168(4)
O1w-H1wA...O12	0.843(18)	2.04(2)	2.855(4)	163(4)
O1w-H1wB...O32 <sup>iii</sup>	0.894(19)	1.86(2)	2.751(4)	178(5)
O2w-H2wA...O22	0.867(18)	1.90(2)	2.740(4)	163(4)
O2w-H2wB...O22 <sup>iv</sup>	0.847(18)	1.952(19)	2.798(4)	176(4)
O3w-H3wA...O32 <sup>v</sup>	0.863(19)	1.98(3)	2.796(4)	158(5)
O3w-H3wB...O12 <sup>vi</sup>	0.841(19)	1.92(2)	2.751(4)	167(4)

Symmetry transformations: i = -x, y, -z + 1/2; ii = x, -y + 1, z - 1/2; iii = -x + 1/2, y + 1/2, -z + 1/2; iv = -x, -y + 1, -z; v = -x + 1/2, y - 1/2, -z + 1/2; vi = x, y - 1, z.

phenanthroline. The final observed weight, 14.9%, is close to that expected for CuO (16.4%).

### Crystal Structure

Table 2 lists selected bond lengths and bond angles, and Table 3 the main hydrogen bonds. Figure 1 shows the molecular structure together with the atom-numbering scheme used.

The structure is based on neutral molecules [Cu(HmL)<sub>2</sub>(phen)], where HmL is a monoanionic O,O'-bidentate 2-methylactato ligand. The copper ions are six-coordinate, being bound to the nitrogen atoms of the 1,10-phenanthroline molecule and to one carboxylate and one hydroxyl oxygen of each of the two 2-methylactato anions. There are thus three five-membered chelate rings. The asymmetric unit con-

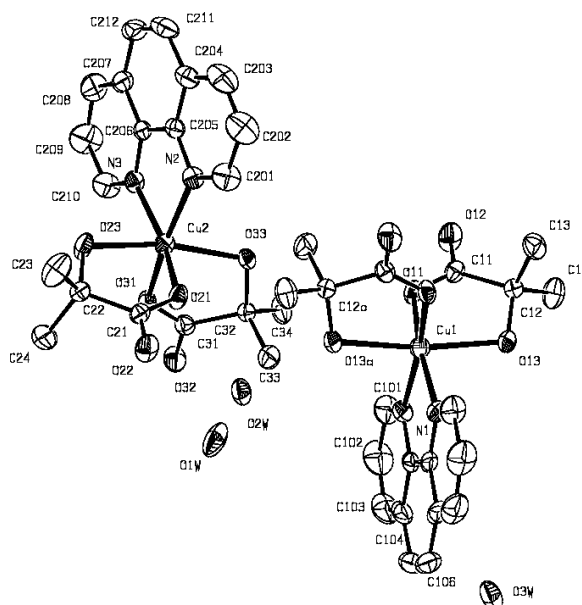


Fig. 1. Molecular structure of [Cu(HmL)<sub>2</sub>(phen)] · 2 H<sub>2</sub>O. Ellipsoids are at the 30% probability, hydrogen atoms are omitted for clarity.

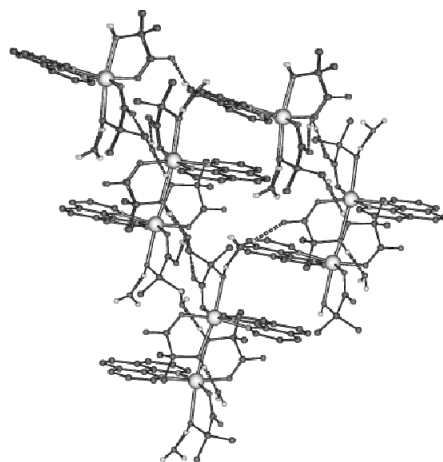


Fig. 2. A view of the three-dimensional hydrogen bond network. (Hydrogen bonds are represented by dashed lines).

tains both enantiomers, one of them (Cu1) located on a twofold axis (e position in the Wyckoff notation). Each copper atom has an elongated octahedral geometry with the two nitrogen atoms and the mutually *cis* O<sub>carboxylate</sub> atoms equatorial and the two α-hydroxyl oxygen atoms axial, the difference between the average equatorial and axial bond lengths being 0.295 and 0.259 Å for the molecule 1 (Cu1) and 2

(Cu2), respectively. Additional deviation from ideal octahedral geometry is shown by the chelating angles ranging from 74.70–81.6° (Table 2) and by some of the *trans* angles, such as O<sub>hydroxyl</sub>–Cu–O<sub>hydroxyl</sub> [172.53(14) and 169.29(10)°]. The Cu–O<sub>carboxylate</sub> distances (between 1.956 and 1.982 Å) are in concordance with the values observed in pentacoordinate copper(II) complexes with 1,10-phenanthroline and other  $\alpha$ -hydroxycarboxylato ligands (bidentate dianions or monodentate monoanions) [3]. Also, the Cu–N distances, 2.011–2.024 Å, are within the normal range for copper(II) complexes with N,N-chelating ligands [3,12]. The Cu–O<sub>hydroxyl</sub> distances (between 2.246 and 2.286 Å) are shorter than in octahedral polymeric copper(II) complexes with 4,4'-bipyridine and lactato or 2-methylactato ligands [13]. The C–O bond lengths of the coordinated carboxylato oxygen atoms [1.257(4) and 1.254(4) Å] are only slightly longer than those of the uncoordinated oxygen atoms [1.234(4) and 1.237(4) Å], which suggests that there is significant electron delocalization in the carboxylato groups.

The nature of the  $\alpha$ -hydroxycarboxylato ligand and the presence of solvated water molecules permit the formation of a supramolecular architecture based on hydrogen bonding. The 2-methylactato ligand and the water molecules act as both hydrogen donors and hydrogen acceptors and the result is a three-dimensional network (Figure 2). Each water molecule accepts the hydroxyl hydrogen of one 2-methylactato ion, and donates hydrogens to the uncoordinated carboxylato oxygen atoms of neighbouring molecules. The strongest hydrogen bonds are those of the O<sub>hydroxyl</sub>...O<sub>w</sub> type with distances and angles in the ranges 2.645–2.682 Å and 168–173°, respectively (Table 3). The O<sub>w</sub>...O<sub>carboxylate</sub> hydrogen bond distances and angles are in the ranges 2.740–2.855 Å and 158–178°, respectively (Table 3).

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