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# Solid state coordination chemistry of copper(II)/\alpha-hydroxycarboxylato/2,2'-bipyridine systems

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#### Abstract

Four new two-ligand complexes of copper(II) with 2,2'-bipyridine and one of three different  $\alpha$ -hydroxycarboxylic acids (lactic, H<sub>2</sub>LACO; 2-methyllactic, H<sub>2</sub>MLACO; and mandelic, H<sub>2</sub>MANO) were prepared. Complexes 1–3 of general formula [Cu(HL)<sub>2</sub>(bipy)]·*n*H<sub>2</sub>O (HL = monodeprotonated acid), were characterized by elemental analysis, IR, electronic and EPR spectroscopy, magnetic measurements and thermogravimetric analysis. Complexes 1 (HL = HLACO, *n* = 2), 2 (HL = HMLACO, *n* = 1) and **3a** (the result of attempted recrystallization of **3**, of formula [Cu(HMANO)(bipy)<sub>2</sub>](HMANO)·H<sub>2</sub>MANO·CH<sub>3</sub>CN were studied by X-ray diffractometry. The copper atom is in an elongated, tetragonally distorted octahedral environment in 1 and 2 and in **3a** has a coordination polyhedron intermediate between a square pyramid and a trigonal bipyramid, as evaluated in terms of the parameter  $\tau$ . In 1 and 2 the  $\alpha$ -hydroxycarboxylato ligand is bidentate and monoanionic but in **3a** there are three forms: a monodentate monoanion, a monoanionic counterion, and a neutral molecule.

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# 1. Introduction

Copper complexes of certain organic acids have biocatalytic activity [1,2].  $\alpha$ -Hydroxycarboxylic acids are involved in a variety of biochemical processes, including vanadium and iron metabolism [3], and are frequently used in pharmaceutical formulations both as excipients and as part of the active principle (lactate, for example, is used for administering bactericidal Bi<sup>III</sup> [4] and for experimental administration of Al<sup>III</sup> to laboratory animals [5]; and the anticancer agents nedaplatin and lobaplatin are mixed-ligand complexes of amines and Pt<sup>II</sup> with glycollate and lactate, respectively [6]. 2,2'-Bipyridine has been reported to form stable mixed complexes with metals and other ligands in solution

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[7], and its aromatic rings make it possible for stacking interactions to stabilize crystals of its complexes. In this paper we describe the synthesis, physical properties and crystal structures of mixed complexes of copper(II) with 2,2'-bipyridine and one of three  $\alpha$ -hydroxycarboxylic acids of differing bulks: lactic acid (H<sub>2</sub>LACO), 2-methyllactic acid (H<sub>2</sub>MLACO) and mandelic acid (H<sub>2</sub>MANO).

# 2. Results and discussion

Reaction of copper(II) hydroxycarbonate with the  $\alpha$ hydroxycarboxylic acids and 2,2'-bipyridine in ethanol afforded powdery blue solids with analytical data corresponding to the general formula [Cu(HL)<sub>2</sub>(bipy)].nH<sub>2</sub>O, where HL = HLACO (1), HMLACO (2) or HMANO (3). These compounds are stable in air, have melting points in the range 190–210 °C, and in general are poorly soluble in both polar and apolar solvents. An

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Table 1				
Crystal	and	structure	refinement	data

Compound	1 (−65 °C)	1 (20 °C)	2	<b>3a</b> (-50 °C)	<b>3a</b> (20 °C)
Empirical formula	$C_{16}H_{22}N_2O_8Cu$	$C_{16}H_{22}N_2O_8Cu$	$C_{18}H_{24}N_2O_7Cu$	C <sub>46</sub> H <sub>41</sub> N <sub>5</sub> O <sub>9</sub> Cu	$C_{46}H_{41}N_5O_9Cu$
Formula weight	433.90	433.90	443.93	871.38	871.38
T (K)	208(2)	293(2)	293(2)	223(2)	293(2)
Crystal system	triclinic	triclinic	tetragonal	monoclinic	monoclinic
Space group	<i>P</i> 1 (no. 2)	<i>P</i> 1 (no. 2)	$I4_1/a$ (no. 88)	<i>Cc</i> (no. 9)	<i>Cc</i> (no. 9)
Unit cell dimensions					
a (Å)	7.9796(12)	8.0143(9)	30.6801(15)	19.9376(11)	19.969(4)
b (Å)	8.6175(17)	8.6833(10)	30.6801(15)	14.6957(11)	14.752(2)
c (Å)	14.639(2)	14.7608(17)	9.9339(6)	15.1213(7)	15.129(2)
α (°)	73.64(2)	73.371(2)	90.00	90.00	90.00
β (°)	84.728(15)	84.341(2)	90.00	109.281(6)	109.393(6)
γ (°)	73.005(13)	72.445(2)	90.00	90.00	90.00
$V(Å^3)$	923.7(3)	938.33(19)	9350.5(9)	4182.0(4)	4203.8(11)
Ζ	2	2	16	4	4
$\rho_{\rm calc} ({\rm g} {\rm cm}^{-3})$	1.560	1.536	1.261	1.384	1.377
Abs. coeff. $(mm^{-1})$	1.229	1.210	0.970	0.586	1.259
F(000)	450	450	3693	1812	1812
Crystal size (mm)	$0.45 \times 0.30 \times 0.25$	$0.39\times0.18\times0.07$	$0.63 \times 0.14 \times 0.12$	$0.25\times0.10\times0.10$	$0.28\times0.28\times0.16$
$\theta$ Range (°)	3.02-30.92	1.44-23.20	1.33-28.03	2.48-25.78	3.81-70.00
Index ranges	$-1 \le h \le 11$ ,	$-8 \le h \le 4$ ,	$-25 \le h \le 40$ ,	$-24 \le h \le 21$ ,	$-24 \le h \le 0$ ,
e	$-12 \le k \le 12$ ,	$-9 \leq k \leq 9$ ,	$-39 \le k \le 40$ ,	$-17 \le k \le 17$ ,	$0 \le k \le 17$ ,
	$-21 \le l \le 12$	$-16 \le l \le 16$	$-12 \le l \le 13$	$-17 \le l \le 16$	$-17 \le l \le 18$
Reflections collected	6092	4195	25973	12845	4104
Independent reflections	5293 [ $R_{\rm int} = 0.050$ ]	2688 [ $R_{\rm int} = 0.060$ ]	5600 $[R_{int} = 0.087]$	6466 [ $R_{\rm int} = 0.038$ ]	4104 [ $R_{\rm int} = 0.000$ ]
Absorption correction	$\Psi$ -scans	SADABS	SADABS	$\Psi$ -scans	Ψ-scans
Max/min transmission	0.915/0.875	1.000/0.657	1.000/0.786	0.944/0.867	0.824/0.719
Data/ parameters	5293/244	2688/252	5600/257	6466/665	4104/551
Goodness-of-fit	0.994	0.973	0.973	0.970	1.017
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0493,$ $wR_2 = 0.1230$	$R_1 = 0.0515,$ $wR_2 = 0.1244$	$R_1 = 0.0639,$ $wR_2 = 0.1898$	$R_1 = 0.0427,$ $wR_2 = 0.0912$	$R_1 = 0.0402,$ $wR_2 = 0.102$

attempt to recrystallize **3** from  $CH_3CN$ , afforded single crystals of a compound of formula [Cu(HMANO)-(bipy)<sub>2</sub>](HMANO)·H<sub>2</sub>MANO·CH<sub>3</sub>CN (**3a**).

In the 3000–3500 cm<sup>-1</sup> region, the IR spectra of **1–3** show two bands, generally of medium intensity, corresponding to OH stretching vibrations. The strong band around 1590 cm<sup>-1</sup> is attributable to  $v_{asym}$ (OCO), and the band between 1330 and 1390 cm<sup>-1</sup> to  $v_{sym}$ (OCO). The values of  $\Delta v = v_{asym}$ (OCO)– $v_{sym}$ (OCO), 209–258 cm<sup>-1</sup>, are typical of monodentate carboxylato groups [8] and very similar to those found in copper(II)/ $\alpha$ -hydroxycarboxylato/1,10-phenanthroline systems [9]. The bands around 1490 and 1450 cm<sup>-1</sup> are due to the C=C and C=N stretching modes of the coordinated 2,2'-bipyridine molecules. A weak band around 400 cm<sup>-1</sup> is assignable to v(CuO), and the band between

250 and 300 cm<sup>-1</sup> is tentatively identified as due to v(CuN) [10].

The three compounds have similar diffuse reflectance spectra (Table 2). They consist of an intense charge transfer band between 26600 and 28600 cm<sup>-1</sup> together with a broad d-d band centred at wavenumbers typical of octahedral copper(II) complexes with tetragonal distortion, 14200–12800 cm<sup>-1</sup> [11].

Table 2 UV–Vis spectra, EPR and magnetic moment data for complexes 1-3

Complex	UV–Vis (cm <sup>-1</sup> )	$G_{  }$	$g_{\perp}$	$g_{\rm av.}$	$\mu_{\rm eff}$ (BM)
1	26 600, 14 200	2.29		2.06	1.47
2	27 030, 12 850	2.30	2.04	2.08	1.67
3	28 570, 12 800	2.25	2.03	2.09	1.56

The magnetic moments of **1** and **3** fall as temperatures rises. At room temperature  $\mu_{eff}$  is only 1.47 BM for **1**, 1.67 BM for **2** and 1.56 BM for **3**. Such low values suggest the possibility of antiferromagnetic coupling between metal centres [12,13], although low magnetic moments are also displayed by mixed complexes of Cu<sup>II</sup> with 1,10-phenanthroline and glycolic or mandelic acid in which there is no antiferromagnetic coupling [9]. At low temperatures (79–200 K for **1** and 79–250 K for **3**), the magnetic moments are within the range reported for copper(II) complexes lacking Cu–Cu interaction, 1.7– 2.2 BM [14].

The room temperature EPR spectrum of polycrystalline 1 (Table 2) is typical of axially symmetric coordination, with  $g_{||} > g_{\perp}$ . The symmetry of the copper atom is thus approximately  $C_{4v}$ , and the unpaired electron occupies a  $3dx^2 - y^2$  orbital. The value of 2.29 for g suggests octahedral coordination with a tetragonal distortion [12,15]. Similar spectra are displayed by complexes of copper(II) with  $\alpha$ -hydroxycarboxylato ligands and 1,10-phenanthroline [9]. The EPR spectra of 2 and 3 (Table 2) are typical of rhombic systems with g values consistent with compressed rhombic-octahedral or *cis*-distorted octahedral stereochemystries [15].

The thermogravimetric behaviour of compounds 1 and 3 (Table 3) is similar to that of mixed complexes containing 1,10-phenanthroline and  $\alpha$ -hydroxycarboxylato ligands [9]. Weakly bound lattice water is largely lost during stabilization of the balance. Decomposition of the ligands begins at 200 °C and in the case of 3 continues up to 400 °C. In 1, ligand decomposition over the range 200–250 °C, is followed by a stable region up to 400 °C and by further weight loss between 400 and 450 °C. For 2, one water molecule is lost between 75 and 150 °C, and the ligands decompose over the range 150– 225 °C. No further weight loss was suffered by any of the compounds. The ratios of final to initial weights

Table 3 Thermogravimetric analyses for the complexes 1-3

Compound	Temperature range (°C)	% Weight loss	Corresponding to
1	RT-200	stable	
	200-250	76.22	bipy+HLACO
	250-400	stable	
	400-450	4.25	
	450-600	stable	
2	RT-75	stable	
	75-150	6.06	1 H <sub>2</sub> O
	150-225	76.82	bipy+HMLACO
	225-700	stable	
3	RT-200	stable	
	200-225	70.80	bipy+HMANO
	225-300	6.12	
	300-400	5.20	
	400-600	stable	

(19.48% for 1, 16.41% for 2 and 17.77% for 3) approximated the values expected for CuO (20.51\% for 1, 17.91\% for 2 and 15.24\% for 3).

# 3. Structural analysis

Selected interatomic distances and angles are listed in Table 4, and the main hydrogen bonds in Table 5. Figs. 1-3 show drawings of the structures of compounds 1, 2 and 3a, respectively, together with the atom-numbering schemes used.

The structure of 1 and 3a are essentially the same at  $-65 \,^{\circ}C(1)$  or  $-50 \,^{\circ}C(3a)$  as at 20  $^{\circ}C$ , the only marginally significant differences being that at room temperature the unit cell volume is slightly greater and the axes slightly longer (Table 1). In what follows, the bond lenghts and angles cited (Table 4) are the values measured at low temperature.

The crystals of 1 and 2 are based on neutral complexes of the form  $[Cu(HL)_2(2,2'-bipy)] \cdot nH_2O$ , where HL is a monoanionic O,O'-bidentate  $\alpha$ -hydroxycarboxylato li-

Table 4

Selected interatomic bond lengths (Å) and bond angles (°) for complexes  $1{-}3$ 

	1	2	3a
Bond lengths			
Cu-O11	1.963(2)	1.956(4)	2.047(3)
Cu-O21	1.969(2)	1.952(4)	
Cu-N1	2.013(3)	2.015(4)	1.988(4)
Cu-N2	2.001(3)	1.995(4)	2.057(4)
Cu-N3			2.157(4)
Cu-N4			2.003(4)
Cu-O13	2.384(3)	2.291(4)	
Cu-O23	2.302(2)	2.310(4)	
Bond angles			
O11-Cu-O21	93.06(11)	91.72(18)	
O11-Cu-N2	93.23(11)	93.27(18)	147.94(14)
O21-Cu-N2	168.54(11)	166.69(18)	
O11-Cu-N1	168.81(11)	166.48(18)	91.97(15)
O21-Cu-N1	94.47(10)	96.57(18)	
N2-Cu-N1	80.80(11)	81.01(18)	80.80(18)
O11-Cu-O23	94.47(10)	99.76(15)	
O21-Cu-O23	74.92(9)	76.10(15)	
N2-Cu-O23	95.04(10)	90.88(15)	
N1-Cu-O23	95.48(9)	92.61(16)	
O11-Cu-O13	75.03(9)	75.90(15)	
O21-Cu-O13	87.59(10)	98.47(17)	
N2-Cu-O13	103.30(10)	94.72(16)	
N1-Cu-O13	97.02(9)	92.28(16)	
O23-Cu-O13	159.21(8)	173.08(13)	
N3-Cu-N1			99.27(16)
N4-Cu-N1			177.28(13)
N3-Cu-N2			113.63(11)
N4-Cu-N2			97.68(17)
N3-Cu-O11			98.32(14)
N4-Cu-O11			90.50(14)
N4-Cu-N3			79.23(17)

Table 5 Main hydrogen bonds in the complexes 1-3

$D - H \cdots A$	d(D–H) (Å)	$d(\mathbf{H} \cdot \cdot \cdot \mathbf{A})$ (Å)	$d(\mathbf{D}\cdots\mathbf{A})$ (Å)	∠ (DHA) (°)
Compound 1 <sup>a</sup>				
O13-H13···O2	0.62	2.16	2.766(4)	164.2
O23-H23···O1	0.68	1.99	2.643(3)	160.5
$O1\!-\!H1A\!\cdots\!O12^i$	0.88	1.90	2.748(4)	162.0
01-	0.96	1.85	2.779(3)	162.1
$H1B \cdot \cdot \cdot O12^{ii}$				
$O2{-}H2A{\cdots}O2^{iii}$	0.91	1.91	2.794(7)	164.5
O2-	1.09	1.90	2.993(4)	178.2
$H2B \cdot \cdot \cdot O22^{iii}$				
C10-H10···O11	0.97	2.41	3.033(4)	121.4
$C3-H3\cdots O22^{iv}$	0.84	2.58	3.338(4)	150.9
$C7-H7\cdots O22^v$	0.80	2.55	3.307(5)	157.8
$C9-H9\cdots O12^{vi}$	0.88	2.73	3.335(5)	127.1
Compound $2^{b}$				
O13-	0.94(6)	1.72(6)	2.657(6)	173(5)
$H13 \cdots O22^{i}$				
$O23-23 \cdot \cdot \cdot O12^{ii}$	0.93	2.06	2.721(5)	126.8
O22···O1			2.958(8)	
$O1 \cdots O1^{i}$			3.086(5)	
C7-H7···O12 <sup>iii</sup>	0.93	2.33	3.256(7)	173.2
C10-H10···O11	0.93	2.53	3.023(7)	113.7
Compound <b>3a</b> °				
O21-	1.25	1.23	2.437(4)	159.2
$H21A \cdots O31^{i}$				
O13-	1.43	1.39	2.765 (7)	157.7
H13A···O32				
O23-	0.74	2.05	2.612(6)	134.0
H23A···O22			( )	
O33-	0.79	2.09	2.755(5)	142.0
H33A···O12				
O33-	0.79	2.26	2.694(5)	115.7
H33A···O32				
C24-H24···O13	0.89	2.36	3.196(6)	158.5
C60-H60···O33	0.93	2.34	3.255(7)	166.2
C47-	0.82	2.58	3.306(7)	147.7
H47···O11 <sup>ii</sup>			~ /	

<sup>a</sup> Symmetry transformations: i, -x, -y+1, -z; ii, x, y-1, z; iii, -x, -y+1, -z+1; iv, -x, -y, -z+1; v, x+1, y-1, z; vi, -x+1, -y+1, -z.

<sup>b</sup> Symmetry transformations: i, y+3/4, -x+3/4, z-1/4; ii; -x+3/2, -y+1/2, -z+1/2; iii, x, y, z-1.

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

gand (lactato in 1, 2-methyllactato in 2). The copper ions are six-coordinate, being bound to the nitrogen atoms of the 2,2'-bipyridine molecule and to one carboxy and one hydroxyl oxygen of each of two  $\alpha$ hydroxycarboxylato anions. There are thus three fivemembered chelate rings. In both 1 and 2 the copper atom has elongated octahedral coordination geometry with the two nitrogen atoms and the mutually *cis*  $O_{carboxy}$  atoms equatorial and the two  $\alpha$ -hydroxyl oxygen atoms axial, the difference between the average equatorial and axial bond lengths being 0.356 Å in 1 and 0.301 Å in 2. This elongation of the coordination polyhedron, due to a Jahn–Teller effect, is also observed



Fig. 1. Molecular structure of [Cu(HLACO)<sub>2</sub>(bipy)]·2H<sub>2</sub>O (1).



Fig. 2. Molecular structure of [Cu(HMLACO)<sub>2</sub>(bipy)]·H<sub>2</sub>O (2).

in polymeric complexes containing lactato or 2-methyllactato ligands and 4,4'-bipyridine [16]. Additional deviation from ideal octahedral geometry is shown by the chelating angles ranging from  $74.92^{\circ}$  to  $80.80^{\circ}$  in 1 and from  $75.90^{\circ}$  to  $81.01^{\circ}$  in 2 (Table 4) and by some of the trans angles, such as O<sub>hydroxyl</sub>-Cu-O<sub>hydroxyl</sub> in 1  $[159.21(8)^\circ]$  and  $O_{carboxy}{-}Cu{-}N$  in 2  $[166.69(18)^\circ$  and 166.48(18)°]. The Cu-O<sub>carboxy</sub> distances fall within the range usually observed in similar copper(II) complexes (1.90-1.97 Å) [16–19], as do the Cu–O<sub>hydroxyl</sub> distances [16], and as in other complexes with a  $CuN_2O_4$  core [16,17,20] the values of the latter depend on their involvement in hydrogen bonds, the hydroxyl oxygens with the shorter Cu-O<sub>hydroxyl</sub> bonds having the shorter hydrogen bond (Table 5). The Cu-N distances, 1.995-2.015 Å, are within the normal range for complexes with N,N-chelating ligands [17,18] but are slightly shorter



Fig. 3. Structure of [Cu(HMANO)(bipy)<sub>2</sub>](HMANO)(H<sub>2</sub>MANO)·CH<sub>3</sub>CN (3a).

than in polymeric copper(II) complexes containing 4,4'-bipyridine [16].

In compound 3a the asymmetric unit is composed of the cationic complex  $[Cu(HMANO)(bipy)_2]^+$  and, in the outer coordination sphere, an HMANO<sup>-</sup> counterion, a nondeprotonated neutral H<sub>2</sub>MANO molecule, and a solvating acetonitrile molecule.  $\alpha$ -Hydroxycarboxylic acids have been reported to show similarly diverse behaviour in mixed complexes containing other diamines [9,21,22], without there apparently being any relation between this behaviour and the bulk of the  $\alpha$ hydroxycarboxylic acid. The copper atom in 3a is fivecoordinated to the four 2,2'-bipyridine nitrogens and to one of the carboxylato oxygens of the monodentate, monodeprotonated mandelic acid; the second carboxylato oxygen, O12, is too far from the metal [2.673(3) Å] for coordination. The Cu-N and Cu-O distances are within the usual ranges for this kind of copper(II) complex [9,13,23]. The coordination polyhedron cannot be described as either a square pyramid or a trigonal bipyramid, having a trigonality index  $\tau = 0.49$  ( $\tau = (\beta - \beta)$  $\alpha$ )/60°, where  $\beta$  and  $\alpha$  are the largest angles in the coordination sphere [24]; its value is zero for a perfect square pyramid and unit for a perfect trigonal bipyramid).

The C–O distances of the coordinated  $\alpha$ -hydroxycarboxylato oxygen atoms are similar in the three complexes (between 1.256 and 1.267 Å) and only slightly longer than those of the uncoordinated oxygen atoms (1.226–1.246 Å). The O–C–O angles are also very similar,  $122.5^{\circ}-125.1^{\circ}$ . As expected, the individual pyridine rings of the bipy ligands are all planar. The bipy ligand as a whole is also planar in **1**, but in **2** and **3a** there are dihedral angles between the pyridyl rings of each bipy:  $7.2(2)^{\circ}$  in **2**, and  $2.3(3)^{\circ}$  and  $8.0(3)^{\circ}$  in **3a**. Twisting around the 2-2' bond is normal in coordinated bipy [25].

All three compounds have both intra- and intermolecular hydrogen bonds (Table 5). In 1 the two solvating water molecules play a key role in the formation of a 2D network, bridging between neighbouring molecules of 1 (Fig. 4). Each water molecule accepts the hydroxyl



Fig. 4. View of the hydrogen bonding linkage in 1.

hydrogen of one of the  $\alpha$ -hydroxycarboxylato ions of its 'own' molecule, and donates hydrogens to the uncoordinated O atoms of neighbouring molecules (and, in the case of H<sub>2</sub>O (**2**), to another O2 oxygen). The O···O hydrogen bond distances and angles are in the ranges 2.643(3)-2.993(4) Å and 160.5°-178.2°, respectively. In **2** the salient feature of the crystal packing is the threedimensional supramolecular arrangement of the molecules around a fourfold screw axis, which is stabilized by hydrogen bonds between the hydroxyl groups and the uncoordinated carboxylato O atoms (Table 5 and Fig. 5). The channels so generated run through the crystal in the direction of the c axis with the water molecules inside them. The O···O hydrogen bond distances are in the range 2.657(6)-2.958(8) Å.

In all three complexes there are also  $C-H\cdots O$ interactions, mainly involving bipy carbons and  $O_{carboxy}$ atoms (Table 5). In **3a**, in which these hydrogen bonds play a decisive role in the crystal packing (Fig. 6), there are also  $C-H\cdots O$  interactions between the mandelic acid and the mandelato anion of the outer sphere. The  $C\cdots O$  distances and  $C-H\cdots O$  angles of these bonds have values indicating significant interactions [26], 3.023-3.338 Å and  $113.7^{\circ}-173.2^{\circ}$ , respectively (Table 5), the strongest of these bonds being intramolecular.

The shortest centroid-to-centroid distances between pyridyl rings belonging to different bipy ligands are 3.655 Å in **1** and **3a** and 3.913 Å in **2** [27]. The latter distance is too large for a  $\pi$  stacking interaction [28], but both are similar to those observed in copper(II) complexes of 1,10-phenanthroline [9,29]



Fig. 5. View of the packing in 2, showing the channel formation along c with the water molecules inside them.



Fig. 6. View of the hydrogen bonding linkage in 3a.

### 4. Experimental

#### 4.1. Materials and instruments

Chemicals were purchased from commercial sources and used without further purification. Elemental analyses (C, H, N) were performed in a Carlo Erba 1108 microanalyser. Melting points were measured in a Büchi melting point apparatus and are uncorrected. The IR spectra of samples incorporated in KBr discs (4000-400  $cm^{-1}$ ) or polyethylene-sandwiched Nujol mulls (500-100 cm<sup>-1</sup>) were recorded on a Bruker IFS66v spectrophotometer. A Shimadzu UV-3101PC spectrophotometer was used to obtain electronic spectra in the region 900-350 nm. Magnetic susceptibility measurements were made at room temperature using a Johnson Matthey magnetic susceptibility balance (for 2) or at variable temperature with a DSM-10 magnetometer (for 1 and 3). X-band (9300 MHz) EPR spectra were obtained at room temperature with a Bruker ESP 300E spectrometer. Thermogravimetric analyses were performed on a Shimadzu TGA-DGT-50H instrument coupled to a Nicolet Magma 550 FT-IR spectrophotometer.

## 4.2. Preparation of the complexes

A mixture of  $CuCO_3 \cdot Cu(OH)_2$  (2.26 mmol) and the appropriate  $\alpha$ -hydroxycarboxylic acid (9.10 mmol) in 35 mL of ethanol was refluxed for 4 h at 75 °C. 2,2'-Bipyridine (4.52 mmol) was added, and refluxing was continued for 2 h, after which the mixture was stirred for several days. The blue solids formed were filtered out, washed with ethanol and dried over CaCl<sub>2</sub>.

# 4.3. $[Cu(HLACO)_2(bipy)] \cdot 2H_2O(1)$

Yield: 55%. M.p.: 206 °C. *Anal.* Found: C, 44.5; H, 5.2; N, 6.6. Calc. for  $C_{16}H_{22}N_2O_8Cu$  (433.9): C, 44.3; H, 5.1; N, 6.5%. IR ( $\nu$  cm<sup>-1</sup>): 3407, 3115,  $\nu$ (OH); 1607,  $\nu$ (CC); 1595,  $\nu_{asym}$ (OCO); 1386,  $\nu_{sym}$ (OCO); 1497, 1450,  $\nu$ (CC, CN); 1084,  $\nu$ (CO); 1049, ring breathing; 733,  $\gamma$ (CH); 396,  $\nu$ (CuO); 310,  $\nu$ (CuN).

Single crystals of **1** were obtained by slow concentration of the mother liquor at room temperature (r.t.).

# 4.4. $[Cu(HMLACO)_2(bipy)] \cdot H_2O(2)$

Yield: 65%. M.p.: 190 °C. *Anal.* Found: C, 47.9; H, 5.6; N, 6.2. Calc. for  $C_{18}H_{24}N_2O_7Cu$  (443.9): C, 48.7; H, 5.4; N, 6.3%. IR ( $\nu$  cm<sup>-1</sup>): 3442, 3205,  $\nu$ (OH); 1642,  $\nu$ (CC); 1593,  $\nu_{asym}$ (OCO); 1359,  $\nu_{sym}$ (OCO); 1492, 1459,  $\nu$ (CC, CN); 1176,  $\nu$ (CO); 1059, ring breathing; 734,  $\gamma$ (CH); 393,  $\nu$ (CuO); 296,  $\nu$ (CuN).

Crystals of 2 were grown at room temperature by slow diffusion of n-hexane into a solution of the compound in acetone.

## 4.5. $[Cu(HMANO)_2(bipy)] \cdot 4H_2O(3)$

Yield: 75%. M.p.: 199 °C. *Anal.* Found: C, 52.3; H, 4.2; N, 4.7. Calc. for  $C_{26}H_{30}N_2O_{10}Cu$  (594.0): C, 52.6; H, 5.1; N, 4.7%. IR ( $\nu$  cm<sup>-1</sup>): 3410, 3110,  $\nu$ (OH); 1607,  $\nu$ (CC); 1597,  $\nu_{asym}$ (OCO); 1339,  $\nu_{sym}$ (OCO); 1490, 1445,  $\nu$ (CC, CN); 1082,  $\nu$ (CO); 1058, ring breathing; 731,  $\gamma$ (CH); 406,  $\nu$ (CuO); 272,  $\nu$ (CuN).

Slow concentration of the mother liquor yielded a blue oil that upon attempted recrystallization from CH<sub>3</sub>CN afforded blue single crystals of formula  $[Cu(HMANO)(bipy)_2](HMANO)(H_2MANO) \cdot CH_3CN$  (**3a**).

## 4.6. X-ray crystallography

Data collection and refinement parameters are listed in Table 1. The diffraction data were collected on an Enraf-Nonius CAD4 (complex 1 at -65 °C and complex 3a at 20 °C), on a Bruker SMART CCD (complexes 1 and 2 at r.t.) and on a STOE-IPDS diffractometer (complex 3a at -50 °C). Graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) or Cu K $\alpha$  radiation ( $\lambda =$ 1.54184 Å) were used and the data were corrected for Lorentz and polarization effects for absorption [30,31]. The structures were solved by direct methods and subsequent Fourier difference techniques (SHELXS [32]), and were refined on  $F^2$  using SHELXL [33]. Hydrogen atoms were inserted at calculated positions and constrained with isotropic thermal parameters, except for those hydroxyl and water H atoms that it was possible to locate from a Fourier difference map, which were refined isotropically. Complex 3a crystallizes in the chiral space group *Cc*, and the analysis unambiguously established its absolute stereochemistry [Flack parameter 0.000(14)]. Neutral atom scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [34]. Geometrical calculations and illustrations were performed or generated with the SHELXL-97 [33], SCHA-KAL-97 [35] and PLATON [27] packages.

## 5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 182331 for 1 (20 °C), 182332 for 1 (-65 °C), 182333 for 2, 182334 for 3a (-50 °C) and 194598 for 3a (20 °C). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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