

Dedicated to Professor Mihaela Hillebrand,  
on the occasion of her 80<sup>th</sup> anniversary

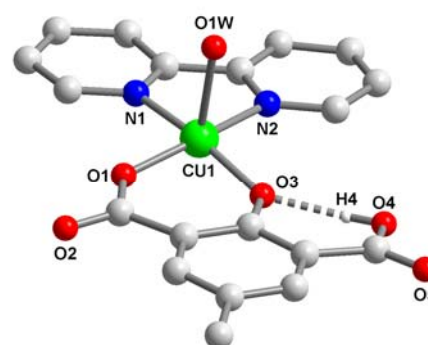
## REACTIONS OF HETEROLEPTIC $[\text{Cu}(\text{acac})(\text{AA})(\text{H}_2\text{O})]^+$ COMPLEXES WITH CARBOXYLATE ANIONS ( $\text{acac}^- = \text{ACETYLACETONATE}$ , $\text{AA} = 2,2'$ -BIPYRIDINE, 1,10-PHENANTHROLINE)

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The reactions of  $[\text{Cu}(\text{acac})(\text{AA})(\text{H}_2\text{O})]^+$  species ( $\text{AA} = 2,2'$ -bipyridine, 1,10-phenanthroline) with anions derived from 4-methylphenol-2,6-dicarboxylic ( $\text{H}_3\text{MeIPA}$ ) and isophthalic acids ( $\text{H}_2\text{IPA}$ ) generate new complexes, which result by substituting the acetylacetonato ligand by carboxylato ones:  $[\text{Cu}(\text{bipy})(\text{HMeIPA})(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{O} \cdot \text{DMF}$  **1** (DMF = dimethylformamide),  $[\text{Cu}(\text{bipy})(\text{IPA})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot \text{DMF}$  **2**, and  $[\text{Cu}(\text{phen})(\text{IPA})(\text{H}_2\text{O})] \cdot \text{DMF}$  **3**. The crystal structures of **1** - **3** have been solved. Compound **1** is a mononuclear complex, while compounds **2** and **3** are one-dimensional coordination polymers with a zigzag topology.



### INTRODUCTION

Heteroleptic copper(II) complexes containing two different chelating ligands (acetylacetonate,  $\text{acac}^-$ , and various  $N$ -donor chelating ligands) are readily obtained by one-pot reactions.<sup>1</sup> In order to avoid the formation of the homo-bis(chelated) copper(II) complexes,  $[\text{Cu}(\text{acac})_2]$  and  $[\text{Cu}(\text{AA})_2]\text{X}_2$ , the solution containing the two ligands has to be added suddenly over the solution of the copper(II) salt. In most of these complexes, the copper(II) ions show a square-pyramidal or a square planar geometry. In the first case, the apical position is occupied by a solvent molecule or by an anion (*e. g.* perchlorate, if the starting material is

copper perchlorate). The geometry of the metal ion is dependent on the nature of the chelating  $N$ -donor ligands. For example, a square pyramidal geometry is observed within  $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})](\text{ClO}_4)$  and  $[\text{Cu}(\text{acac})(\text{bipy})(\text{H}_2\text{O})](\text{ClO}_4)$  mononuclear complexes (phen = 1,10-phenanthroline; bipy = 2,2'-bipyridine),<sup>1b,c</sup> while in the case of 4,4'-dimethyl-2,2'-bipyridine ( $\text{Me}_2\text{bipy}$ ), the copper ion shows a square planar geometry:  $[\text{Cu}(\text{acac})(\text{Me}_2\text{bipy})](\text{ClO}_4)$ .<sup>2</sup> If the phenanthroline derivative is crystallized from an acetonitrile solution by slow diffusion of ether, two mononuclear square-pyramidal compounds co-crystallize:  $[\text{Cu}(\text{acac})(\text{phen})(\text{OCIO}_3)]$  and  $[\text{Cu}(\text{acac})(\text{phen})(\text{CH}_3\text{CN})](\text{ClO}_4)$ .<sup>3</sup> On the other hand, the bipyrimidine

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derivative, [Cu(acac)(bipym)(OCIO<sub>3</sub>)], is a 1D coordination polymer with the perchlorato ligands acting as bridges, the coordination sphere of the copper ions being described by an elongated octahedron.<sup>1b</sup> Starting from copper nitrate, Fukuda *et al.* described square-pyramidal complexes with the nitrate ligand in apical position: [Cu(acac)(phen)(ONO<sub>2</sub>)]·H<sub>2</sub>O and [Cu(acac)(Me<sub>2</sub>phen)(ONO<sub>2</sub>)] (Me<sub>2</sub>phen = 2,9-dimethyl-1,10-phenanthroline).<sup>1a</sup> Copper(II) halides were also employed as starting materials. Onawumi, Paul *et al.* reported on two such systems: starting from copper(II) chloride, two complexes co-crystallize: ([Cu(acac)(bipy)Cl] and [Cu(acac)(bipy)(H<sub>2</sub>O)]Cl), while copper(II) bromide leads to [Cu(acac)(bipy)(Br)]·H<sub>2</sub>O.<sup>4</sup> These complexes show antibacterial and antifungal activity.

Apart from the aromatic *N*-donor chelating ligands mentioned above, aliphatic tertiary diamines have been employed also to generate similar mixed-ligand complexes, for example [Cu(acac)(tmen)(H<sub>2</sub>O)]X, [Cu(acac)(tmen)(X)]; tmen = *N,N,N',N'*-tetramethylethylenediamine.<sup>5-7</sup> All these complexes show a remarkable stability in solution toward dissociation of the chelating ligands, while the apical position is labile and therefore accessible for other potential ligands. This explains one of the properties of these complexes, namely their solvatochromism: upon the dissolution, the solvent molecules coordinate into the apical positions, influence the splitting of the *d* orbitals and, consequently, the color of the resulting species.<sup>5-8</sup>

In a series of papers we have shown that [Cu(acac)(AA)]<sup>+</sup> species can be further employed as building-blocks in designing homo- and heteronuclear complexes, by simply playing with the apical position of the copper(II) ions. Various potentially bridging ligands (neutral or anionic) can be attached into the apical position, while the two chelating ligands preserve their position in the basal plane. For example, binuclear complexes, [{Cu(acac)(AA)}-bridge-{Cu(acac)(AA)}]<sup>q</sup>, are assembled using azido or bis-(4-pyridyl) *exo*-dentate ligands.<sup>9,10</sup> Metalloligands can be employed as well, resulting in heterometallic complexes: [{Cu(acac)(AA)}-NC-M-CN-{Cu(acac)(AA)}](ClO<sub>4</sub>) (M = Ag, Au),<sup>11</sup> [{Cu(acac)(AA)}-X-HgX<sub>2</sub>-X-{Cu(acac)(AA)}] (X = Cl, SCN).<sup>12</sup> The analysis of the packing diagrams of all these complexes revealed the occurrence of  $\pi$ - $\pi$  stacking interactions between the phen or bipy ligands, with

an important role in stabilizing the solid state architectures.<sup>11-13</sup> On the other hand, we observed that the reaction of [Cu(acac)(tmen)]<sup>+</sup> with the dianion of the trimesic acid results in the substitution of the acetylacetonato ligand by chelating carboxylate groups.<sup>14</sup> In this work, we provide new examples illustrating this substitution reaction and its consequences for the synthesis of new compounds.

## RESULTS AND DISCUSSION

In order to check the generality of the substitution process of the acac<sup>-</sup> ligand by carboxylato groups, we have chosen the following systems: (i) [Cu(acac)(bipy)(H<sub>2</sub>O)](ClO<sub>4</sub>) and 4-methylphenol-2,6-dicarboxylic acid (H<sub>3</sub>MeIPA); (ii) [Cu(acac)(bipy)(H<sub>2</sub>O)](ClO<sub>4</sub>) and isophthalic acid (H<sub>2</sub>IPA); (iii) [Cu(acac)(phen)(H<sub>2</sub>O)](ClO<sub>4</sub>) and isophthalic acid. Two reactions have been carried out in the presence of triethylamine, in order to generate the carboxylato ligands. Three new complexes are assembled by replacing the acetylacetonato ligands with carboxylato ones: [Cu(bipy)(HMeIPA)(H<sub>2</sub>O)]·0.5H<sub>2</sub>O·DMF **1** (DMF = dimethylformamide), <sup>1</sup><sub>∞</sub>[Cu(bipy)(IPA)(H<sub>2</sub>O)<sub>2</sub>]·H<sub>2</sub>O·DMF **2**, and <sup>1</sup><sub>∞</sub>[Cu(phen)(IPA)(H<sub>2</sub>O)]·DMF **3**.

The 4-methylphenol-2,6-dicarboxylic acid can be readily synthesized starting from the corresponding dialdehyde (2,6-diformyl-*p*-cresol).<sup>15</sup> Surprisingly, this dicarboxylic acid was not employed as a ligand so far. Related compounds, 2-hydroxy-isophthalic acid,<sup>16</sup> and 4,6-dimethyl-2-hydroxy-isophthalic acid,<sup>17</sup> have a quite interesting, but still scarce, coordination chemistry. Another derivative, 5-*tert*-butyl-2-hydroxy-isophthalic acid, was employed to generate a luminescent Tb(III) complex.<sup>18</sup>

The crystallographic investigation of crystal **1** reveals that HMeIPA<sup>2-</sup>, resulting from the deprotonation of one carboxyl and one phenolic group, acts as a chelating ligand (Figure 1). Compound **1** is a mononuclear complex, with the copper(II) ion showing a square pyramidal geometry: the basal plane is formed by the two chelating ligands, bipy and HMeIPA<sup>2-</sup> [Cu1 – N1 = 2.010(6), Cu1 – N2 = 2.010(6), Cu1 – O3 = 1.933(5), Cu1 – O1 = 1.898(5) Å] and the apical position is occupied by the aqua ligand [Cu1 – O1w = 2.279(7) Å]. The analysis of the

supramolecular interactions occurring in crystal is particularly interesting. First of all, the expected intramolecular hydrogen bond between the COOH group and the vicinal phenoxido oxygen atom is observed, with  $O3\cdots O4 = 2.467 \text{ \AA}$ . Supramolecular dimers (Figure 2a) are generated through hydrogen bonds established between the aqua ligand from one complex and the carboxylate oxygen atom from another one ( $O1w\cdots O2' = 2.701 \text{ \AA}$ ,  $' = 2-x, 2-y, 1-z$ ). Each molecule from a H-bonded dimer interacts through  $\pi$ - $\pi$  stacking with a molecule from another dimer (Figure 2b). These interactions occur between one ring of the bipy ligand and the phenyl moiety of the HMeIPA<sup>2-</sup> ligand from the neighboring molecule (centroid $\cdots$ centroid distance =  $3.61 \text{ \AA}$ ). The alternate hydrogen bond and  $\pi$ - $\pi$  interactions described above generate supramolecular chains running along the crystallographic  $b$  axis (Figure 2c).

Both compounds **2** and **3** are 1D coordination polymers, constructed from mononuclear copper(II) nodes and IPA<sup>2-</sup> spacers. Let us discuss first the crystal structure of **2** (Figure 3). It consists of zigzag chains paralleling the  $b$  axis. Each carboxylate group coordinates the metal ion by one oxygen atom. The copper(II) ion shows an elongated octahedral geometry: The basal plane is formed by two bipy nitrogen atoms and by the oxygen atoms arising from two of the carboxylate groups [ $Cu1 - O1 = 1.945(3)$ ,  $Cu1 - N1 = 2.008(3) \text{ \AA}$ ], while the apical positions are occupied by two aqua ligands [ $Cu1 - O1w = 2.282(4)$ ,  $Cu1 - O2w = 2.867 \text{ \AA}$ ]. The O2w aqua ligand is hydrogen bonded to two uncoordinated oxygen atoms arising from two carboxylate groups ( $O2w\cdots O2 = 2.729 \text{ \AA}$ ).

The shortest distance between the copper ions within a chain is  $10.807 \text{ \AA}$ .

Compound **3** shows also a zigzag topology (Figure 4), but the carboxylate groups of each IPA<sup>2-</sup> spacer are not equivalent: one of them is coordinated to the copper ion through only one oxygen atom, while the second one is chelating another copper ion (*syn-syn* asymmetric mode). The stereochemistry of the copper ions is again an elongated octahedron. The basal plane is made by two nitrogen and two oxygen atoms arising from two carboxylate groups; one is monodentate, the other one is chelating [ $Cu1 - N1 = 2.034(4)$ ,  $Cu1 - N2 = 2.001(4)$ ,  $Cu1 - O3 = 1.991(3)$ ,  $Cu1 - O5 = 1.927(3) \text{ \AA}$ ]. The apical positions are occupied by the aqua ligand as well as by the carboxylate oxygen atom from the chelating group [ $Cu1 - O1w = 2.349(4)$ ,  $Cu1 - O1 = 2.557(3) \text{ \AA}$ ]. A hydrogen bond is established between the aqua ligand and the uncoordinated oxygen atom from the monodentate carboxylate group ( $O1w\cdots O4 = 2.653 \text{ \AA}$ ). The different coordination modes of the two carboxylate groups lead to shorter intrachain distances between the metal centers ( $9.983 \text{ \AA}$ ), in comparison with compound **2** ( $10.807 \text{ \AA}$ ).

Selected bond distances and angles for the three compounds are collected in Table 2.

The electronic spectra of the three compounds (diffuse reflectance technique) are shown in Figure 5. Each spectrum is dominated by a broad band in the visible range (**1**: 675, **2**: 692, **3**:  $\sim 800 \text{ nm}$ ), arising from the  $d_{z^2} \rightarrow d_{x^2-y^2}$ ,  $d_{xz}$ ,  $d_{yz} \rightarrow d_{x^2-y^2}$ , and  $d_{xy} \rightarrow d_{x^2-y^2}$  transitions.<sup>19</sup>

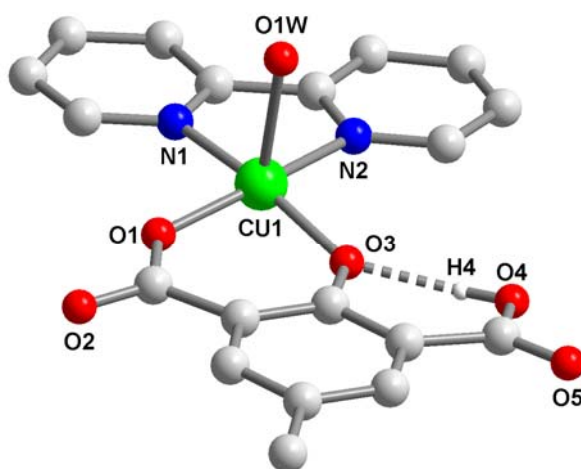


Fig. 1 – Perspective view of  $[Cu(bipy)(HMeIPA)(H_2O)] \cdot 0.5H_2O \cdot DMF$  **1**, along with the atom numbering scheme.

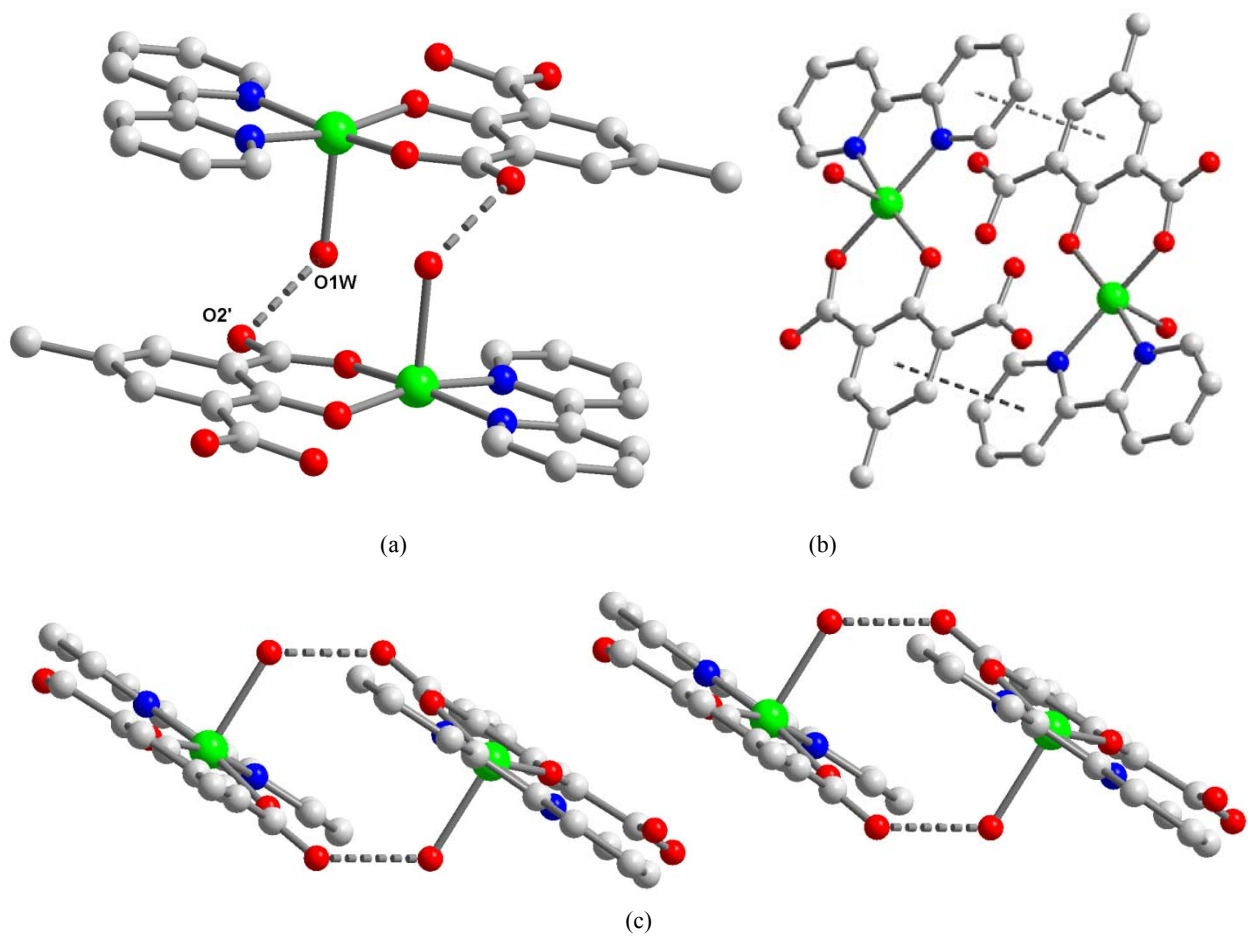


Fig. 2 – Details of the packing diagrams in crystal 1: (a) H-bonded supramolecular dimers ( $\bar{c}' = 2-x, 2-y, 1-z$ ); (b) Perspective view showing the  $\pi$ - $\pi$  stacking interactions; (c) Supramolecular chains assembled by H-bond and  $\pi$ - $\pi$  stacking interactions.

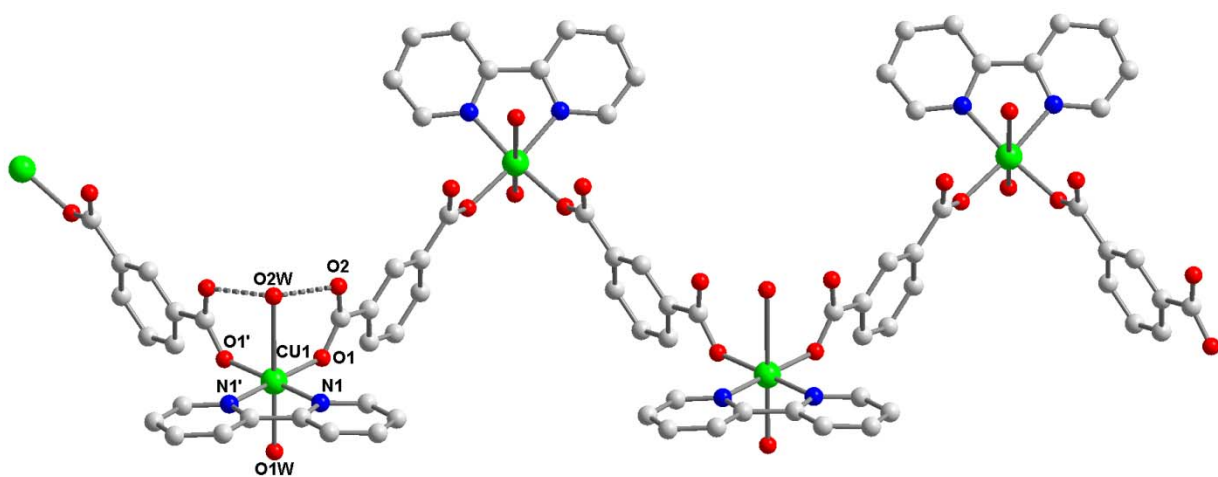


Fig. 3 – View of the 1D coordination polymer in crystal 2 along with the atom numbering scheme ( $\bar{c}' = x, 0.5-y, z$ ).

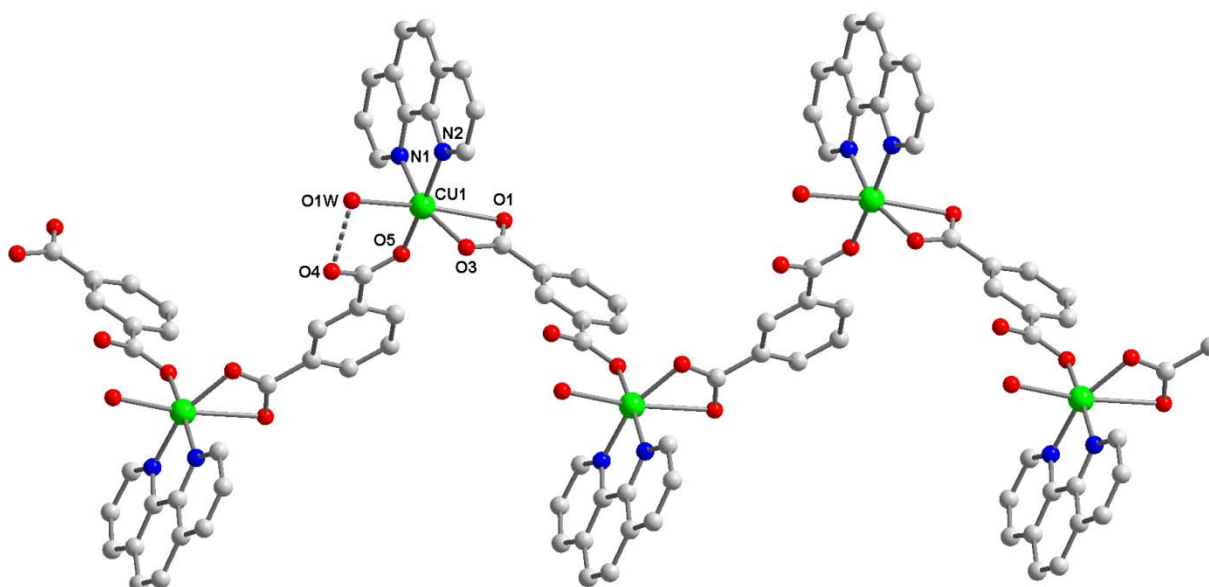


Fig. 4 – Perspective view of the 1D coordination polymer in crystal 3.

Table 1

Crystallographic data, details of *data* collection and structure refinement parameters for compounds 1 - 3

Compound	1	2	3
Formula	C <sub>22</sub> H <sub>24</sub> CuN <sub>3</sub> O <sub>7.5</sub>	C <sub>21</sub> H <sub>23</sub> CuN <sub>3</sub> O <sub>8</sub>	C <sub>23</sub> H <sub>21</sub> CuN <sub>3</sub> O <sub>6</sub>
Molecular weight	513.98	508.96	498.97
Crystal system	<i>triclinic</i>	<i>orthorhombic</i>	<i>monoclinic</i>
Space group	<i>P</i> -1	<i>Pcmb</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>
a(Å)	10.2398(2)	7.1813(2)	7.1009(2)
b(Å)	11.0534(3)	14.0209(3)	19.9665(3)
c(Å)	11.3874(4)	22.4908(4)	15.7223(4)
<i>a</i> /	114.916(2)	90	90
<i>β</i> (deg)	99.671(3)	90	100.809(3)
<i>γ</i> /	100.661(4)	90	90
V(Å <sup>3</sup> )	1104.14	2264.56(9)	2189.56(9)
Z	2	4	4
Dcalc (gcm <sup>-3</sup> )	1.546	1.493	1.043
F(000)	532	1052	1028
<i>μ</i> (mm <sup>-1</sup> )	1.042	1.016	1.514
Wavelength (Å)	0.71073	0.71073	0.71073
Final <i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> [ <i>I</i> > 2σ( <i>I</i> )]	0.0885, 0.2565	0.0584, 0.1373	0.0583, 0.1519
<i>R</i> <sub>1</sub> <sup>a</sup> , <i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.1012, 0.2681	0.1595, 0.1773	0.0766, 0.1691
Goodness-of-fit on F <sup>2</sup>	1.227	0.909	1.055
Largest peak in final difference (eÅ <sup>-3</sup> )	-1.164, 1.073	-0.450, 0.474	-1.164, 1.240

<sup>a</sup> $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . <sup>b</sup> $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$ ;  $w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]$  where  $P = [\max(F_o^2, 0) + 2F_c^2] / 3$ .

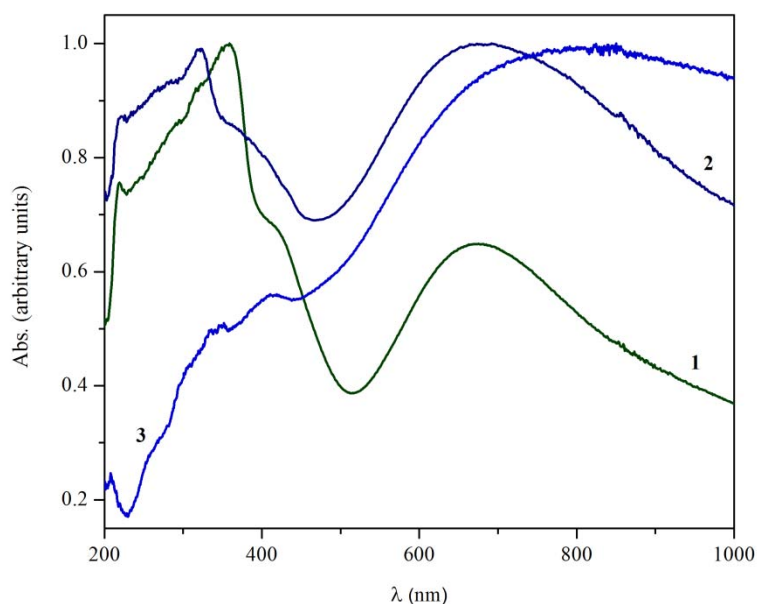


Fig. 5 – Diffuse reflectance spectra for compounds **1** – **3**.

The reactions described herein show that the reactions between  $[\text{Cu}(\text{acac})(\text{AA})]^+$  complexes with carboxylate ions represent a useful strategy for the synthesis of mixed-ligand complexes (discrete species and coordination polymers) with terminal or bridging carboxylato ligands.

## EXPERIMENTAL

### Materials and methods

All reagents and solvents for synthesis were commercially purchased and used without any further purification. 4-methylphenol-2,6-dicarboxylic acid ( $\text{H}_3\text{MeIPA}$ ) has been obtained by following the synthetic procedure reported by Okawa *et al.*<sup>15</sup> The mononuclear copper(II) precursors,  $[\text{Cu}(\text{acac})(\text{bipy})(\text{H}_2\text{O})](\text{ClO}_4)$  and  $[\text{Cu}(\text{acac})(\text{phen})(\text{H}_2\text{O})](\text{ClO}_4)$ , have been obtained as previously reported.<sup>1b,c</sup>

**$[\text{Cu}(\text{bipy})(\text{HMeIPA})(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{O} \cdot \text{DMF}$  (**1**).** A solution of  $\text{H}_3\text{MeIPA}$  (25 mg) in DMF (5 mL) was added quickly to a solution containing the copper precursor (55.5 mg) dissolved in 6 mL DMF, resulting in a blue solution. The color of the solution changed to dark green overnight. Slow evaporation of the solution at room temperature over two months produced prismatic dark green single crystals. FTIR (KBr,  $\text{cm}^{-1}$ ): 3433(m), 3058(w), 2922(vw), 1656(vs), 1621(s), 1605(m), 1574(s), 1532(m), 1449 (vs), 1418(m), 1395(m), 1373(w), 1302(w), 1260(m), 1166(w), 1102(w), 1065(w), 1031(w), 1019(vw), 959(vw), 921(vw), 812(wm), 771(m), 732(w), 661(w), 637(w), 555(w), 540(w), 420(w).

**$[\text{Cu}(\text{bipy})(\text{IPA})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O} \cdot \text{DMF}$  (**2**).** A DMF solution (3 mL) of isophthalic acid (15 mg) deprotonated with triethylamine (64 mL) was added to an ethanolic solution (23 mL) of the copper precursor (78.8 mg). The resulting blue solution was covered with a parafilm. Slow evaporation of the

solution at room temperature produced prismatic dark blue crystals after 4 weeks. FTIR (KBr,  $\text{cm}^{-1}$ ): 3713(vw), 3202(w), 3108(w), 2926(w), 2853(w), 1658(wm), 1609(vs), 1559(s), 1495(w), 1474(w), 1446(ms), 1390(vs), 1321(w), 1253(w), 1159(w), 1098(w), 1075(w), 1058(w), 1032(w), 774(w), 751(w), 732(m), 661(w), 639(vw), 418(vw). The dark blue crystals of **2** are stable in the mother liquor. In air, the crystals start to disintegrate after several hours.

**$[\text{Cu}(\text{phen})(\text{IPA})(\text{H}_2\text{O})] \cdot \text{DMF}$  (**3**).** A DMF solution (1 mL) of isophthalic acid (15 mg) deprotonated with triethylamine (66 mL) was added to the solution of the copper precursor (41.6 mg) dissolved in 14 mL acetone. A white precipitate was formed, which was dissolved by adding 5 mL methanol. The resulting light blue solution was covered with parafilm. Slow evaporation of the solution at room temperature produced cubic blue crystals after two weeks. FTIR (KBr,  $\text{cm}^{-1}$ ): 3339(wm), 3078(w), 2953(w), 2926(w), 1674(ms), 1609(s), 1558(vs), 1518(wm), 1493(w), 1477(w), 1425(m), 1383(s), 1366(vs), 1352(vs), 1259(w), 1219(w), 1149(w), 1107(w), 1088(w), 937(vw), 874(w), 854(wm), 827(w), 754(ms), 723(m), 660(w), 648(w), 613(w), 600(w), 540(w), 471(vw), 430(w).

### Physical measurements

IR spectra were recorded on a FTIR Bruker Tensor V-37 spectrophotometer (KBr pellets) in the range of 4000–400  $\text{cm}^{-1}$ . UV–Vis diffuse reflectance spectra were recorded on a JASCO V-670 spectrophotometer, using MgO as a standard.

### X-Ray crystallography

Single X-ray studies were performed on a STOE IPDS II diffractometer using graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structures were solved by direct methods and they were refined with the ShelXL refinement package.<sup>20</sup> Data collection and refinement parameters for the two compounds are summarized in Table 1. CCDC reference numbers: 2052214–2052216.

Table 2

Selected bond lengths and angles for compounds **1**, **2**, and **3**.

Compound	Distances (Å)		Angles (°)	
<b>1</b>	O(3)-Cu(1)	1.933(5)	O(3)-Cu(1)-O(1)	92.2(3)
	O(1)-Cu(1)	1.898(5)	O(3)-Cu(1)-O(1W)	95.9(3)
	O(1W)-Cu(1)	2.279(7)	O(3)-Cu(1)-N(1)	167.5(3)
	N(1)-Cu(1)	2.010(6)	O(3)-Cu(1)-N(2)	95.6(3)
	N(2)-Cu(1)	2.010(6)	O(1)-Cu(1)-O(1W)	96.9(3)
<b>2</b>			O(1)-Cu(1)-N(1)	89.8(3)
			O(1)-Cu(1)-N(2)	167.4(3)
			O(1W)-Cu(1)-N(1)	96.2(3)
			O(1W)-Cu(1)-N(2)	92.2(3)
			N(1)-Cu(1)-N(2)	80.5(3)
<b>3</b>	Cu(1)-O(1)	1.945(3)	O(1)-Cu(1)-O(1w)	89.44(12)
	Cu(1)-O(1w)	2.282(4)	O(1)-Cu(1)-N(1)	94.36(12)
	Cu(1)-N(1)	2.008(3)	N(1)-Cu(1)-O(1w)	93.35(11)
			N(1)-Cu(1)-O(1)'	174.17(13)
			N(1)-Cu(1)-N(1)'	80.38(17)
<b>3</b>	O(1W)-Cu(1)	2.349(4)	O(1W)-Cu(1)-O(5)	93.8(1)
	O(5)-Cu(1)	1.927(3)	O(1W)-Cu(1)-N(2)	87.4(1)
	N(2)-Cu(1)	2.001(4)	O(1W)-Cu(1)-N(1)	87.6(1)
	N(1)-Cu(1)	2.034(4)	O(1W)-Cu(1)-O(1)	168.8(1)
	O(1)-Cu(1)	2.557(3)	O(1W)-Cu(1)-O(3)	112.5(1)
	O(3)-Cu(1)	1.991(3)	O(5)-Cu(1)-N(2)	174.1(2)
			O(5)-Cu(1)-N(1)	92.8(1)
			O(5)-Cu(1)-O(1)	88.6(1)
			O(5)-Cu(1)-O(3)	92.8(1)
			N(2)-Cu(1)-N(1)	81.4(1)
		N(2)-Cu(1)-O(1)	91.3(1)	
		N(2)-Cu(1)-O(3)	92.1(1)	
		N(1)-Cu(1)-O(1)	103.2(1)	
		N(1)-Cu(1)-O(3)	158.7(1)	

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