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## Synthesis, characterization, electrochemical studies and X-ray structures of mixed-ligand polypyridyl copper(II) complexes with the acetate

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**Abstract:** [Cu(phen)<sub>2</sub>(CH<sub>3</sub>COO)](ClO<sub>4</sub>)·2H<sub>2</sub>O (**1**) and [Cu(bipy)<sub>2</sub>(CH<sub>3</sub>COO)](ClO<sub>4</sub>)·H<sub>2</sub>O (**2**) (phen = 1,10-phenanthroline, bipy = 2,2'-bipyridine) were synthesized and characterized. The complexes were characterized by employing elemental analyses, infrared and UV–Vis spectroscopy, room temperature magnetic measurements and the crystal structures were elucidated using X-ray diffraction experiments. The redox properties of the complexes were also investigated. Both structures have a square pyramidal CuN<sub>4</sub>O chromophore, which exhibit significant distortions due to long Cu–O (2.217(3) Å for **1** and 2.179(1) Å for **2**) and Cu–N (2.631(2) Å for **1** and 2.714(1) Å for **2**) bonds. This distortion was further shown by the O–Cu–N bond angles (147.71(8)° for **1** and 153.40(5)° for **2**). Elemental analyses further supported the structural details unveiled by the single crystal X-ray diffraction analysis. The infrared spectra show the acetate vibrational frequencies at 1587, 1428 and 1314 cm<sup>-1</sup> for **1**, 1571, 1441 and 1319 cm<sup>-1</sup> for **2**, and the perchlorate bands at 1059 and 720 cm<sup>-1</sup> for **1** and 1080 and 768 cm<sup>-1</sup> for **2**. The broad d–d bands for the copper ion at 14.514 cm<sup>-1</sup> for **1** and 14535 cm<sup>-1</sup> for **2** support the adoption of square pyramid geometries. The magnetic moments for the two complexes were 1.83 μ<sub>B</sub> for **1** and 1.72 μ<sub>B</sub> for **2**. The peak-to-peak values of the two complexes show that the electrode reactions are quasi-reversible with ΔE<sub>p</sub> of 0.023 V for **1** and 0.025 V for **2**. In both structures, there are π–π intermolecular interactions in addition to hydrogen bonding between the units.

**Keywords:** X-ray structure determination; copper polypyridyl complexes; π–π interactions; CuN<sub>4</sub>O chromophore, quasi-reversible.

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## INTRODUCTION

Modern coordination chemistry employs polypyridine ligands as chelating agents, among such commonly used ligands are 2,2'-bipyridine and 1,10-phenanthroline (phen).<sup>1–5</sup> These ligands as well as their compounds find a number of applications including their use in building molecular structure, herbicides, solar energy conversion, colorimetric analysis, molecular recognition, as anti-neoplastic agents, pharmaceuticals and nucleic acid probes.<sup>1,6</sup> The metal complexes of these ligands are also known to exhibit biological activities, such as antitumor, anti-*Candida*, antimycobacterial and other antimicrobial activities, and also in mimic chemistry as a substitute for amino acid side group.<sup>7–9</sup> In addition, the metal complexes of these ligands find use in electrochemistry, catalysis, *etc.*<sup>10–13</sup> The complexes of these ligands have attracted much attention due to the presence of an extended  $\pi$ -system with various non-covalent  $\pi$ -interactions, which mimic various biological processes.<sup>14</sup> The coordination geometry of the copper(II) complexes is known to depend largely on the ligands, co-ligands and counter ions.<sup>14</sup> The study of the supramolecular Cu networks utilized the different coordination environments in which several copper ions exist.<sup>14</sup> Five-coordinate copper(II) complexes with *N,N'*-chelating ligands and monodentate co-ligands were studied and found to have diverse stereochemical and physicochemical properties.<sup>14</sup> Co-ligands, such as the acetate, were reported to coordinate to the copper centre of copper polypyridyl (polypyridyl = 1,10-phenanthroline and 2,2'-bipyridine) complexes in a bidentate fashion,<sup>15–17</sup> resulting in six-coordinate geometries around the copper(II) ion centers.

Herein, the synthesis, infrared (IR) and UV–Vis spectroscopic analyses, room temperature magnetic measurements, X-ray diffraction studies and the redox properties of the copper(II) mixed ligand complexes of 1,10-phenanthroline, 2,2'-bipyridine and the acetate, which acts as a monodentate ligand, are reported.

## EXPERIMENTAL

*Materials and methods*

2,2'-Bipyridine, 1,10-phenanthroline, copper(II) perchlorate hexahydrate, tetrabutylammonium hexafluorophosphate (TBAHFP) and other reagents were purchased from Aldrich Chemical Co., and sodium acetate was obtained from J.T. Baker Chemical Co. These chemical were used without further purification. Bis(2,2'-bipyridine)copper perchlorate,  $\text{Cu}(\text{bipy})_2(\text{ClO}_4)_2$ , and  $\text{Cu}(\text{phen})_2(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  were synthesized according to the literature.<sup>18,19</sup> CHN analyses were performed by Atlantic Microlab, Atlanta, GA, USA. The electronic spectra were recorded on a Genesys 10 UV–Vis spectrophotometer. The infrared spectra were recorded on a Perkin–Elmer PE 100 spectrometer with an attenuated total reflectance (ATR) window. The room temperature magnetic susceptibility measurements were determined employing a Sherwood Scientific MK1 MSB magnetic susceptibility balance. The susceptibilities were corrected considering the sample holder as the background and the diamagnetic contribution was calculated from Pascal constants. The redox properties of the

mixed-ligand complexes were studied by cyclic voltammetry. The cyclic voltammograms were recorded using a BAS 100 electrochemical analyzer. Three electrodes were employed in this system, a glassy carbon working electrode, a platinum wire electrode and saturated calomel electrode as the reference electrode. The glassy carbon working electrode was manually cleaned with alumina polish prior to each scan. Tetrabutylammonium hexafluorophosphate was used as the supporting electrolyte. The redox properties of the copper(II) mixed-ligand complexes were studied in  $10^{-3}$  M acetonitrile solutions. All solutions were de-oxygenated by passing a stream of pre-purified  $N_2$  through the solutions for 10 min before recording the voltammograms. All reported potentials were measured at 25 °C and referenced to the SCE.

#### *X-Ray diffraction analysis*

Single crystals of the  $[Cu(phen)_2(CH_3COO)](ClO_4) \cdot 2H_2O$  and  $[Cu(bipy)_2(CH_3COO)](ClO_4) \cdot H_2O$  complexes suitable for X-ray diffraction experiments were obtained by slow evaporation of the acetonitrile solution of the compounds. Data were collected by a Bruker Apex 2 CCD diffractometer using standard programs. The structures were solved, refined and publication material prepared using the Shelx suite of programs within the WinGX package.<sup>20-23</sup> The perchlorate anion was disordered in **2**. This was modeled as two sets of tetrahedral O atoms with occupancy factors of 0.870(5) and 0.130(5).

#### *Synthesis of $[Cu(phen)_2(CH_3COO)](ClO_4) \cdot 2H_2O$ (1)*

$[Cu(phen)_2](ClO_4)_2$  (0.80 mmol, 0.513 g) and 7.2 mmol (0.590 g) sodium acetate in distilled water (50 mL) was refluxed for 3 h. The bluish-green compound obtained after cooling the solution to room temperature was filtered by suction, washed with distilled water and air-dried. The crude compound was recrystallized using distilled water. Single crystals suitable for X-ray diffraction experiment were obtained by the slow evaporation of an acetonitrile solution of the compound. Yield: 0.1506 g (30 %). The characterization data for **1** are given in the Supplementary material to this paper.

#### *Synthesis of $[Cu(bipy)_2(CH_3COO)](ClO_4) \cdot H_2O$ (2)*

To a solution of 0.46 g (0.8 mmol,  $[Cu(bipy)_2](ClO_4)_2$  in 50 mL distilled water, 7.2 mmol (0.59 g) of sodium acetate were added and the mixture was stirred and heated to reflux for 3 h. The blue crystalline compound obtained on cooling to ambient temperature was filtered by suction, washed with distilled water, and then air-dried. Single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in  $CH_3CN$ . Yield: 0.2354 g (44 %).

*Caution!* Care should be taken during the handling of perchlorate salts since they are potentially explosive.<sup>24</sup> Though we have never encountered any accidents during this work, it is therefore advisable to prepare the compounds in small quantities.

## RESULTS AND DISCUSSION

### *Crystal structures*

Crystal data and structural refinement for  $[Cu(phen)_2(CH_3COO)](ClO_4) \cdot 2H_2O$  and  $[Cu(bipy)_2(CH_3COO)](ClO_4) \cdot H_2O$  are given in Table S-I of the Supplementary material to this paper.

The X-ray structure of **1** is shown in Figs. 1 and 2 and selected bond lengths and angles for the complex are presented in Table I. The crystal structure of **1** was

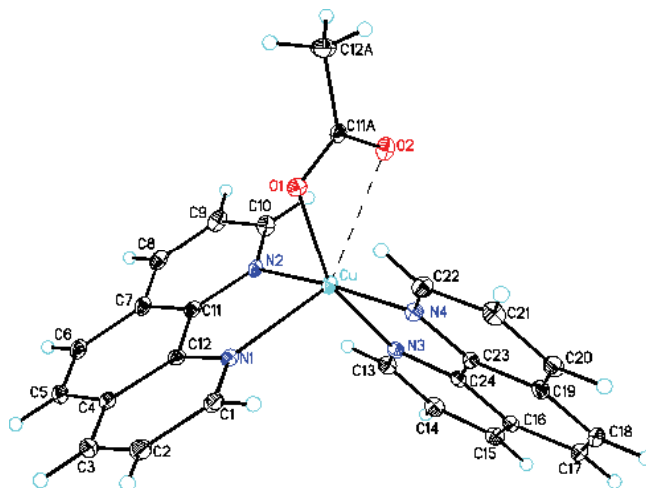


Fig. 1. ORTEP representation of the solid-state molecular structure for  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{COO})]^+$ .

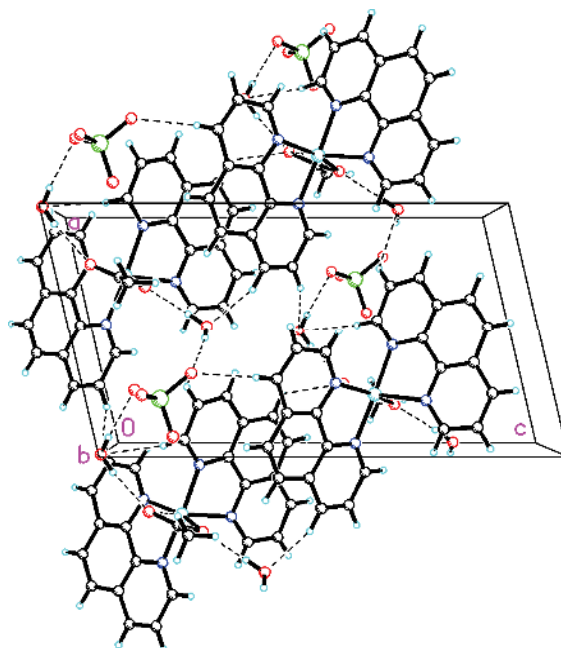


Fig. 2.  $\pi$ - $\pi$  stacking and  $\text{C-H}\cdots\text{O}(\text{W})$ ,  $\text{Cl-O}\cdots\text{H}(\text{W})$ ,  $\text{C-O}\cdots\text{H}(\text{W})$  interactions in the crystal packing of  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{COO})](\text{ClO}_4)\cdot 2\text{H}_2\text{O}$ .

unveiled in the non-symmetric monoclinic  $Pn$  space group. The two phenanthrolines are coordinated to the copper atom in a bidentate way while the acetate anion is bound to the metal in a false bidentate fashion through one shorter car-

boxylate oxygen–Cu bond (O1) and a second longer Cu–O (O2) pseudo-bond giving rise to a distorted false octahedral geometry (Fig. 1) with the longer axis involving Cu–O2 (2.631(2) Å) and Cu–N1 (2.217(3) Å) with the O2–Cu–N1 angle 147.71(8)°.

TABLE I. Selected bond lengths and angles for [Cu(phen)<sub>2</sub>(CH<sub>3</sub>COO)](ClO<sub>4</sub>)·2H<sub>2</sub>O and [Cu(bipy)<sub>2</sub>(CH<sub>3</sub>COO)](ClO<sub>4</sub>)·H<sub>2</sub>O

Bond	1	2
	Lengths, Å	
Cu–N1	2.217(3)	1.9899(13)
Cu–N2	2.009(3)	2.1786(14)
Cu–N3	2.038(2)	2.0422(13)
Cu–N4	2.007(3)	1.9750(14)
Cu–O1	1.995(2)	1.9896(12)
Cu–O2	2.631(2)	2.7136(15)
	Angles, °	
N1–Cu–N2	79.22(11)	79.16(5)
N1–Cu–N3	108.48(9)	97.46(5)
N1–Cu–N4	100.38(11)	174.48(6)
N1–Cu–O1	95.09(9)	89.80(5)
N1–Cu–O2	147.71(8)	101.73(5)
N2–Cu–N3	93.33(11)	110.70(5)
N2–Cu–N4	174.75(12)	96.31(5)
N2–Cu–O1	92.65(10)	100.18(5)
N2–Cu–O2	89.62(9)	153.40(5)
N3–Cu–N4	81.81(11)	81.11(5)
N3–Cu–O1	156.38(9)	149.08(5)
N3–Cu–O2	102.30(8)	95.63(5)
N4–Cu–O1	92.60(10)	94.13(5)
N4–Cu–O2	93.34(9)	83.73(5)
O1–Cu–O2	108.48(9)	53.45(4)

The distortion from an ideal square is more obvious in the angles for N(4)–Cu–N(2) (174.75(10)°) and N(4)–Cu–O(1) (92.65(10)°), showing partial deviation from the ideal angles 180 and 90°, respectively (Table I). The carboxylate group, the perchlorate anion and the molecules of solvation (H<sub>2</sub>O) cause extensive hydrogen bonding interactions in complex **1**. In each monomer, the carboxylate oxygen (O1) participates in a C(22)–H(22A)···O(1) interaction with the phenanthroline ligand, as well as with O(2W)–H(2W1)···O(1) hydrogen bonding. In addition, there is hydrogen bond between the perchlorate anion and a second lattice water molecule [O(1W)–H(1W1)···O(3)]. The formula units are also connected to each other by weak C–H···O intermolecular interactions [C(2)–H(2A)···O(1W)#2 and O(2W)–H(2W2)···O(6) #5 (#2  $x-1/2, -y+1, z+1/2$ ; #5  $x-1, y, z$ )], Table II. Consequently, a layer pattern is observed involving

C–H $\cdots$ O interactions and O–H $\cdots$ O hydrogen bonds, as shown in Fig. 2. In addition, the monomer is linked to another along the crystallographic *c*-axis through “herring bone”-like  $\pi$ – $\pi$  stacking interactions between the phenanthroline rings. Phenanthroline ligands were reported to favor both intramolecular and intermolecular  $\pi$ – $\pi$  interactions.<sup>25</sup> The stacked molecules further extend into chains by C–H $\cdots$ N interactions leading to the formation of supramolecular 1D structure along the *c*-axis.

TABLE II. Hydrogen bonds for [Cu(phen)<sub>2</sub>(CH<sub>3</sub>COO)](ClO<sub>4</sub>)·2H<sub>2</sub>O; symmetry transformations used to generate equivalent atoms: #1 *x*–1, *y*+1, *z*; #2 *x*–1/2, –*y*+1, *z*+1/2; #3 *x*+1, *y*, *z*; #4 *x*, *y*+1, *z*; #5 *x*–1, *y*, *z*

D–H $\cdots$ A	<i>d</i> (D–H) / Å	<i>d</i> (H $\cdots$ A) / Å	<i>d</i> (D $\cdots$ A) / Å	$\angle$ (DHA) / °
C(2)–H(2A) $\cdots$ O(6)#1	0.95	2.53	3.101(4)	119.2
C(2)–H(2A) $\cdots$ O(1W)#2	0.95	2.59	3.153(4)	117.9
C(9)–H(9A) $\cdots$ O(2W)#3	0.95	2.56	3.283(4)	133.5
C(10)–H(10A) $\cdots$ O(2)	0.95	–	3.243(4)	123.6
C(10)–H(10A) $\cdots$ O(1W)	0.95	2.53	3.474(4)	169.7
C(13)–H(13A) $\cdots$ N(2)	0.95	–	–	113.5
C(13)–H(13A) $\cdots$ O(4)#4	0.95	2.56	3.302(4)	135.0
C(21)–H(21A) $\cdots$ O(1W)#5	0.95	2.56	3.416(4)	150.5
C(22)–H(22A) $\cdots$ O(1)	0.95	–	3.118(4)	110.4
O(1W)–H(1W1) $\cdots$ O(3)	0.85(2)	2.09(3)	2.912(4)	162(7)
O(1W)–H(1W2) $\cdots$ O(2)	0.84(2)	1.98(4)	2.747(4)	151(6)
O(2W)–H(2W1) $\cdots$ O(1)	0.84(2)	1.93(2)	2.758(3)	169(5)
O(2W)–H(2W2) $\cdots$ O(6)#5	0.83(2)	2.11(3)	2.930(4)	170(5)

For **2**, the single crystal diffraction measurement also reveals a discrete monomer of the complex, [Cu(bipy)<sub>2</sub>(CH<sub>3</sub>COO)](ClO<sub>4</sub>)·H<sub>2</sub>O, in which the copper(II) ion displays a distorted square pyramidal geometry with a CuN<sub>4</sub>O chromophore. The molecular structure showing the arrangement about the Cu(II)

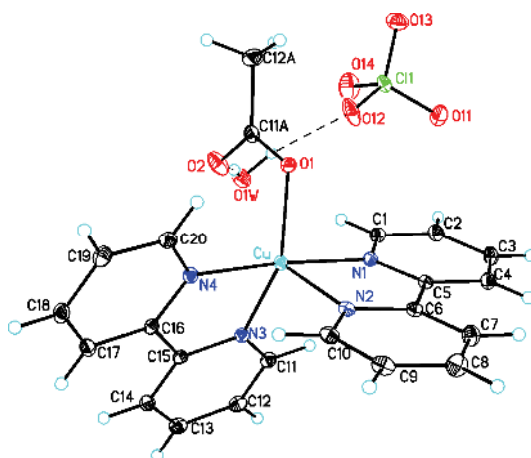


Fig. 3. ORTEP representation of the solid-state molecular structure for [Cu(bipy)<sub>2</sub>(CH<sub>3</sub>COO)](ClO<sub>4</sub>)·H<sub>2</sub>O.

metal center is shown in Fig. 3. In the crystal structure of **2**, each unit is linked to the other by hydrogen bonding (Table III) between the bonded oxygen atom of the carboxylate group and the hydrogen of the bipyridine ring.

TABLE III. Hydrogen bonds for  $[\text{Cu}(\text{bipy})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot \text{H}_2\text{O}$

D-H...A	$d(\text{D-H}) / \text{\AA}$	$d(\text{H}\cdots\text{A}) / \text{\AA}$	$d(\text{D}\cdots\text{A}) / \text{\AA}$	$\angle(\text{DHA}) / ^\circ$
O(1W)-H(1W1)···O(2)	0.88(3)	1.88(3)	2.758(2)	172(3)
O(1W)-H(1W2)···O(12)	0.87(3)	1.97(3)	2.793(2)	158(3)
O(1W)-H(1W2)···O(12A)	0.87(3)	2.29(3)	3.107(11)	156(3)

The distortion from the square pyramidal geometry is reflected in the structural index  $\tau = 0.07$  (where  $\tau = (\beta - \alpha)/60$ ),<sup>26</sup> which is rather small. Complex **2** is similar to **1** in which the coordinated carboxylate anion and perchlorate counter ion are linked through hydrogen bonds to the lattice water molecule and this results in formation of a Y-shaped arrangement (Fig. 4). The presence of lattice water in complex **2** gives stronger intramolecular bonding in the complex compared to a similar reported system.<sup>27</sup> Complex **2** shows intermolecular  $\pi$ - $\pi$  interactions similar to those observed in **1**. The striking feature of these two complexes is the presence of the hydrogen bonds in the carboxylate anion, perchlorate and the solvation molecules ( $\text{H}_2\text{O}$ ), which resulted in very similar crystal packing of the two compounds in spite of the fact that they crystallized in different crystal systems (monoclinic for **1** and triclinic for **2**) with **1** being non-centric and **2** centric.

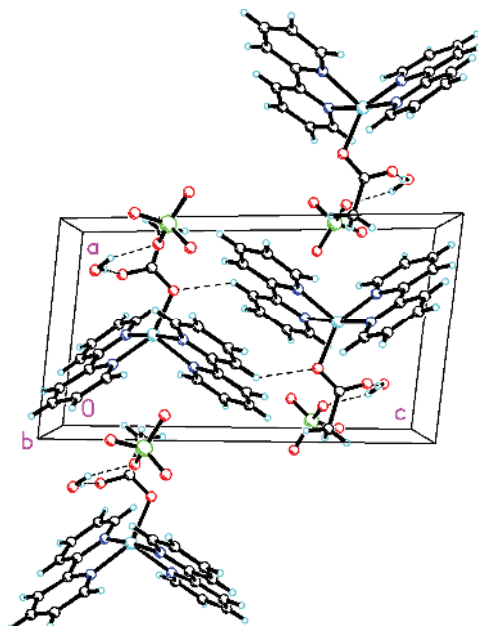


Fig. 4. *b*-Axis projection of the crystal structure of  $[\text{Cu}(\text{bipy})_2(\text{CH}_3\text{COO})]_2(\text{ClO}_4) \cdot \text{H}_2\text{O}$ .

### Spectroscopic characterization

In the infrared spectra of  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{COO})](\text{ClO}_4)\cdot 2\text{H}_2\text{O}$ , some guide peaks were observed which indicated coordination of the acetate ion to the copper(II) center. The characteristic asymmetric stretching,  $\nu_{\text{as}}$ , of the carboxylate group of the acetate ion ( $\text{COO}^-$ ) was observed at  $1587\text{ cm}^{-1}$  and of the symmetric stretching ( $\nu_{\text{s}}$ ) at  $1428\text{ cm}^{-1}$  confirmed the participation of the acetate as a monodentate ligand.<sup>24,26</sup> Unidentate carboxylate complexes exhibited  $\Delta\nu$  values of  $>200\text{ cm}^{-1}$ ,  $\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$ <sup>28</sup> but in complex **1** this is smaller ( $159\text{ cm}^{-1}$ ) than  $200\text{ cm}^{-1}$ , which may be attributed to the weak coordination of the second oxygen atom of the carboxylate group and also to the hydrogen bonding that existed in the solid state structure. The  $\nu(\text{C}-\text{O})$  stretching was observed for this complex at  $1314\text{ cm}^{-1}$ .<sup>29</sup> The presence of a broad absorption band at  $3382\text{ cm}^{-1}$  supported the presence of water molecules in the complex. The infrared spectrum of this complex showed peaks of the perchlorate anion at  $1059$  and  $720\text{ cm}^{-1}$ .<sup>30,31</sup> In complex **2**, the asymmetrical stretching of the carboxylate,  $\nu_{\text{as}}$ , was observed at  $1571\text{ cm}^{-1}$  and the symmetrical stretching,  $\nu_{\text{s}}$ , at  $1441\text{ cm}^{-1}$  while the  $\nu(\text{C}-\text{O})$  stretching was at  $1319\text{ cm}^{-1}$ .<sup>32</sup> The  $\Delta\nu$  value for the unidentate carboxylate ( $\text{COO}^-$ ),  $\Delta\nu = \nu_{\text{as}}(\text{COO}^-) - \nu_{\text{s}}(\text{COO}^-)$ , is  $139\text{ cm}^{-1}$ , which is also lower than expected for unidentate carboxylate complexes probably due to the presence of the hydrogen bonding that exists in the complex. In the spectrum of the complex, the band at  $3399\text{ cm}^{-1}$  was attributed to water molecules in the lattice. The perchlorate anion bands were found at  $1060$  and  $764\text{ cm}^{-1}$ , which are similar to those reported.<sup>31</sup>

The electronic spectra of the complexes show broad bands at  $14514$  and  $14535\text{ cm}^{-1}$ , respectively, for **1** and **2**. In a five-coordinate complex, either square pyramidal or trigonal bipyramidal geometries are adopted by the complexes. The absence of constraints of chelating ligands and ligand–ligand repulsion favors the trigonal bipyramidal geometry in a five-coordinate transition metal complex.<sup>33</sup> In the studied complexes, the presence of constraints of the chelating 1,10-phenanthroline and 2,2'-bipyridine ligand, and also the reduction in ligand–ligand repulsion favors the distorted square pyramidal arrangement of these complexes. The square pyramidal stereochemistries of these complexes exhibited a high-energy, high intensity peak at  $14514$  and  $14535\text{ cm}^{-1}$ , respectively, for **1** and **2**.<sup>34</sup> The one-electron ground-state configuration is  $d_x^2-y^2 > d_z^2 > d_{xy} > d_{xz} \approx d_{yz}$  and therefore, the broad bands observed in these complexes are attributed to  $d_z^2 \rightarrow d_x^2-y^2$  transitions.<sup>33</sup> The room temperature magnetic moment values of complexes **1** and **2** are  $1.83$  and  $1.72\ \mu_{\text{B}}$ , respectively. The moment for **1** is slightly higher than the value expected for the spin only value of  $1.73\ \mu_{\text{B}}$ . This is attributed to mixing of angular momentum from excited states, *i.e.*, spin orbit coupling.<sup>34</sup> while that for complex **2** is slightly lower which may be due to anti-ferromagnetic interaction present in the complex.<sup>35</sup>



*Electrochemistry*

The cyclic voltammograms were scanned at  $0.1 \text{ V s}^{-1}$  in different potential ranges ( $-0.8$  to  $0.4 \text{ V}$  and  $-0.8$  to  $0.8 \text{ V}$ ). The cyclic voltammograms, Figs. 5 and 6, for both complexes **1** and **2**, respectively, show that both reactions are rever-

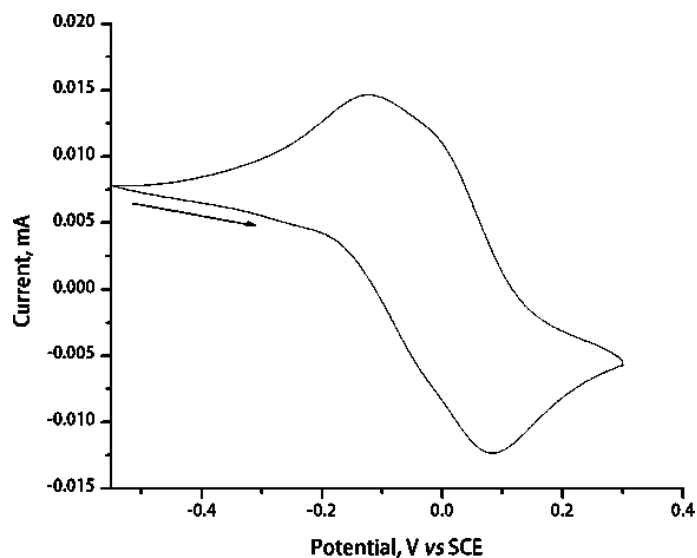


Fig. 5. Cyclic voltammogram for 1 mM  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$  containing 0.1 M TBAHFP, scan rate  $0.1 \text{ V s}^{-1}$ .

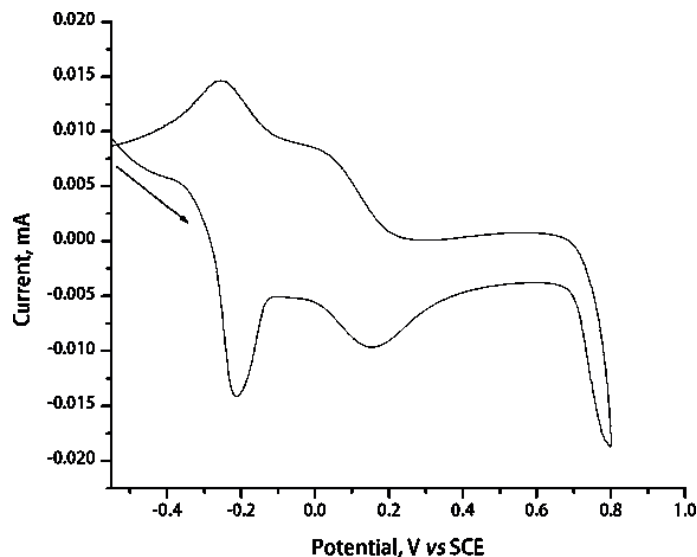


Fig. 6. Cyclic voltammogram for 1 mM  $[\text{Cu}(\text{bipy})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot \text{H}_2\text{O}$  in  $\text{CH}_3\text{CN}$  containing 0.1 M TBAHFP, scan rate  $0.1 \text{ V s}^{-1}$ .

sible. In Fig. 5, a well-defined redox process corresponding to the formation of the quasi-reversible Cu(II)/Cu(III) couple is visible for **1**. The anodic peak at 0.082 V *vs.* SCE and the associated cathodic peak at -0.105 V correspond to the Cu(II)/Cu(III) couple. The peak-to-peak separation,  $\Delta E_p = 0.023$  V, indicates a quasi-reversible one-electron transfer process. The redox property displayed by complex **2** has a counter ion redox process in addition to the Cu(II)/Cu(III) couple, Fig. 6. The first anodic peak is at -0.213 V *vs.* SCE, with the corresponding cathodic wave at -0.238 V on the reverse scan. The peak separation value,  $\Delta E_p$ , of 0.025 V also indicates a quasi-reversible character for the one-electron transfer reaction of the Cu(II)/Cu(III) couple. The second anodic peak at 0.149 V and the associated cathodic peak at 0.054 V, with the peak separation value ( $\Delta E_p$ ) of 0.095 V is attributed to the oxidation of the oxygen atoms of the  $\text{ClO}_4^-$ :<sup>36</sup>  $\text{ClO}_4^- \rightarrow \text{ClO}_4^+ + e^-$ .

#### CONCLUSIONS

$[\text{Cu}(\text{phen})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$  and  $[\text{Cu}(\text{bipy})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot \text{H}_2\text{O}$  complexes, **1** and **2**, were synthesized and their solid-state structures elucidated. Complex **1**, although it has a distorted square pyramidal geometry, shows a pseudo octahedral geometry, as revealed by the X-ray studies, due to a weak bond with the second oxygen atom of the carboxylate anion. On the other hand, complex **2**, which had the same co-ligand but different primary ligand, has five-coordinate coordination with a distorted square pyramidal geometry in the solid-state structure. In the complexes, the phenanthroline ligand in **1** exhibited a property that favors its molecular structure, *i.e.*, intermolecular  $\pi$ - $\pi$  interactions, which results in the formation of a considerably dense crystalline packing arrangement. Complex **2**, on the other hand, with the bipyridine ligands showing no such interaction, has an open structure. The  $d_z^2 \rightarrow d_{x^2-y^2}$  transitions at 14,514 and 14,535  $\text{cm}^{-1}$ , respectively, for **1** and **2**, further supported the square pyramidal stereochemistries of these complexes. The room temperature magnetic moment values of the complexes correspond to a single unpaired electron. The cyclic voltammograms of the two complexes show the redox properties to be quasi-reversible.

#### SUPPLEMENTARY MATERIAL

The crystallographic data of the structural analyses of the complexes have been deposited with the Crystallographic Data Centre with the CCDC No 1418811 and 1418812. The data are available free of charge *via* [www.ccdc.cam.uk/data\\_request.cif](http://www.ccdc.cam.uk/data_request.cif) (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, +44 1223 336033, E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

The characterization data and the crystallographic data (Tables S-I-S-XIII) for the complexes are available electronically at the pages of journal website: <http://www.shd.org.rs/JSCS/>, or from the corresponding author on request.

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## ИЗВОД

СИНТЕЗА, КАРАКТЕРИЗАЦИЈА, ЕЛЕКТРОХЕМИЈСКА ИСПИТИВАЊА  
И КРИСТАЛНЕ СТРУКТУРЕ МЕШОВИТИХ ПОЛИПИРИДИЛ-БАКАР(II)  
КОМПЛЕКСА СА АЦЕТАТОМ

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Синтетизовани и окарактерисани су  $[\text{Cu}(\text{phen})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot 2\text{H}_2\text{O}$  (**1**) и  $[\text{Cu}(\text{bipy})_2(\text{CH}_3\text{COO})](\text{ClO}_4) \cdot \text{H}_2\text{O}$  (**2**) комплекси (phen = 1,10-фенантролин, bipy = 2,2'-бипиридин). Комплекси су окарактерисани применом елементарне микроанализе, инфрацрвене и UV-Vis спектроскопије. Магнетна мерења комплекса су извршена на собној температури, док су кристалне структуре комплекса одређене методом дифракције рендгенских зрака са кристала. Поред тога, испитиване су редокс особине комплекса. Нађено је да оба комплекса имају квадратно-пирамидалну геометрију са  $\text{CuN}_4\text{O}$  хромофором лигандног поља. Структурна испитивања комплекса су показала да њихове структуре показују значајну дисторзију дуж  $\text{Cu}-\text{O}$  (2,217(3) Å за **1** и 2,179(1) Å за **2**) и  $\text{Cu}-\text{N}$  веза (2,631(2) Å за **1** и 2,714(1) Å за **2**). Поред тога, ова дисторзија се додатно манифестује кроз одговарајуће  $\text{O}-\text{Cu}-\text{N}$  углове веза (147,71(8)° за **1** и 153,40(5)° за **2**). Резултати елементарне микроанализе су у складу са резултатима рендгенских структурних испитивања. Инфрацрвени спектри испитиваних комплекса показују вибрациону фреквенцију за ацетатни ањон на 1587, 1428 и 1314  $\text{cm}^{-1}$  за **1** и 1571, 1441 и 1319  $\text{cm}^{-1}$  за **2**, као и одговарајућу фреквенцију за перхлорат на 1059 и 720  $\text{cm}^{-1}$  за **1** и 1080 и 768  $\text{cm}^{-1}$  за **2**. Постојање широких d-d апсорпционих максимумума у UV-Vis спектрима за бакар(II) јон на 14514  $\text{cm}^{-1}$  за **1** и 14535  $\text{cm}^{-1}$  за **2** је у складу са квадратно-пирамидалном геометријом испитиваних комплекса. Магнетни моменти испитиваних комплекса су 1,83  $\mu_B$  за **1** и 1,72  $\mu_B$  за **2**. Вредности пикова за два комплекса показују да су електродне реакције псевдореверзибилне са потенцијалима  $\Delta E_p = 0,023$  V за **1** и 0,025 V за **2**. У структурама код оба комплекса утврђено је постојање  $\pi-\pi$  интермолекулских интеракција са додатним водоничним везама између одговарајућих структурних јединица.

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