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# Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry

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# Synthesis, Spectral Characterization, and Fungicidal Activity of Transition Metal Complexes With Benzimidazolyl-2-hydrazones of Glyoxal, Diacetyl, and Benzil

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A series of complexes of the type  $[ML_2].nH_2O$ , where L = 2-(benzimidazolyl-2'-amino) imino ethanone (HBAIE), 2-(benzi midazolyl-2'-amino) imino-1,2-dimethyl ethanone (HBAIME), 2-(benzimidazolyl-2'-amino) imino-1,2-diphenyl ethanone (HBAIPE), M = Cu(II), Co(II), Ni(II), and Zn(II), have been synthesized and characterized. The results are in consistent with tridentate chelation of ligand with azo nitrogen, ring nitrogen, and oxygen atom of glyoxal, diacetyl, and benzil. The fungi toxicity of the ligands and their complexes against some fungal pathogen has been studied.

Keywords benzil, benzimidazolyl-2-hydrazones, diacetyl, glyoxal, transition metal complexes

### INTRODUCTION

Schiff bases are an important class of ligands in coordination chemistry and their complexing ability containing different donor atoms are widely reported.<sup>[1,2]</sup> In this way, the synthesis, structural investigation, and reaction of transition metal Schiff bases have received a special attention, because of their biological activities as antitumoral, antifungal, and antiviral activities.<sup>[3]</sup> Thus, Schiff base hydrazones are also interesting from the point of view of pharmacology. Hydrazone derivatives are found to possess antimicrobial,<sup>[4]</sup> antitubercular,<sup>[5]</sup> anticonvulsant,<sup>[6]</sup> and anti-inflammatory<sup>[7]</sup> activities. Particularly, the antibacterial and antifungal properties of hydrazones and their complexes with some transition metal ions were studied and reported by Carcelli et al.<sup>[8]</sup> In addition, complexes of salicylaldehyde benzoylhydrazone were shown to be a potent inhibitor of DNA synthesis and cell growth.<sup>[9]</sup> This hydrazone also has mild bacteriostatic activity and a range of analogues has been investigated as potential oral ion chelating drugs for genetic disorders such as thalasemia.<sup>[10,11]</sup>

Following all these observations and as a part of our continuing research on the coordination chemistry of multidentate ligands,<sup>[12–19]</sup> we report here the synthesis and structural studies on the complexes of Cu(II), Co(II), Ni(II), and Zn(II) with some hydrazone derivatives containing benzimidazole moiety such as 2-(benzimidazolyl-2'-amino) imino ethanone (HBAIE), 2-(benzimidazolyl-2'-amino) imino-1,2dimethyl ethanone (HBAIME), and 2-(benzimidazolyl-2'amino) imino-1,2-diphenyl ethanone (HBAIPE).

# **EXPERIMENTAL**

## Material and Method

All the chemicals used of AR grade. The solvents were purified before use by standard procedures. The starting material such as 2-hydrazinobenzimidazole was synthesized according to literature method.<sup>[20]</sup>

#### **Preparation of Ligands**

The ligands used in the present investigation were benzimidazolyl-2-hydrazones of aldehydes and ketones such as glyoxal, diacetyl, and benzil have been synthesized by condensing 2-hydrazinobenzimidazole with respective aldehydes and ketone in the following manner.

Ethanolic solution of 2-hydrazinobenzimidazole (0.01 mol in 20 mL) was added to ethanolic solution of glyoxal/diacetyl/benzil (0.01 mol in 20 mL) and the resulting solution was refluxed on a water bath for 6–8 h. It was concentrated and allowed to stand overnight when colored precipitate was separated out. It was filtered, washed, and recrystallized from ethanol. The sample was dried *in vacuo* over fused calcium chloride and then analyzed.

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#### **Preparation of the Complexes**

The complexes were synthesized by refluxing ethanolic solution of the ligand HBAIE/HBAIME/HBAIPE (0.02 mol in 20 mL) with a hot ethanolic solution of corresponding hydrated metal (II) chloride (0.01 mol in 20 mL) for about 4 h when colored complexes precipitated out in each case. The complexes were filtered, washed with ethanol followed by ether and finally dried in vacuo over fused CaCl<sub>2</sub>.

#### **Analysis and Physical Measurements**

A weighed quantity of the compound (0.2-0.3 g) was treated with a few drops of concentrated H<sub>2</sub>SO<sub>4</sub> and 1 cc. of concentrated HNO<sub>3</sub>. It was heated till all the organic matter decomposed and sulfur trioxide fumes came out. The same process was repeated 2–3 times to decompose the substance completely. Then it was dissolved in water and the resulting solution was used for analysis of metal ions. The metal contents in the complexes were determined gravimetrically following standard procedure.<sup>[21]</sup> The molar conductance measurements were carried out at room temperature with a Toshniwal conductivity Bridge (model CL-01–06, cell constant 0.5 cm<sup>-1</sup>) using  $1 \times 10^{-3}$ M solution of the complexes in DMSO. Carbon, hydrogen, and nitrogen contents of the complexes were determined by using a MLW-CHN micro analyzer. FTIR spectra in KBr pallets were recorded on a Varian FTIR spectrophotometer, Australia. The electronic spectra of the complexes in DMSO were recorded on a Perkin-Elmer spectrophotometer. Thermo gravimetric analysis was done by Netzch-429 thermo analyzer. The <sup>1</sup>H-NMR spectra of the complexes were recorded in DMSO-d<sub>6</sub> medium on JEOL, GSX-400 model equipment.

#### **RESULTS AND DISCUSSION**

The complexes were formulated from the analytical data and molar conductance data support the suggested formulae (Table 1). The complexes are highly colored and insoluble in water and common organic solvent but soluble in highly coordinating solvents such as dioxane, DMF, and DMSO. They are non hygroscopic, highly stable under normal conditions, and all of them decompose above 250°C. The molar conductance data values in DMSO for the complexes indicate them to be nonelectrolyte in nature.

#### IR Spectra

In the high frequency region, 2-hydrazinobenzimidazole exhibits a pair of strong bands precisely located at ~3310 and ~3275 cm<sup>-1</sup> which may be assigned to asymmetric and symmetric stretching modes of vibrations of the -NH<sub>2</sub> group. Apart from these bands a multiple band system of medium intensity is observed at ~3150 and ~3100 cm<sup>-1</sup>, which may be attributed to v (N-H) benzimidazolyl group and v (N-H) exocyclic,

 TABLE 1

 Analytical and physical data of the compounds

Sl no	Compound	Color	Yield (%)	$\Lambda^a_{\ m}$	C Found (Calcd.)	H Found (Calcd.)	N Found (Calcd.)	M Found (Calcd.)
1	HBAIE	Brick red	80		37.82	0.32	39.26	
					(37.89)	(0.35)	(39.30)	
2	HBAIME	Light brown	75		36.11	0.24	46.00	
		-			(36.16)	(0.27)	(46.03)	
3	HBAIPE	Light brown	80	—	46.55	0.16	41.35	_
		-			(46.58)	(0.18)	(41.40)	
4	$[Co(BAIE)_2]H_2O$	Brown	62	7.9	47.85	3.51	24.79	13.05
					(47.89)	(3.54)	(24.83)	(13.08)
5	[Ni(BAIE) <sub>2</sub> ]H <sub>2</sub> O	Dark yellow	63	14.3	47.91	3.52	24.82	12.93
					(47.94)	(3.55)	(24.86)	(12.98)
6	[Cu(BAIE) <sub>2</sub> ] 2H <sub>2</sub> O	Yellow	65	12.6	45.58	3.76	23.61	13.38
					(45.61)	(3.80)	(23.65)	(13.41)
7	$[Zn(BAIE)_2] H_2O$	Green	62	10.6	47.21	3.48	24.47	14.18
					(47.26)	(3.50)	(24.50)	(14.22)
8	$[Co(BAIME)_2]$	Light Green	62	8.4	52.04	4.69	22.05	11.58
	$H_2O$				(52.07)	(4.73)	(22.09)	(11.63)
9	[Ni(BAIME)2] H2O	Red	65	7.2	52.09	4.69	22.07	11.51
					(52.12)	(4.73)	(22.11)	(11.54)
10	$[Cu(BAIME)_2]$	Brown	58	13.4	49.81	4.88	21.11	11.95
	$2H_2O$				(49.85)	(4.91)	(21.15)	(11.99)
11	$[Zn(BAIME)_2]$	Yellow	61	10.4	51.43	4.64	21.79	12.63
	$H_2O$				(51.46)	(4.67)	(21.83)	(12.67)
12	[Co(BAIPE) <sub>2</sub> ] H <sub>2</sub> O	Brown	63	11.2	66.71	4.18	14.79	7.78
					(66.75)	(4.23)	(14.83)	(7.81)
13	[Ni(BAIPE)2] H2O	Dark Green	60	5.7	66.76	4.19	14.81	7.71
					(66.79)	(4.24)	(14.84)	(7.75)
14	$[Cu(BAIPE)_2]$	Yellowish	60	7.8	64.78	4.34	14.35	8.12
	$2H_2O$	green			(64.82)	(4.37)	(14.40)	(8.16)
15	[Zn(BAIPE) <sub>2</sub> ] H <sub>2</sub> O	Pale yellow	64	10.2	66.19	4.16	14.66	8.50
					(66.22)	(4.20)	(14.71)	(8.54)

 $^{\mathrm{a}}\mathrm{Ohm}^{-1}\mathrm{\,cm}^{2}\mathrm{\,mol}^{-1}.$ 

respectively. Apart from these bands, a multiple band system of medium intensity is observed at ~1540 v (C=N) cyclic and -1340 v (C=N) cyclic, which may be due to ring stretching vibrations mode of benzimidazole moiety. The N-H bending vibrations for primary amine occur at 1600–1575 cm<sup>-1</sup>. The band occurring at 1620 cm<sup>-1</sup> may be assigned due to N-H bending vibrational mode. The band observed at 1230 cm<sup>-1</sup> and at ~1000 cm<sup>-1</sup> may be due to the C-N (exocyclic) stretching vibrations and N-N stretching vibrations respectively.

Reaction of 2-hydrazinobenzimidazole with glyoxal, diacetyl, and benzil brings about significant changes in the IR spectra of the product, which has been used as ligand in the present investigation. The most notable feature of the spectrum is the disappearance of band at  $\sim$ 3310 cm<sup>-1</sup> and at 3275 cm<sup>-1</sup> and appearance of additional band systems at  $\sim$ 2900 cm<sup>-1</sup>,  $\sim$ 1710 cm<sup>-1</sup>, and  $\sim$ 1590 cm<sup>-1</sup> due to v(C–H) phenyl ring in case of (HBAIPE) methyl, v(C=O) carbonyl, and v(C-N) azomethine vibration, respectively, and suggesting thereby the condensation of 2-hydrazinobenzimidazole with glyoxal, diacetyl, and benzil occurs in 1:1 proportion with conversion of NH<sub>2</sub> group to azomethine group. The previous spectral data thus provide a logical and self consistent picture to indicate the structural feature of the ligands.

The position of bands due to v (C=N) cyclic, and v (C=N) cyclic remains practically unaltered in the present complexes indicating non–coordination of ring nitrogen atom to the metal ions. Whereas, the position of benzimidazole v (N–H) band occurring at 3150 cm<sup>-1</sup> is shifted by 20–25 cm<sup>-1</sup> to lower frequency region indicating involvement of –NH group of benzimidazole in coordination to Co(II), Ni(II), Cu(II), and Zn(II) ions. In the spectra of the complexes the band due to v(C=O) was found to be absent and two new bands of medium intensity

are observed at  $\sim 1550 \text{ cm}^{-1}$  and  $\sim 1450 \text{ cm}^{-1}$ , which may be assigned to v(C=C) and v(C=O), respectively, indicating that the ligands coordinate to the metal ions through deprotonation of enolic –OH after enolization via tautomerization.<sup>[22,23]</sup> The bands observed at 1610 cm<sup>-1</sup> due to v(C=N) azomethine and at ~1050 cm<sup>-1</sup> due to v(N-N) of the ligand is also found to be absent and a new band due to -N=N- (azo group) appears at  $\sim 1630 \text{ cm}^{-1}$ , indicating thereby coordination of one of the nitrogen atom of the azo group with metal ion. A pair of sharp bands of moderate intensity is observed in the IR spectra of all the metal complexes, the first band appears at  $\sim$ 530 cm<sup>-1</sup> and the second one at  $\sim 450 \text{ cm}^{-1}$ . These bands are distinctly absent in the spectra of ligands. Considering the sharpness and intensity, higher band is attributed to v(M-N) and lower band is attributed to v(M–O) vibrations.<sup>[24,25]</sup> These observations clearly support our assumptions that oxygen (enolized), nitrogen (azo group), and ring nitrogen (benzimidazole moiety) atoms are coordinated to the metal ions. This is supported by the disappearance of band at  $\sim$ 3100 cm<sup>-I</sup> due to v (N-H) vibration. Thus IR spectral investigation of ligand as well as its metal complexes provides unequivocal evidence of coordination of ligand to the metal center through conversion of keto form to the enolic form.

Besides the previous bands, a broad band at  $\sim$ 3400 cm<sup>-1</sup> is observed in the IR spectra of all the complexes indicating the presence of coordinated or lattice water due to vOH vibration. However, all the complexes lose water when heated to  $\sim$ 100°C as indicated by thermal analysis conforms presence of lattice water molecules. The representative spectrum of the [Cu(BAIPE)<sub>2</sub>] 2H<sub>2</sub>O complex is shown in Figure 1.

#### **Thermal Analysis**

Thermal characteristics of the metal complexes are recorded in Table 2. These complexes follow the same pattern of thermal decomposition. The complexes remain almost unaffected up to  $\sim 40^{\circ}$ C. After this a slight depression up to  $\sim 120^{\circ}$ C is observed. The weight loss at this temperature range is equivalent to two water molecules in case of copper(II) complexes and one molecule in case of other complexes indicating them to be lattice water<sup>[26]</sup> in conformity with our earlier observations from analytical and IR spectral investigations. The anhydrous complexes remain stable up to 240-340°C and thereafter the complexes show rapid degradation presumably due to decomposition of organic constituents of the complex molecules as indicated by the steep fall in the percentage weight loss. The decomposition continues up to  $\sim$ 500°C and reaches to a stable product in each complex as indicated by the consistency in weight in the plateau of the thermogram. This corresponds to the composition of their stable oxides. The decomposition temperature varies for different complexes. Thermal stability of the complexes is found to be in the following order:

$$\begin{split} HBAIEComplexes: Co(II) < Zn(II) < Cu(II) < Ni(II) \\ HBAIMEComplexes: Ni(II) < Co(II) < Cu(II) < Zn(II) \\ HBAIPEComplexes: Ni(II) < Cu(II) < Zn(II) < Co(II) \end{split}$$

#### **Electronic Spectra and Magnetic Properties**

The electronic spectral data of Co(II) complexes in DMSO exhibit a band system at  $\sim 10,000$  cm<sup>-1</sup> (1000 nm) and



FIG. 1. IR spectrum of [Cu(BAIPE)<sub>2</sub>] 2H<sub>2</sub>O.

 TABLE 2

 Important features of thermo gravimetric analysis (TGA)

Compound	Total wt. for TG (mg)	Temp. range of water loss (°C)	% of water loss		Decomposition	% of residue		Composition of
			Found	Calcd.	temperature (°C)	Found	Calcd.	the residue
4	22.2	50-110	3.66	3.70	250	16.59	16.63	CoO
5	18.8	56-125	3.64	3.71	295	16.51	16.54	NiO
6	20.1	50-118	7.15	7.08	285	16.74	16.79	CuO
7	10.9	50-119	3.79	3.65	275	17.68	17.72	ZnO
8	20.0	55-125	3.37	3.33	285	14.74	14.79	CoO
9	17.6	50-120	3.22	3.34	276	14.68	14.71	NiO
10	22.3	55-118	6.47	6.38	294	14.96	15.01	CuO
11	14.6	50-120	3.20	3.29	320	15.75	15.79	ZnO
12	20.3	50-115	2.36	2.28	325	9.89	9.93	CoO
13	9.9	50-115	2.34	2.29	268	9.82	9.87	NiO
14	11.6	50-122	4.35	4.42	282	10.18	10.22	CuO
15	24.8	50-125	2.33	2.25	308	10.61	10.64	ZnO

 ${\sim}23,000\,cm^{-1}\,(434\,nm)$  corresponding to  ${}^{4}T_{1g}(F){\rightarrow}{}^{4}T_{2g}(F)\,(\nu_{1})$  transition and  ${}^{4}T_{1g}(F){\rightarrow}{}^{4}T_{1g}(P)\,(\nu_{3})$  transition, respectively, under octahedral symmetry. The electronic spectra of Ni(II) complexes show three well-resolved bands at  ${\sim}9,800\,\,cm^{-1}$  (1020 nm),  ${\sim}16,400\,\,cm^{-1}\,\,(609\,\,nm)$ , and  ${\sim}25,800\,\,cm^{-1}\,\,(387\,nm)$  assignable to  ${}^{3}A_{2g}(F){\rightarrow}{}^{3}T_{2g}(F)\,(\nu_{1}),\,{}^{3}A_{2g}(F){\rightarrow}{}^{3}T_{1g}(F)\,(\nu_{2})$ , and  ${}^{3}A_{2g}(F){\rightarrow}{}^{3}T_{1g}(P)\,(\nu_{3})$  transitions, respectively, under octahedral field. The electronic spectra of Cu(II) complexes show two main bands at  ${\sim}14,600\,\,cm^{-1}\,\,(684\,\,nm)\,\,(\nu_{2})$  and  ${}^{\sim}16,340\,\,cm^{-1}\,\,(611\,\,nm)\,\,(\nu_{3})$  assignable to  ${}^{2}B_{1g}{\rightarrow}{}^{2}E_{g}$  transitions, respectively, under D<sub>4h</sub> symmetry.

The magnetic moment values of octahedral Co(II) complexes, specially in weak and medium field strength, generally lie in the range 4.7–5.2 B.M., indicating much higher value than expected spin only value for three unpaired electrons. The higher value can be attributed to large orbital contribution, which is reinforced by spin orbit coupling. The magnetic moment values of tetrahedral Ni(II) complexes usually lie in the range 3.7–4.0 B.M. that are higher than those of octahedral complexes. Magnetic moment of mononuclear Cu(II) complexes lie in the



 $FIG.\ 2. \quad Electronic\ spectrum\ of\ [Cu(BAIME)_2].2H_2O.$ 

range 1.75–2.20 B.M. and is temperature independent in nature and dose not indicate major interaction between unpaired electrons of neighboring Cu(II) ions. The representative spectrum of the [Cu(BAIME)<sub>2</sub>].2H<sub>2</sub>O complex is shown in Figure 2.

# <sup>1</sup>H-NMR Spectra

The <sup>1</sup>H NMR spectrum of the ligand HBAIPE displays a complex multiplet in the region  $\delta$  8.0–8.7 ppm pertaining to 14 aromatic protons of the three phenyl groups only, while the signals due to ring NH proton and exocyclic NH proton appear at  $\delta$  7.0 and  $\delta$  9.0 ppm, respectively. On the other hand, the ligand HBAIME shows a complex broad multiplet in the region  $\delta$  8.0–8.5 ppm corresponding to four aromatic protons while the singlet due to ring NH proton and ring exocyclic NH proton appear at  $\delta$  7.1 and  $\delta$  9.1 ppm, respectively, and a singlet at  $\delta$  9.1 ppm for ring NH proton and exocyclic NH proton, respectively. It is to be noted that, instead of getting two peaks as observed in case of ligand HBAIME due to -CH<sub>3</sub> protons, only one <sup>1</sup>H NMR peak at  $\delta$  2.5 ppm is observed in the ligand HBAIME. But in case of HBAIE complexes a new signal at  $\sim \delta$ 6.5 ppm (-CH-CH-) is observed, conforms the coordination of ligand to the metal center through conversion of keto form to the enolic form. The signal due to ring NH proton shows a downfield shifts appearing at  $\delta$  7.5 ppm indicating coordination through ring NH group of benzimidazolyl moiety in the complexes. The proton signals due to exocyclic NH proton is absent in the <sup>1</sup>H NMR spectra of the complexes indicating deprotonation of enolic OH via tautomerization after complexation in conformity with the results of IR investigations, while the positions of other <sup>1</sup>H NMR peak of the ligands remain practically unaltered in the present complexes.

Based on the foregoing observations the following tentative structures (Figure 3) have been proposed for the present complexes.





# Antifungal Activity

The antifungal activities of the compounds were determined against two fungal strains (i.e., *A. niger* and *A. flavus*) by potato dextrose agar diffusion method.<sup>[27]</sup> The ligands and its complexes were mixed directly at different concentrations as 100, 200, 400, 800, and 1000  $\mu$ mg mL<sup>-1</sup>. All the newly synthesized compounds show considerable inhibition capacity against all the species screened. The results of the antifungal screening are presented in Table 3. DMSO was used as a control and

Gentamycin as a standard drug. At concentration 1000  $\mu$ mg mL<sup>-1</sup> compounds show better antifungal screening (i.e., inhibition was found to increase with increasing concentration of metal complex).<sup>[28]</sup>

It has been observed that on comparison with reference to fungicides the complexes were found to be more effective than ligands. It is suggested that complexation tends to make the ligand to act as more potent fungal agent than the free ligand. Moreover, coordination reduces the polarity<sup>[29,30]</sup> of the metal ion mainly because of the partial sharing of its positive charge within the chelate ring formed during coordination. This process increases the lipophilic nature of the central metal atom, which favors its permeation more efficiently through the lipid layer of the microorganism<sup>[31–33]</sup> thus destroying them more aggressively. In addition to this, many other factors, such as solubility, dipole moment, and conductivity, which are influenced by the metal ion may be the possible reasons for the antifungal activities of these metal complexes.<sup>[34]</sup>

#### **Electrochemical Study**

The cyclic voltammogram of copper complexes was recorded in DMSO solution (1.1 to -1.5 V potential range). The nature of cyclic voltammogram is similar for all the complexes. Hence the representative Cu(II) (6) is discussed here. A cyclic voltammogram of [Cu(BAIE)<sub>2</sub>] 2H<sub>2</sub>O (6) (Figure 5) displays a well defined redox process corresponding to the formation of Cu(II)/Cu(III) couple at Epa = 0.53 V and the associated anodic peak at Epc = 0.46 V. This couple is found to be reversible with  $\Delta Ep = 0.07$  V and the ratio of anodic to cathodic

 TABLE 3

 Antifungal activities of the ligands and their metal complexes

	Representation zone of inhibition ( $\mu$ mg mL <sup>-1</sup> )											
	Aspergillus niger						Aspergillus flavus					
Compound	100	200	400	800	1000	100	200	400	800	1000		
1	9.2	13.1	16.2	28.7	53.6	7.3	11.9	15.7	25.4	49.6		
2	11.6	15.4	19.8	34.3	50.7	12.4	17.5	24.3	33.5	53.6		
3	14.2	18.5	23.4	40.6	58.1	15.2	19.1	24.3	34.4	56.2		
4	16.5	21.6	27.3	35.2	64.1	13.6	18.3	24.8	32.6	60.3		
5	13.2	17.6	22.4	33.7	58.6	13.3	17.2	22.3	31.6	57.8		
6	15.2	19.6	23.4	32.5	57.6	14.6	17.2	22.4	33.2	56.8		
7	11.3	14.8	18.3	30.4	55.5	12.2	16.7	20.3	31.2	55.7		
8	18.6	23.1	33.2	46.6	64.2	17.1	25.3	31.5	43.4	67.3		
9	16.7	20.3	27.1	42.3	61.0	16.3	23.4	32.4	44.3	65.2		
10	15.7	19.3	27.2	40.1	59.3	17.5	21.2	31.2	42.5	64.4		
11	14.2	18.4	25.7	38.6	55.3	18.3	23.2	28.3	35.6	58.2		
12	19.4	26.2	34.3	66.3	78.5	18.5	26.6	36.1	68.5	76.7		
13	18.2	24.6	32.7	60.2	74.6	16.5	23.6	34.7	62.7	72.3		
14	17.4	23.5	30.4	54.7	70.3	16.3	22.5	31.8	53.7	70.2		
15	16.5	21.6	26.4	48.4	64.2	16.7	21.3	28.3	45.2	65.3		
Gentamycin (std.)	57.4	62.1	73.6	82.4	90.3	51.8	58.3	76.2	85.7	94.4		



FIG. 4. Cyclic voltammogram of [Cu(BAIE)<sub>2</sub>] .2H<sub>2</sub>O.

peak currents corresponding to a simple one electron process. The complexes also show a reversible peak in the negative region, characteristic of the Cu(II)/Cu(I) couple at Epc = -0.92 V, with the associated anodic peak at Epa = -0.35 V and  $\Delta$ Ep = 0.57 V for Cu(I) $\rightarrow$ Cu(II) oxidation.<sup>[35–37]</sup> The representative cyclic voltammogram of [Cu(BAIE)<sub>2</sub>] 2H<sub>2</sub>O complex is shown in Figure 4.

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