

Gold(I) Complexes of 2,2'-Biimidazolate Ligand: Syntheses and Spectral Properties of Hetero-polymetallic Complexes Having Ru₂Au₂ Core

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ABSTRACT: The reaction of $[Ru(L)_2(H_2biim)](ClO_4)_2$ [$L^1 = 2,2'$ -bipyridine (bpy) or $L^2 = 2$ -(phenylazo)pyridine (pap) and $H_2biim = 2,2'$ -biimidazole] with $Au(tht)Cl$ ($tht =$ tetrahydrothiophene) in presence of base in methanol produced a terametallic cationic complex $[Ru(L)_2(biim)_2Au_2]^{2+}$, $[1]^{2+}$ which was isolated as its perchlorate salt. The compounds were characterized by various spectroscopic techniques. ESIMS data of these fully corroborate with their formulation. Spectral data of all the polymetallic systems are reported and compared. The redox properties of the complexes are interesting. The complex $[Ru(bpy)_2(biim)_2Au_2](ClO_4)_2$ showed one irreversible metal based oxidation at 1.43 V whereas the compound $[Ru(pap)_2(biim)_2Au_2](ClO_4)_2$ showed one irreversible ligand based oxidation at 1.34 V. This type of binding mode of the biimidazolate anion containing Ru_2Au_2 core is rare in the literature. 'Metal complex as ligand' strategy provides a platform for the synthesis novel polymetallic complexes of gold(I).

KEYWORDS: Biimidazole ligand; Gold(I) complexes; Hetero-polymetallic complex; Self-assembly.

INTRODUCTION

The chemistry of polynuclear complexes obtained by the controlled assembly of mononuclear transition metal complexes is an area of considerable interests [1]. Transition metal complexes particularly of ruthenium and osmium are the subjects of extensive investigations due to their photophysical properties making them ideal components for photochemically and electrochemically driven molecular devices [2]. They are also prime candidates for application as luminophores for the detection of metal ions. The luminophore approach to the development of sensors has been widely used [3].

Oligonuclear complexes, which are bridged by π -conjugated ligands, have attracted as model compounds for the study of cooperative effects in, for example, homogeneous catalysis [4]. Studies of di- and polynuclear transition metal complexes with interesting structure and magnetic properties have gained much interest [5]. A variety of synthetic strategies have been applied to build such molecular architecture with different terminal and bridging ligands to facilitate ferro- and anti-ferromagnetic interactions among the metal centers. Synthesis and structural characterization of some mixed ligand

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1021-9986/2019/1/73-82

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polymetallic systems like M_2Ag_2 , M_4Cu_2 , and M_4Ni_2 by making use of unusual trimetallic coordination mode of the 2,2'-biimidazolate ion have been explored [5c, 6].

The controlled assembly of monometallic transition metal complexes of coordinately unsaturated bridging ligands can lead to the synthesis [7-19] of oligomers, polymers or clusters showing unusual structures and fascinating properties. In this context, monometallic complexes of 2,2'-biimidazole (H_2biim) and its derivatives are interesting due to their ability to enter into various modes of coordination (Scheme 1). The usual binding mode [20-27] of the conjugate dianion base $[biim]^{2-}$ is bis-bidentate (Type-A). This, however, can also bridge across [28-31] three metal centers simultaneously (Type-B) and thus provides a platform for design and construction of polymetallic systems with unusual structural features.

Synthesis and structural characterization of some mixed ligand polymetallic systems by making use of unusual trimetallic coordination mode of the 2,2'-biimidazolate ion have been explored. A series of di-nuclear complexes of ruthenium and osmium containing the terminal ligands 2,2'-bipyridine (bpy) and the bridging ligand 2,2'-biimidazole (H_2biim) are synthesized. The mono-nuclear complexes $[M(bpy)_2(H_2biim)]^{2+}$ ($M = Ru^{II}$ or Os^{II}) act as dibasic acids and undergo deprotonation to afford $[(bpy)_2M(biim)]$ which behave as reacting building units ("metal complex as ligand") [32] and react smoothly with other metal ions to produce hetero-polynuclear complexes.

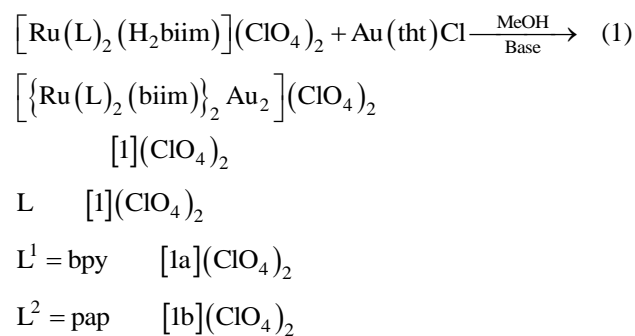
In recent years, the structure of a hetero-metallic complex with a Ru_2Ag_2 core wherein two $Ag(I)$ ions are held in proximity has been reported [28]. In this compound two units of a ruthenium complex, $[Ru(L)_2(biim)]$ assemble around two silver(I) ions using Type-B coordination. Since silver(I) has a strong preference for linear coordination, a tetrametallic coordination is expected. The novel structural features of the polymetallic Ru_2Ag_2 systems arose due to trimetallic binding of bridging $[biim]^{2-}$ ion. In view of our above results, it was incumbent on us to investigate the reactions of $[Ru(L)_2(biim)]$ further with other metal ions to establish the generality of this unusual coordination of biim. In this respect, copper(II) and nickel(II) ion which have the preference for tetra-coordination are known

to adopt a square planar geometry. It was anticipated that a trimetallic coordination mode of $[Ru(L)_2(biim)]$ with these metal ions would produce interesting mixed metal polymetallic systems (Scheme II). Heterometallic complexes having Ru_4Cu_2 and Ru_2Ni_2 are synthesized and reported [33].

In the presence of a strong π -acid co-ligand 2-(phenylazo)pyridine (pap), the complexes $[M(pap)_2(BiimH_2)]^{2+}$ ($M=Ru, Os$), exhibit relatively low pKa values (pKa: $M=Ru$, 4.2 and 8.0; $M=Os$, 3.8 and 6.5). The neutral conjugate base, $[M(pap)(Biim)]$, behave as a potential chelating ligand and react with appropriate metal complexes to yield di- and tri-metallic complexes.

The reaction of $[Ru(L)_2(H_2biim)](ClO_4)_2$ with $Au(tht)Cl$ solution [$L^1 = bpy$ and $L^2 = pap$]:

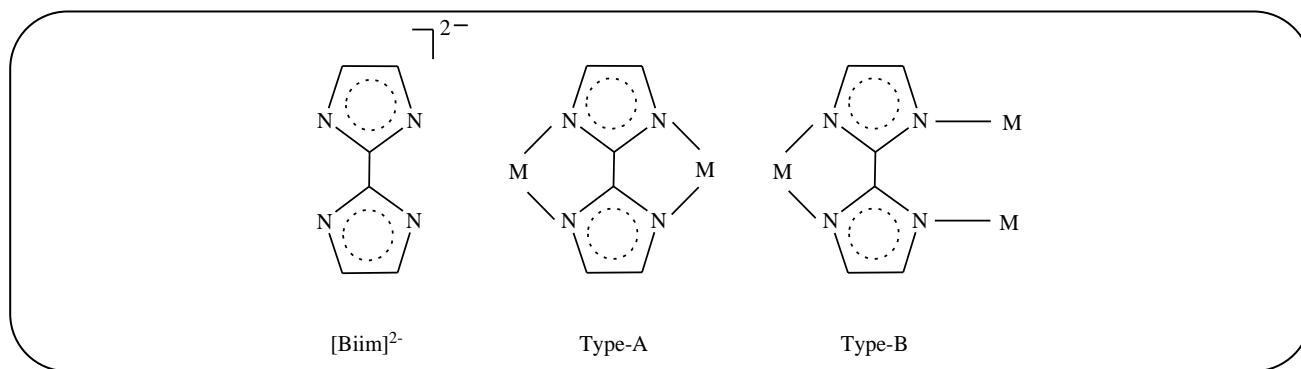
In search for the similar type of aurophilic [34-40] compounds, the reaction of $[Ru(L)_2(biim)]$ with $Au(tht)Cl$ in methanol had been performed [Equation(i)] and a tetranuclear complex having Ru_2Au_2 core resulted.



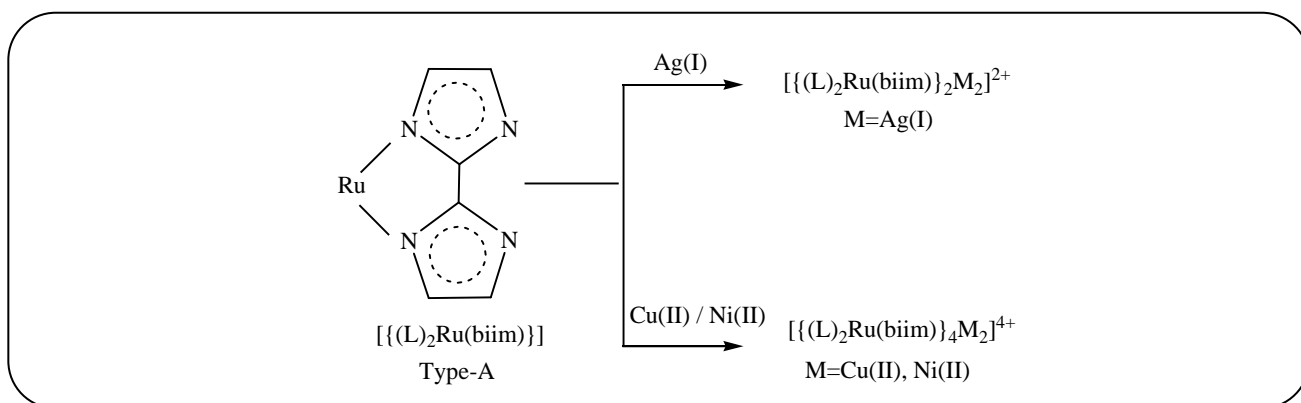
EXPERIMENTAL SECTION

Preparation of the complex, $\{[Ru(L)_2(biim)]_2Au_2\}(ClO_4)_2$, $[1](ClO_4)_2$ [$L = bpy$ or pap]

The compound $[Ru(bpy)_2(biim)](ClO_4)_2$ (0.1g, 0.134 mmol) was dissolved in methanol (30 mL) and NaOMe was added to deprotonate it. The colour of the solution became intense pink. To it, a solution of $Au(tht)Cl$ (42mg, 0.130 mmol) in acetone (10 mL) was added and the mixture was refluxed on a steam bath for 2h. The colour of the solution changed to reddish-pink. Recrystallization of the product for acetonitrile-toluene solvent mixture yielded crystalline compound $[1a](ClO_4)_2$. Yield: ca. 75%. A similar reaction of $[Ru(pap)_2(biim)]$ with $Au(tht)Cl$ in methanol afforded $[1b](ClO_4)_2$. In this case, dilute NEt_3 was used as a base. Yield ca. 80%. Chloro(tetrahydrothiophene)gold(I),



Scheme 1:



Scheme 2:

Au(tht)Cl was prepared by a published procedure reported earlier [41]. Anal. Calcd. for $C_{52}H_{40}N_{16}Cl_2O_8Au_2Ru_2$ (**1a**): C, 37.07; H, 2.38; N, 13.30. Found: C, 37.05; H, 2.40; N, 13.32; $C_{56}H_{44}N_{20}Cl_2O_8Au_2Ru_2$ (**1b**): C, 37.52; H, 2.46; N, 15.63. Found: C, 37.50; H, 2.45; N, 15.65.

Physical measurements

Elemental analysis of carbon, hydrogen, and nitrogen was carried out with a Perkin-Elmer 240C elemental analyser. Infrared Spectra were obtained in KBr disk ($4000-400\text{ cm}^{-1}$) using a Perkin Elmer 783 spectrophotometer. A JASCO V570 UV-VIS-NIR spectrophotometer was used to record electronic spectra in acetonitrile solutions. Quartz cell of path length 1 cm was used. 1H NMR Spectra measurements were done with a Bruker Avance DPX 300 Spectrophotometer in $CDCl_3$ or $DMSO-d_6$ and $SiMe_4$ was used as an internal standard. The ElectroSpray Ionization Mass Spectra (ESIMS) were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. The ESI capillary was set

at 3.5 kV and the cone voltage was 40 V. The spectra were collected in a 6 s scans and the print outs are averaged spectra of 6-8 scans. Electrochemical Measurements were done under dry nitrogen atmosphere on an EG&G PAR model 273A Potentiostat/Galvanostat based electrochemistry system. The data were collected at 298K by using a precision thermostat. All potentials were uncorrected for junction potentials. Potentials were referred against Standard Calomel Electrode (SCE). The value of ferrocenium-ferrocene couple under our experimental conditions was 0.40V. Electrical Conductance Measurements were measured in acetonitrile solution on a Systronics 304 Direct Reading Conductivity meter.

RESULTS AND DISCUSSION

The heteropolymetallic Au complex does not form good X-ray quality crystal in spite of several attempts for the structure determination. However, the mass spectral data along with other spectral as well as electrochemical data are in good agreement with the tetrametallic formulation of the compound similar to Ru_2Ag_2 core.

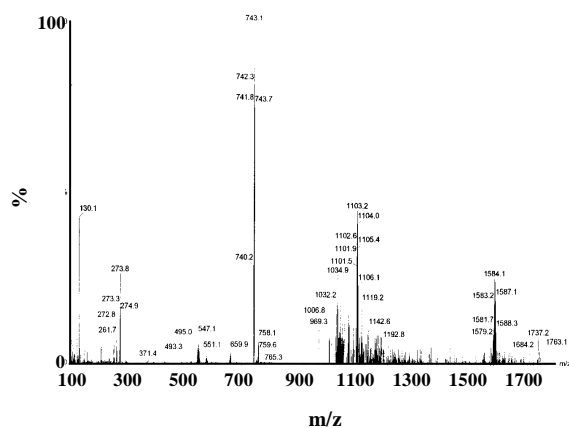


Fig. 1: ESI mass spectrum of $[Ru(bpy)_2(biim)_2]_2Au_2(ClO_4)_2$.

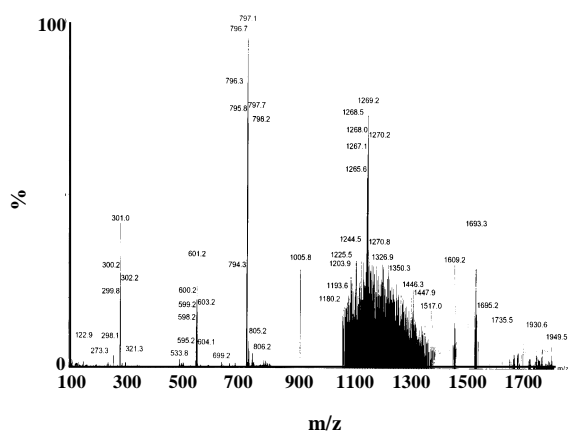


Fig. 2: ESI mass spectrum of $[Ru(pap)_2(biim)_2]_2Au_2(ClO_4)_2$.

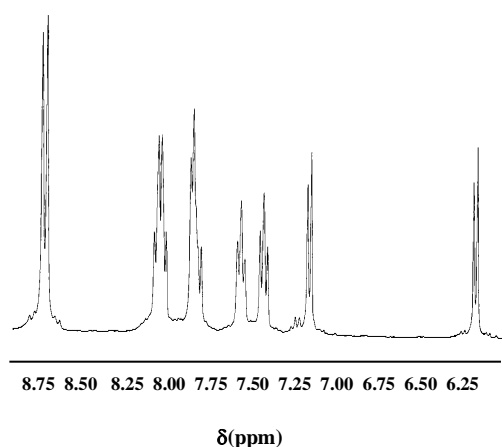


Fig. 3: 1H NMR spectrum of $[Ru(bpy)_2(biim)_2]_2Au_2$ in $DMSO-d_6$.

ESIMS Measurement

The ESIMS spectral data of $[Ru(L)_2(biim)_2]_2Au_2(ClO_4)_2$ strongly points to the formulation of the complexes. The positive ion ESI mass spectra of the complex $[1](ClO_4)_2$ are shown in Fig. 1 and Fig. 2, respectively. The multiply charged ions were generated due to loss of negative counter ions, which is denoted by $[M-nX]^{2+}$, where M and X represent the molecule and ClO_4^- , respectively. The complex $[Ru(bpy)_2(biim)_2]_2Au_2(ClO_4)_2$ exhibited peak at 1584.1 a.m.u. which is assigned to $[M-X]^+$, while that of 743.1 a.m.u. is due to $[M-2X]^{2+}$.

The pap analogue of the complex, $[Ru(pap)_2(biim)_2]_2Au_2(ClO_4)_2$ also showed similar peaks at 1693.3 and 797.1 a.m.u., respectively. Besides these, there are many weak peaks which may be due to fragmentation or unknown combination of fragmented ions. Thus the ESIMS measurement confirmed the actual composition of the complexes.

1H NMR Spectra

The 1H NMR spectrum of the compound $[Ru(bpy)_2(biim)_2]_2Au_2(ClO_4)_2$ was recorded in $DMSO-d_6$ and is displayed in Fig. 3. This showed resolved 1H NMR spectrum. From the spectral pattern, it is clear that the compound retains its C_2 -symmetry in solution and the spectral pattern is similar to the building block, $[Ru(bpy)_2(H_2biim)]^{2+}$. The signals from bipyridine protons appeared in the range 7.5 to 8.8 δ . Two imidazole protons resonate at 6.2 and 7.2 δ , respectively. The pap analogue of the compound, $[Ru(pap)_2(biim)_2]_2Au_2(ClO_4)_2$ showed similar spectral pattern with the building block, $[Ru(pap)_2(H_2biim)]^{2+}$. The signals from pap protons appeared in the range 7.2 to 9.0 δ and two imidazole protons resonate at 6.7 and 7.0 δ , respectively.

Electronic Spectra

Electronic spectral data of the Ru-Au complexes are collected and the representative spectrum of $[1a]^{2+}$ is displayed in Fig. 4 and the data are collected in Table 1. The spectral pattern of the compounds is similar to that of deprotonated building units, $[Ru(L)_2(biim)]$. The visible range absorption spectra of the complex $[Ru(bpy)_2(biim)_2]_2Au_2^{2+}$, $[1a]^{2+}$ are dominated by a strong band at 510 nm. This is assigned to metal to ligand charge transfer involving $Ru(t_{2g})$ and π^* (bpy). It also

**Table 1: Electronic spectral data for $[\{Ru(L)_2(biim)\}_2Au_2](ClO_4)_2$;
^a Data obtained from absorption spectra: solvent CH_3CN ; ^b Shoulder**

Compound	Absorption ^a λ_{max}/nm ($\epsilon/M^{-1}cm^{-1}$)
$[\{Ru(bpy)_2(biim)\}_2Au_2](ClO_4)_2$, $[1a](ClO_4)_2$	510(22535), 450 ^b (13840), 365 ^b (21320), 340(30575), 290(131275), 240(59095)
$[\{Ru(pap)_2(biim)\}_2Au_2](ClO_4)_2$, $[1b](ClO_4)_2$	540(15585), 360 ^b (26420), 315(39680), 230(38065)

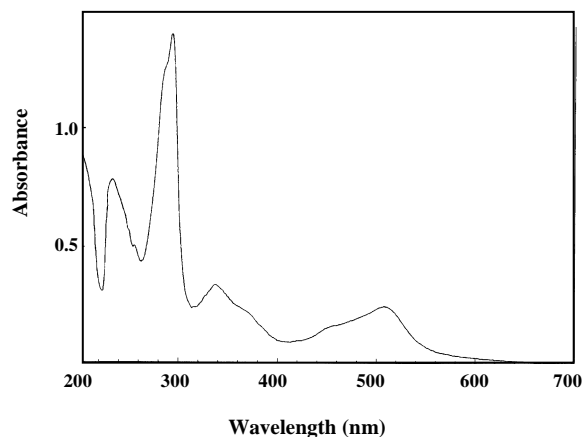


Fig. 4: Electronic spectrum of $[\{Ru(bpy)_2(biim)\}_2Au_2](ClO_4)_2$ in CH_3CN .

showed bands at 450, 365, 340, 290 and 240 nm, respectively. The pap analogue of the compound, $[\{Ru(pap)_2(biim)\}_2Au_2]^{2+}$, $[1b]^{2+}$ also showed bands at 540, 360, 315 and 230 nm of which the lowest energy transition is assigned as metal to ligand charge transfer involving $Ru(t_{2g})$ and π^* (pap). Notably, the intensities of the metal to ligand charge transfer transitions are [25, 42-44] almost double of the intensity for the corresponding monomer, $[Ru(L)_2(biim)]$. This indeed is a strong indication of the presence of two units of $[Ru(L)_2(biim)]$ in the Ru-Au complexes. The intense absorptions in the UV region are due to the superposition of pap, bpy and biimidazolate based $\pi \rightarrow \pi^*$ transitions.

Redox Properties

All the compounds are characterized by cyclic voltametry [45]. Representative voltammograms of $[1a]^{2+}$ are displayed in Fig. 5. All potentials are referenced to the Standard Calomel Electrode (SCE). The complex $[\{Ru(bpy)_2(biim)\}_2Au_2](ClO_4)_2$ showed one irreversible anodic response at 1.43 V. This may be assigned to metal based oxidation. In contrast, the pap analogue of the compound $[\{Ru(pap)_2(biim)\}_2Au_2](ClO_4)_2$ showed one irreversible ligand based oxidation at 1.34 V.

The cathodic responses in the complexes are due to the reductions of coordinated ligands. It may be noted here that the ligand, pap being a superior π -acid, undergoes reductions at lower cathodic potentials than the bpy analogue.

Infrared Spectra

Infrared spectral measurements of the complexes were carried out in the range 4000-400 cm^{-1} in KBr disk. The spectrum consists of characteristic absorption [46] for the coordinated pap, bpy and $[biim]^{2-}$ ligands. A strong band near 1250 cm^{-1} is assigned as N=N vibration of the coordinated pap ligands. Notably, the N=N stretching frequency in the free pap appears at 1425 cm^{-1} . The lowering of frequency may be attributed to the presence of extensive $d(M) \rightarrow \pi^*(pap)$ backbonding in the ground state of ruthenium(II). The C=N stretching frequency appeared at ca. 1600 cm^{-1} . All the complexes showed bands near 1100 and 630 cm^{-1} assignable to ionic perchlorate. A broad transition at ca. 3400 cm^{-1} was recorded which is due to the presence of water molecule as a solvent of crystallization.

In acetonitrile solution, the complex, $[1]^{2+}$ behaves [47] as a 1:2 electrolyte ($\Lambda_M = 220 \Omega^{-1}cm^2mol^{-1}$ in 1×10^{-3} M acetonitrile).

CONCLUSIONS

By unusual trimetallic coordination of biimidazolate dianion $[biim]^{2-}$, we are able to synthesize heteropolymetallic complexes having Ru_2Au_2 core. The complex should show metallophilic interactions in their complexes similar to Ru-Ag complexes. Hydrogen-bonded assemblies of ruthenium(II)-biimidazole complex cations and cyanometallate anions are important due to their photophysics. A number of nitrogen and sulphur donor homo- and hetero-nuclear bimetallic complexes of Pd and Pt are also important in the context of anticancer activity and interaction with DNA [48]. Synthesis of multimetallic systems using biimidazolate ligand in other

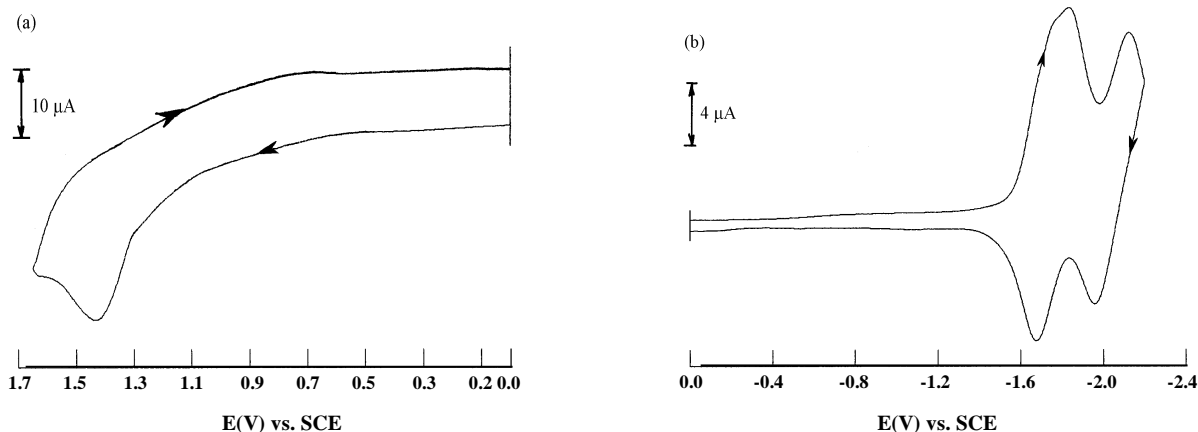


Fig. 5: Cyclic voltammograms of $[\{Ru(bpy)_2(biim)\}_2Au_2](ClO_4)_2$ in CH_3CN containing $0.1M NEt_4ClO_4$ as supporting electrolyte: (a) anodic scan using platinum electrode and (b) cathodic scan using glassy-carbon electrode.

coordinations and studies of their photophysical properties and biological interaction are also in progress.

Acknowledgement

I am thankful to the Indian Association for the Cultivation of Science, Kolkata for giving me funding in doing the research work there. I owe to my parents for giving me constant inspiration in doing the research work.

Received : Apr. 25, 2017 ; Accepted : Jan. 15, 2018

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