

# Synthesis and characterization of Co (II) and Cu (II) complexes with bidentate O,O-donor of 2,3-dihydro-9,10-dihydroxy-1,4-anthracenedione

Palash Setua<sup>1</sup>, Surajit Maiti<sup>2</sup>, Gobinda Prasad Sahoo<sup>2\*</sup>, and Animesh Patra<sup>2\*</sup>

<sup>1</sup>Department of Chemistry, Pingla Thana Mahavidyalaya, Maligram-721140, India

<sup>2</sup>Postgraduate Department of Chemistry, Midnapore College, Midnapore- 721101, India

**Abstract:** My present work is to investigate the synthesis of new Co(II) and Cu(II) complexes with the commercially obtained bidentate O,O-donor ligand (HL=2,3-dihydro-9,10-dihydroxy-1,4-anthracenedione) in 2:1 ligand to metal ratio with the general formula  $ML_2$  (M= Co, Cu) having square planar geometry. The complexes are characterised by elemental analysis and electronic spectral studies such as UV-VIS spectroscopy and cyclic voltammetry. These study shows that the ligand behaves as a bidentate chelating ligand.

**Keyword:** Metal complex, Anthracenedione; UV-VIS spectroscopy, Cyclic Voltammetry.

\*Corresponding author: E-mail: animeshpatrar1@yahoo.com; gobindaprasadsahoo@gmail.com

## I. INTRODUCTION

Antraquinone, is an aromatic organic compound, more preferably as group of functionally diverse aromatic compound, structurally related to anthracene, having the parent structure 9,10-anthracenedione, where keto groups are located on the central ring, [1] is a building block of many dyes and is used in bleaching pulp for papermaking.

Antraquinones are one of such compounds which occur naturally in some plants, fungi and insects where they serve as a basic skeleton for their pigments [2]. Both the natural and synthetic antraquinones have wide spread application throughout all industry and medicinal chemistry [3]. Natural and synthetic antraquinones have attracted all researchers due to their biological activities such as antitumor [4-6], anti-inflammatory [7], antimalarial [7,8], antimicrobial [9], antifungal [10], antiviral and anti-HIV properties [11,12]. Antraquinones and their derivatives are also used as antioxidants [13], dyes [14] or in photo imaging [15]. It is reported that substituted 1,4-anthracenediones are used to quench bacterio rhodopsin tryptophan fluorescence.

Metal complexes of antraquinones have attracted considerable attention due to their remarkable importance in medicinal, pharmaceutical field, field of analytical chemistry and high molecular chemistry [16]. It is of interest that some of metabolic products produced by microorganisms especially by pathogenic organisms are found to be chelate reagents such as kojic acid [17], fusaric acid [18], and hydroxyl antraquinones. Flumiani [19] has reported on the copper chelates of some hydroxyl antraquinones, in which he concluded that the presence of

hydroxyl group at the alpha position was decisive for the formation of normal chelate of 2:1, whereas for the formation of an addition compound the presence of a hydroxyl group at the beta position is decisive.

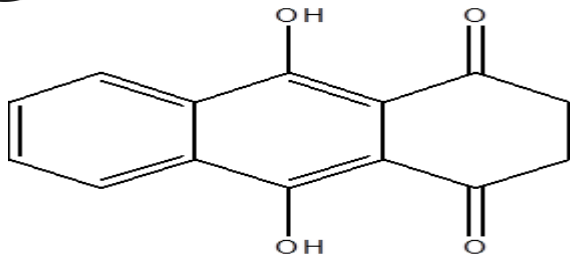
In this respect, present work was done by using one of the substituted 1,4-antraquinones named 2,3-dihydro-9,10-dihydroxy-1,4-anthracenedione having synonym Leucoquinizarine as a ligand. The complexes are prepared by mixing ligand and metal (II) acetate in 2:1 molar ratio respectively. The prepared complexes are characterised by elemental analysis, electronic spectral data and cyclic voltammetry study; described in details.

## II. EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES

All chemicals and reagents were obtained from commercial sources and used as received, unless otherwise stated. Solvents (MeOH, DMF) were distilled from an appropriate drying agent. The complexes were synthesised by using the following procedure. Electronic absorption spectra were recorded on a SHIMADZU UV-1800 spectrophotometer. Cyclic voltammetry study has been examined.

### ABOUT THE LIGAND (HL)

The ligand, 2,3-dihydro-9,10-dihydroxy-1,4-anthracenedione (Leucoquinizarin) was obtained from commercial sources with the known physical properties. The structure of the ligand was given below in fig 1:



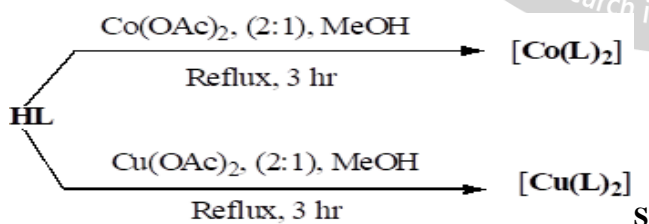
**Fig.1.** Structure of 2,3-dihydro-9,10-dihydroxy-1,4-anthracenedione

### PREPARATION OF Co (II)-LIGAND COMPLEX (1)

To prepare Cobalt (II) complex (1), a common procedure was followed described below, using the cobalt acetate salt and the organic ligand (HL) in the molar ratio 1:2 respectively. For this, 0.81 gm (2 mmol) of the ligand was dissolved in a round bottom flask by DMF and methanolic solution of 0.415 gm (1 mmol) of the cobalt(II) acetate was added drop wise into the ligand with constant stirring condition for 2 hours followed by refluxing 2 hours. The crude product was collected from the vacuum filtration in a crucible and then washed with methanol and kept aside to dry. The reaction was done in the methanolic medium.

### PREPARATION OF Cu (II) LIGAND COMPLEX (2)

To prepare Copper (II) complex (2) the reactants were properly weighed such that the ratio of ligand and metal became 2:1 respectively. For this, 0.81 gm (2 mmol) of ligand was dissolved in a round bottom flask by DMF and methanolic solution of 0.443 gm (1 mmol) of the copper (II) acetate was added drop wise into the ligand with constant stirring condition for 2 hours, followed by refluxing the mixture for 2 hours. The crude product was collected by vacuum filtration in a crucible, washed with methanol and kept aside to dry. The reaction was done in methanolic medium.



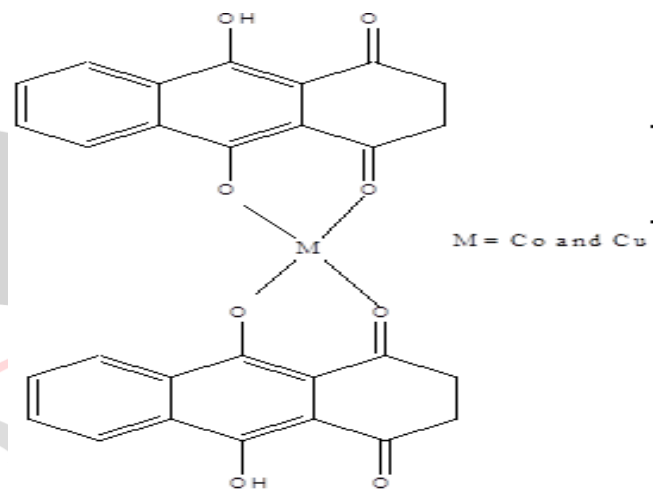
**CHEME 1:** Synthetic strategy of the Co(II) and Cu(II) complexes

**Table-1.** Elemental analysis of Ligand and complexes

Formula	Compound	Molecular Weight	Colour	Calculated percentage			Melting point (°c)
				C (%)	H(%)	M(%)	
C <sub>14</sub> H <sub>10</sub> O <sub>4</sub>	HL	242	Straw yellow	69.42	4.13	–	153
C <sub>14</sub> H <sub>10</sub> O <sub>4</sub> Co	1	541	Black	62.12	3.33	10.89	> 200
C <sub>14</sub> H <sub>10</sub> O <sub>4</sub> Cu	2	545	Brown	61.59	3.29	11.64	>230

### III. RESULT AND DISCUSSION

The direct reaction of 2,3-dihydro-9,10-dihydroxy-1,4-anthracenedione (HL) with Co(II) and Cu(II) ions in methanolic medium using 2:1 ligand to metal ratio afford complexes of the type [ML<sub>2</sub>], where M=Co(II) and Cu(II). In these complexes the ligand acts as a bidentate chelating ligand through O,O-donor sites. These complexes are air stable, coloured solids, amorphous and soluble in DMF and DMSO. The elemental analysis data of the ligand and their complexes (given in the table 1) are consistent with the calculated results from the empirical formula of each compound. The probable structure of the complexes is given in fig. 2.



**Fig.2.** Probable structure of complexes

#### IV. ELECTRONIC ABSORPTION SPECTRAL STUDY

The electronic spectral study of the ligand and the complexes were recorded in DMSO at room temperature and combined diagram of them are summarized in the given fig.3. The spectra of the ligand exhibit main peak nearly at 325nm and 400nm. All these spectra indicate due to intramolecular  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions for the aromatic ring. An intense band at 338 nm (for Co complex) is assigned to  $\pi \rightarrow \pi^*$  intra-ligand transition along with the intense bands at 447 nm corresponding to the d-d transition. A broad band observed for copper complex at 452 nm is well in agreement with the d-d transition for copper (II) in the square planar geometry.

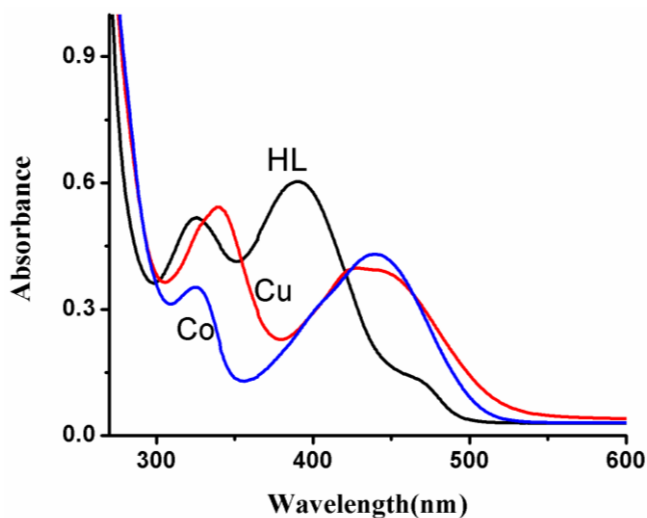


Fig. 3. UV spectra of ligand (HL) and its corresponding complexes

#### V. CV STUDY

The electrochemical study of Cu(II) complex was examined by cyclic voltammetry using Pt-disk working electrode and a Pt-wire auxiliary electrode in dimethylformamide using [n-Bu<sub>4</sub>N]ClO<sub>4</sub> (0.1 M) as the supporting electrode. The cyclic voltammograms exhibit quasi reversible transfer process with a reduction peak at  $E_{pc} = -0.07V$  with a corresponding oxidation peak at  $E_{pa} = 0.35V$  for Cu complex at a scan rate interval 50-400 Mv/s. this electrode potential data indicates copper(II) complex is a Cu(II)/Cu(I) couple given in the fig.4. The ratio of cathodic to anodic peak height was less than one. However, the peak current increases with the increase of the square root of scan rates. From the data indicates the redox couple is related to a quasi-reversible one electron transfer process controlled by diffusion.

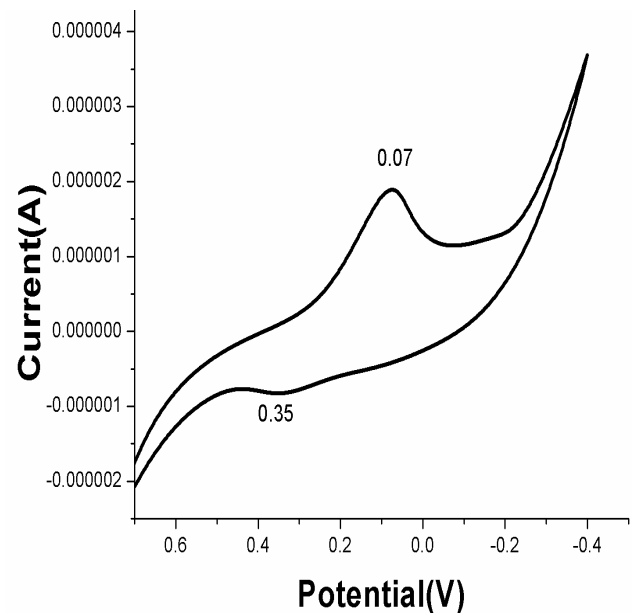


Fig.4. Cyclic Voltammetry study of Cu(II) complex

#### VI. CONCLUSION

Here the synthesis and characterisation of mononuclear Co(II) and Cu(II) complexes with a bidentate O,O-donor chelating ligand have been performed. These complexation affords a new class of metal ligand complex with the general formula [ML<sub>2</sub>]. Two complexes are synthesised by a common method and characterised by spectroscopic method and electrochemical analysis. On the basis of the above result and discussion one can assume that the metal ions are bonded to the ligand through the Oxygen of keto(C=O) group, Oxygen of -OH group of the ligand and the metal complexes have square planer geometry. The cyclic Voltammetric study indicates copper (II) is readily reduced to Cu (I) and the data indicates the redox couple is related to a quasi-reversible one electron transfer process controlled by diffusion.

#### VII. ACKNOWLEDGEMENT

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