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## Synthesis and characterization of heterotrinnuclear bis ( $\mu_2$ -chlorido)dicopper (II) mono zinc(II) complexes derived from succinoyldihydrazones

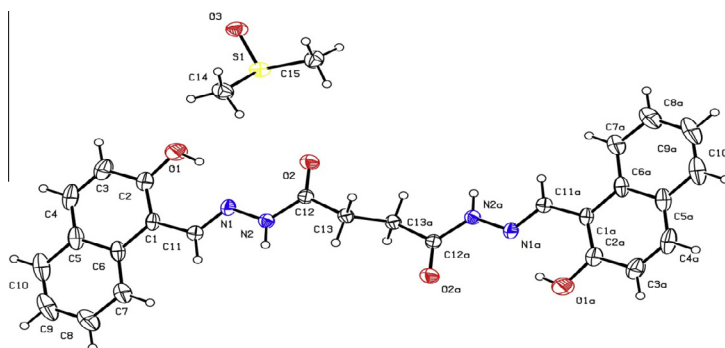
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### HIGHLIGHTS

- Three new zinc (II)–copper (II) heterotrinnuclear complexes have been synthesized.
- The structure of the ligand  $H_4L^2$  has been established by X-ray crystallography.
- The dihydrazone ligand is present in enol form in all of the complexes.
- Copper centre has tetragonally distorted octahedral stereochemistry.
- EPR parameters indicate that copper centre has doublet state as the ground state.

### GRAPHICAL ABSTRACT

Three new heterotrinnuclear copper (II)–zinc (II) complexes having composition  $[Cu_2Zn(L)(\mu_2-Cl)_2(H_2O)_6] \cdot 2H_2O$  ( $H_4L = N, O$  donor schiff base ligands) were prepared and characterised by UV–vis, IR, magnetic moment and EPR spectroscopy. The electron transfer reactions for the complexes have been studied by cyclic voltammetry. Single crystal structure of  $H_4L^2$ .



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### ABSTRACT

Three new zinc (II)–copper (II) heterometallic trinuclear complexes of the composition  $[ZnCu_2(L^n)(\mu_2-Cl)_2(H_2O)_6] \cdot 2H_2O$  ( $H_4L^n = H_4L^1, H_4L^2, H_4L^3$ ) have been synthesized from substituted succinoyldihydrazones ( $H_4L^n$ ) in methanol medium. The composition of the complexes has been established on the basis of data obtained from analytical, mass spectral studies and molecular weight determinations in DMSO. The structure of the ligand  $H_4L^2$  has been established by X-ray crystallography. The structure of the complexes has been discussed in the light of molar conductance, magnetic moment, electronic, EPR, IR and FT-IR spectral studies. The molar conductance values for the complexes fall in the region  $1.2$ – $1.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in DMSO solution indicating that all of these are non-electrolyte. The magnetic moment values suggest weak M–M interaction in the structural unit of the complexes. The dihydrazone ligand is present in enol form in all of the complexes. Copper centre has tetragonally distorted octahedral stereochemistry. The EPR parameters of the complexes indicate that the copper centre has doublet state as the ground state. The electron transfer reactions of the complexes have been investigated by cyclic voltammetry.

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## Introduction

Copper is a biologically important metal and occurs in enzymes and metalloproteins like ascorbate oxidase copper monooxygenase, copper dioxygenase, superoxide dismutase, cytochrome oxidase and blue oxidase [1]. In living organisms, it is often present in mono-, di-, or trinuclear assemblies. When blue copper site in multinuclear copper oxidases is substituted by a redox innocent mercuric ion, O<sub>2</sub>-bond cleavage by the fully reduced trinuclear site is significantly impeded [2]. The multimetallic copper complexes are also important because of their relevance in the development of novel functional materials showing molecular ferromagnetism [3] and specific catalytic properties [4]. Homo- and hetero-trimetallic copper complexes offer the opportunities to test magnetic exchange models on more complicated systems. Copper (II) complexes find application as catalyst for the oxidation of alcohols into aldehydes and ketones [5].

Hydrazones are special kind of polyfunctional Schiff base ligands derived from condensation of organic acid hydrazines and o-hydroxy aromatic aldehydes and ketones [6–10] which have potential for yielding homo- and hetero-metallic complexes. The dihydrazones derived from condensation of succinoyldihydrazines and o-hydroxy-aromatic aldehydes and ketones are unique in the sense that their succinoyl fraction offers greater flexibility in three dimensional space because of their capability for free rotation about C–C single bond as compared to those in which the two hydrazone groupings are joined together either directly (oxaloyl) or through phenyl or pyridyl groups. Such dihydrazones, although, might exist in only one configuration in free state, in metal complexes can exist in staggered, anti-cis or syn-cis configuration [10]. The resulting dihydrazones contain salicylaldimine, 2-hydroxy-naphthalaldimine and 5-bromo-salicylaldimine in their molecular skeleton. Further, as we go from salicylaldimine dihydrazone to naphthalaldimine dihydrazone to 5-bromo-salicylaldimine dihydrazone, the bulkyness and electronegativity both increase in the same order. It is quite interesting to see how the properties of the complexes change as we go from one dihydrazone to next one.

A survey of literature reveals that although some isolated studies are available on metal complexes of succinoyldihydrazones [10] and related dihydrazones [6–10] yet the synthesis and characterization of heterotrinnuclear complexes of dihydrazones is quite meagre [11]. Moreover, a systematic study on trinuclear metal complexes of succinoyldihydrazones is absent to the best of our knowledge inspite of their highly flexible nature. In view of the above importance of copper complexes, absence of work on heterotrinnuclear complexes of succinoyldihydrazones and highly flexible polyfunctional nature of succinoyldihydrazones, it was of interest to synthesize the heterotrinnuclear copper complexes of the title dihydrazones (Fig. 1) and to characterize them by various physico-chemical and spectroscopic studies. Further, it was of

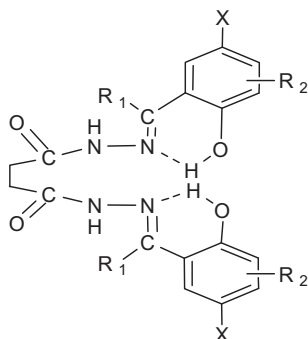


Fig. 1. Structure of ligands.

interest to investigate the electron transfer reactions of the complexes by cyclic voltammetry. The results of such an investigations are presented in this paper.

R <sub>1</sub>	R <sub>2</sub>	X	Dihydrazone ligand
H	H	H	Disalicylaldehydesuccinoyldihydrazone ( <b>H<sub>4</sub>L<sup>1</sup></b> )
H	5,6-benzo	H	Bis(2-hydroxy-1-naphthaldehyde) succinoyldihydrazone ( <b>H<sub>4</sub>L<sup>2</sup></b> )
H	H	Br	Bis(5-bromosalicylaldehyde) succinoyldihydrazone ( <b>H<sub>4</sub>L<sup>3</sup></b> )

## Experimental

### Materials

Zinc acetate dihydrate, copper chloride dihydrate, diethyl succinate, hydrazine hydrate, substituted salicylaldehyde and 2-hydroxy-1-naphthaldehyde were E-Merck, Qualigens, Hi-Media or equivalent grade reagents.

### Instrumentation and measurement

Copper and zinc were determined by standard literature procedure [12]. Chloride was determined as AgCl [12]. C, H, N were determined by micro-analytical method using Perkin-Elmer, 2400 CHNS/O Analyser II. All conductance measurements were made at 1 kHz using Wayne Kerr B905 Automatic Precision Bridge. A dip-type conductivity cell having a platinised platinum electrode. The cell constant was determined using a standard KCl solution. Room temperature magnetic susceptibility measurements were made on a Sherwood Magnetic Susceptibility Balance MSB-Auto. Diamagnetic corrections were carried out using Pascals Constant [13]. Electronic spectra of the complexes were recorded in DMSO solution at  $\sim 10^{-3}$  M concentration on a Perkin-Elmer Lambda-25 spectrophotometer. Electron paramagnetic resonance spectra of the complexes were recorded at X-band frequency on a Varian E-112 E-Line Century Service EPR spectrometer using TCNE ( $g = 2.0027$ ) as an internal field marker. Variable temperature experiments were carried out with a Varian Variable Temperature accessory. Infrared spectra were recorded on a BX-III/FT-IR Perkin-Elmer Spectrophotometer in the range 4000–400 cm<sup>-1</sup> in KBr discs and 600–50 cm<sup>-1</sup> in CsI discs. The molecular weights of the complexes were determined in DMSO by freezing point depression method. Mass losses were determined by heating the complexes at 110 °C and 180 °C in an electronic oven. APCI mass spectra of the complexes were recorded on a water Zg 4000 Micromass Spectrometer in DMSO solution. Cyclic voltammetric measurements of the compounds in DMSO were done using a CH instruments Electrochemical analyzer under dinitrogen. The electrolytic cell comprises of three electrodes, the working electrode was a Pt disk while the reference and auxiliary electrodes were Ag/AgCl separated from the sample solution by a salt bridge; 0.1 mol L<sup>-1</sup>, TBAP was used as the supporting electrolyte.

### Molecular weight determination

The molecular weight of the complexes were determined in DMSO ( $K_f = 4.07$ ) [14] as a solvent, by lowering of the freezing point of DMSO (f.p. 18.5 °C) using Beckman's freezing point depression instruments. The instrument consisted of a Beckman thermometer and a stirrer with a non-conducting handle of wood fitted into a tube through a rubber stopper fixed at its upper end. This tube was supported through a rubber stopper in a bigger glass

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