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# Synthesis, characterization, structure and properties of heterobimetallic complexes $[CuNi(\mu\text{-}OAc)\,(\mu\text{-}OH)\,(\mu\text{-}OH_2)\,(bpy)_2](BF_4)_2$ and $[CuNi(bz)_3(bpy)_2]\,ClO_4$ from 2,2′ bipyridine

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ABSTRACT

Heterobimetallic complexes of the composition $[CuNi(bpy)_2\,(\mu\text{-}OAc)\,(\mu\text{-}OH)\,(\mu\text{-}OH_2)](BF_4)_2$ (1) and $[CuNi(bz)_3\,(bpy)_2]ClO_4$ (2) were synthesized in moderate yield through solid state reaction and have been characterized by elemental analyses, molar conductance, mass spectra, magnetic moment, EPR, UV–Vis, IR spectroscopies and cyclic voltammetry. The ground state in complex (1) is doublet while that in complex (2), the ground state is a mixture of doublet and quartet, respectively. The structure of the complexes has been established by X-ray crystallography. The electron transfer reactions of the complexes have been investigated by cyclic voltammetry.

## 1. Introduction

Study of heterometallic complexes constitutes an active area of research in contemporary inorganic chemistry because of their importance in magneto-structural, bioinorganic chemistry and catalysis [1–4]. The bimetallic combinations are found in the active sites of many metalloenzymes such as acetyl co-enzyme A synthase [5,6], heme-copper oxidases [7], and hydrogenases [8,9], and dinuclear hydrolases [10]. In the enzymes, the metal ions discharge their functions either by redox cooperativity or by acting as a support for another metal ion. It has been found that heterometal compounds are potential novel magnetic materials [11] and simple source precursors for the synthesis of mixed-metal oxides [12]. Hence investigation of heteropolynuclear complexes might be more informative in comparison to those of homopolynuclear complexes. However, the catalysis by coordination compounds is still a field of continuous exploration not only for hetero-multimetallic complexes but even for heterobimetallic ones [13,14].

The design of new heterobimetallic complexes presents a challenge in comparison to monometallic or homo-metallic complexes as linking two electronically different metal centres in close proximity to each other is highly dependent on ligand architecture and close matching of the hard/soft donor/acceptor properties of the metal and ligand[4]. Several synthetic approaches are available in the literature to design discrete polynuclear complexes. One of them consists of the introduction of bidentate or tridentate ligands and multi-atom bridging ligands [15]. Another method consists of utilization of spontaneous self-assembly strategy, which represent a thermodynamically based assembly of free metal ions with many simple, flexible ligands that impart little or no geometrical restrictions [16]. This synthetic strategy, the direct synthesis is based on self-assembly of the building blocks, generated in situ, into crystalline materials. Further, use of compartmental ligands, which are organic molecules, being able to hold together two or more metal ions [17] have also been done. Metal complexes have also been used as ligands to give multi-atom complexes via a reaction between a preformed metal-containing ligands and second type of metal ions via coordination donors [18]. The solution to this problem lies in the utilization of a spontaneous self-assembly strategy, the synthesis, which is based on self-assembly of building blocks, generated in situ, into crystalline materials [19]. As we more interested in synthesizing multi-atom system, we used simple carboxylic ligand in our work in an optimism that it would lead to desired system.

A survey of literature reveals that although some heterobimetallic complexes incorporating copper and nickel have been

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synthesized and characterized and their properties investigated [17,20], still much remains to be learnt about catalysis promoted by multimetallic complexes containing copper and nickel in same metal complex systems. In view of the above importance of multimetallic complexes in general and heterobimetallic complexes in particular and meager amount of work on catalysis by heterometallic complexes of copper and nickel, we set out our aim to isolate heterometal complexes containing copper as one metal and other first row transition metal ions as second metal from simple carboxylic acids and characterize them by various physicochemical, and spectroscopic techniques and establish their structure by X-ray crystallography. Further, it was decided to explore the catalytic properties of the resulting complexes in organic reactions. Accordingly, the present communication reports the results of preparation and characterization of two copper (II) and nickel (II) heterobimetallic complexes and short study of their catalytic property.

## 2. Experimental

### 2.1. Materials and general methods

Copper and nickel were determined by standard literature procedure [21]. C, H and N were determined by microanalytical method using Perkin-Elmer 2400 CHNS/O Analyzer 11. Mass spectra of the complexes were recorded on a Water ZQ-4000 Micromass Spectrometer. Conductance measurements were done using Wayne Kerr B 95 Automatic Precision Bridge with a dip-type conductivity cell having a platinised platinum electrode. The cell constant was determined using a standard KCl solution. Room temperature magnetic data of the powdered sample were measured using Sherwood Scientific Magnetic Susceptibility Balance. The magnetic data were corrected for diamagnetism using Pascal's constants [22]. The X-band EPR spectra at room temperature and at variable temperature were recorded from powdered samples and from $CH_3CN$ solution on a Varian E-112 ESR Spectrometer using TCNE ($g = 2.0027$) as an internal standard. Solid state and solution electronic spectra were recorded on a Perkin-Elmer Lambda-25 spectrophotometer. Infrared spectra in the range 4000 - 200 $cm^{-1}$ were recorded as KBr discs by using a BX-III/FTIR Perkin Elmer Spectrophotometer. Cyclic voltammogram were recorded on a CH Electrochemical Analyzer using a standard three electrode assembly (glassy-carbon working, Pt wire auxiliary, SCE reference) and 0.1 M $NBu_nClO_4$ as supporting electrolyte. Gas Chromatographic (GC) analysis was performed on a Bruker 430-GC Gas Chromatograph equipped with a 30 m × 0.32 mm x 0.5 μm HP-Innowax capillary column and a flame ionization detector (FID).

### 2.2. Synthesis of $[CuNi(\mu\text{-}OAc)\ (\mu\text{-}OH)\ (\mu\text{-}OH_2)\ (bpy)_2](BF_4)_2$ (1)

Warning: perchlorate salts are potential explosive. Although during the preparation of the complex, no detonation tendencies of the reaction mixture was observed, caution is advised and it is recommended that small quantities of the reactants be handled.

A mixture of $Ni(OAc)_2.4H_2O$ (0.125 g, 0.5 mmol), $Cu(OAc)_2.H_2O$ (0.1 g, 0.5 mmol), 2, 2′ bipyridine (0.393 g, 2.52 mmol), $NaBF_4$ (0.165 g, 1.5 mmol) was taken in a pestle mortar and heated in a hot air oven at 150 °C for 5 h and recrystallized from methanol solution. The violet colour crystals were isolated from methanol solution after 1 day. Yield: 62.7%. Colour: Dark violet. Anal (%): Calcd for $C_{22}H_{22}\ N_4\ O_4B_2\ F_8$ CuNi: C, 37.60; H, 3.16; N, 7.98; Cu, 9.05; Ni, 8.40. Found: C, 37.40; H, 3.13; N, 8.09; Cu, 8.81; Ni, 8.63. Mass ($m/z$): Expt. 529.15, theo. 528.23. Molar conductance ($\Omega^{-1}mol^{-1}cm^2$): 210.7. Magnetic Moment (μB): 2.92 B.M. IR data ($cm^{-1}$ KBr): 1560 s ($\nu_{as}$ COO), 1444 ($\nu_s$ COO), 775 s (out-of -plane deformation mode of 2,2′-bipyridine), 1083 s ($BF_4$), 737 m (in-plane ring deformation mode of 2,2′-bipyridine). Electronic spectrum: $CH_3CN$ Solution, $\lambda_{max}$ nm ($\varepsilon_{max}$, $dm^3\ mol^{-1}\ cm^{-1}$): 307 (3650), 674 (185), 892 (95).

### 2.3. Synthesis of $[CuNi(bz)_3(bpy)_2]ClO_4$ (2)

This complex was also prepared by essentially the above method mixing $Ni(OAc)_2.4H_2O$ (0.125 g, 0.5 mmol), $Cu(OAc)_2.H_2O$ (0.1 g, 0.5 mmol), benzoic acid (0.43 g, 3.5 mmol), 2, 2′ bipyridine (0.197 g, 1.26 mmol), $NaClO_4$ (0.123 g, 2.5 mmol) was powdered in a pestle mortar for 1 h and then heated in a hot air oven for 5 h at 150 °C. The reaction mixture was then cooled to room temperature, followed by dissolution in hot methanol. The resulting hot violet solution was filtered in hot condition to remove small quantities of undissolved residue and then cooled to room temperature. Violet single crystals suitable for X-ray analysis were successfully obtained from the resultant solution after 1 day. Yield**:** 70.5%. Colour: Dark violet. Anal (%): Calcd for $C_{41}\ H_{31}\ N_4\ O_{10}$ ClCuNi: C, 54.85; H, 3.46; N, 6.24; Cu, 7.08; Ni, 6.48. Found: C, 54.40; H, 3.50; N, 6.46; Cu, 7.35; Ni, 6.60. Mass ($m/z$): Expt. 796.20, theo. 797.49. Molar conductance ($\Omega^{-1}mol^{-1}cm^2$): 93.3. Magnetic Moment (μB): 2.70 B.M.IR data ($cm^{-1}$, KBr): 1599 s, 1567 s ($\nu_{as}$COO), 1446 s, 1384 s $\nu_s$ (COO); 729 s (out-of- plane ring deformation mode of 2,2′-bipyridine), 678 s (in-plane ring deformation mode of 2,2′-bipyridine), 1055 $\nu$ ($ClO_4^-$). Electronic spectrum ($\varepsilon_{max}$, $dm^3\ mol^{-1}\ cm^{-1}$)]: Solid, $\lambda_{max}$ (nm): 250, 550–1000 sbr); Solution, $\lambda_{max}$ (nm): 300 (9000), 625 (223).

### 2.4. X-ray crystallography

A dark violet crystal of complexes 1 and 2, suitable for X-ray analysis was obtained from methanol solution at room temperature. The intensity measurement were made on Gemini-co-mounted fine focus dual source single Crystal X-Ray diffractometer using graphite-monochromated Mo $K_\alpha$ radiation ($\lambda = 0.7107$ Å) at 292 K. Crysalispro Agilent technology software were used for data collection, indexing reflection and determination of lattice constant, empirical absorption correction. The structure were solved by direct method (SHELXT-2014) and refined full matrix least square (SHELXL-2014) on $F^2$. Anisotropically thermal parameters were employed for the non-hydrogen atom and isotropic parameter for all hydrogen atoms. The position of the hydrogen atoms were placed at a geometrical position after the final refinements.

Crystallographic data of the complexes have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1484766, 1484767 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

## 3. Results and discussion

### 3.1. Synthesis and characterization

The complexes were identified by elemental analyses and mass spectrometry. The observed $m/z$ value 529.23 (theo: 528.23), 796.20 (theo: 797.24) in the mass spectra Figs. (S3 and S4) clearly demonstrate the formation of the heterodinuclear complex ions $[CuNi(\mu\text{-}OAc)\ (\mu\text{-}OH)\ (\mu\text{-}OH_2)\ (bpy)_2]^{2+}$ (1) and $[CuNi(bz)_3(bpy)_2]^{2+}$ (2), respectively, rather than a mixture of mononuclear or corresponding homodinuclear copper or nickel complexes. However, when only Cu(II) or Ni(II) acetate is employed in the synthesis,