Synthesis and Electrochemistry of M(II) \( \text{N}_2\text{O}_2 \) Schiff Base Complexes: X-Ray Structure of \{\text{Ni[Bis(3-chloroacetylacetone)ethylenediimine]}\} \\

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The synthesis and characterization of \([\text{Ni(BCE)}]\) and \([\text{Cu(BCE)}]\) (where BCE = bis(3-chloroacetylacetone)ethylenediimine) are described. The coordination geometry of \([\text{Ni(BCE)}]\) was determined by X-ray crystallography. It was found to be planar and four coordinate in the solid state. The electrochemical properties of \(\text{M(Chel)}\), where \(\text{M} = \text{Co(II)}, \text{Ni(II)}\) and \(\text{Cu(II)}\), and \(\text{Chel} = \text{BAE}\) (bis(acetylacetone)ethylenediimine), \(\text{BBE} = \text{bis(benzoylacetone)ethylenediimine}\), \(\text{BFE}\) (bis(1,1,1-triflouroacetylacetone) ethylenediimine) and BCE ligands were investigated in DMF and DMSO as solvents. The oxidation potentials changed from left to right in the periodic table in the trend: \(\text{Co} < \text{Ni} < \text{Cu}\), while the reduction potentials changed according to the trend: \(\text{Ni} > \text{Co} > \text{Cu}\). The oxidation potentials of \(\text{M(II)}\) to \(\text{M(III)}\) (\(\text{M} = \text{Ni and Cu}\)) increased according to the Schiff base ligands in the trend: \(\text{BAE} < \text{BBE} < \text{BCE} < \text{BFE}\), while the reduction potentials followed a reverse trend: \(\text{BAE} > \text{BBE} > \text{BCE} > \text{BFE}\). The oxidation potentials of \(\text{M(II)}\) to \(\text{M(III)}\) increased according to the solvent in the trend: \(\text{DMSO} < \text{DMF}\).

Keywords: Cobalt(II), Nickel(II), Cu(II), Schiff base complexes, Electrochemistry

INTRODUCTION

Schiff bases have been widely used as ligands because of the high stability of coordination compounds with different oxidation states. The \(\pi\)-system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well. Transition metal Schiff base complexes have been studied as catalysts in organic redox and electrochemical reduction reactions [1-4]. Cyclic voltammetry has been a useful instrument to study the mechanisms of the catalysis property of metal Schiff base complexes and their reactivity [2,4-5]. To explore the catalytic activity, the electrochemical properties of \(\text{Co(III)}\) BAE and Salen Schiff base complexes were studied intensively [6-12]. Also, the electrochemical properties of tetradentate Ni(II) and Cu(II) Schiff base complexes were investigated [13-19]. The Ni(I) complexes can act as powerful catalysts on chemical or electrochemical reduction of alkyl and aryl halides [15,20]. Also, the Ni(I) and Ni(III) oxidation states play a crucial role in the activity of several hydrogenase reactions [21]. The electronic effects of the different Schiff base complexes with different donor and acceptor functional groups were studied by cyclic voltammetry method. The results show that there is a good relationship between the electron-donating power of Schiff base ligands and redox potentials [19,22-24].

In the present work, we report the synthesis and characterization of \([\text{Ni(BCE)}]\), and \([\text{Cu(BCE)}]\). The electrochemical properties of \(\text{Co(II)}, \text{Ni(II)}\) and \(\text{Cu(II)}\) complexes with tetradentate BAE Schiff base ligands (Fig. 1)
**EXPERIMENTAL**

**Chemicals and Apparatus**

All the chemicals and solvents were used as received, except for the 3-chloroacetylacetone which was distilled to be used. All the Schiff base ligands were prepared using the known methods [12,26-28]. The M(II) BAE, BBE and BFE complexes were prepared following the literature procedure [26]. The elemental analyses were determined on a Heraeus CHN-O-RAPID elemental analyzer. Infrared spectra were recorded as KBr discs on a Perkin Elmer 781 spectrophotometer in the 4000-400 cm\(^{-1}\) range. UV-Vis spectra were recorded on a JASCO V-570 spectrophotometer in the 190-900 nm range.

Cyclic Voltammetric measurements were carried out under argon in DMF and DMSO solutions with 0.1 M tetraethylammonium perchlorate as the supporting electrolyte at room temperature using an autolab modeler electrochemical system (ECO Chemie, Ultrecht, The Netherlands) equipped with a PSTA 20 module and driven by GPES (ECO Chemie). A conventional three electrode cell was used with an Ag/AgCl (saturated KCl)/3 M KCl reference electrode, a Pt wire as counter electrode and a glassy carbon electrode as working electrode.

**X-Ray analysis.** The X-ray crystallography measurements were made on a STOE IPDS-II diffractometer with graphite monochromated Mo-K\(_{\alpha}\) radiation. For this complex, a yellow plate crystal with dimensions 0.34 × 0.207 × 0.07 mm was chosen and mounted on a glass fiber and used for data collection. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of diffraction data from 3763 unique reflections. Data were collected at a temperature of 298(2) K to a maximum 2\(\theta\) value of 58.46° in a series of \(\omega\) scans in 1° oscillations and integrated using the Stoe X-AREA [29] software package. The numerical absorption coefficient, \(\mu\), for Mo-K\(_{\alpha}\) radiation was 1.752 mm\(^{-1}\). A numerical absorption correction was applied using X-RED [30] and X-SHAPE [31] softwares. The data were corrected for Lorentz and Polarizing effects. The direct method structure solution [32], different Fourier calculations, and full-matrix least-squares refinement against \(F^2\), were performed using X-STEP32 crystallographic software package [33]. All hydrogen atoms were included in the structure factor calculations at idealized positions and were allowed to ride on the neighboring atoms with relative isotropic displacement coefficients. Atomic factors were used from the International Tables for X-ray Crystallography [34]. Crystal data and the details of data collection and refinement are summarized in Table 1.

**Synthesis of the [Ni(BCE)] Complex**

Nickel(II) acetate tetrahydrate (1 mmol, 0.2487 g) was added to a refluxed solution of BCE (1 mmol, 0.2933 g) Schiff