

New insight into electrochemical behavior of copper complexes and their applications as bifunctional electrocatalysts for CO₂ activation



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ABSTRACT

The electrochemical behaviors of two copper Schiff base complexes, [*N,N'*-bis(2-*R*-phenyl-salicylidene-aminato)Cu(II)] complex, (CuL₂-Me for *R*=Me, and CuL₂-Cl for *R*=Cl), and [*N,N'*-bis(salicylaldimine)propylenediimino Cu(II)] (CuL'), as well as the stability of their reduced forms in a *N,N*-dimethylformamide (DMF) solution were studied using cyclic voltammetry. We also investigated the homogeneous activity of the CuL' complex as a bifunctional electrocatalyst for direct electrocatalytic reduction of CO₂ to CO₂^{•-} and indirect CO₂ activation by the product of O₂ electrocatalytic reduction to yield peroxydicarbonate anions, C₂O₆²⁻. In each case, the complex exhibited an excellent electrocatalytic behavior for the activation of carbon dioxide. Both electrocatalytic reduction of CO₂ and that of O₂ are ligand-based. However, the complex promotes the electrocatalytic reduction of CO₂ better as compared to the free ligand.

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1. Introduction

The use of carbon dioxide has received considerable attention due to its natural abundance, nontoxicity and good potentiality as a renewable carbon resource. However, the thermodynamic stability and relative kinetic inertness of CO₂ may cause difficulties in its transformation [1–5]. Therefore, devising simple and efficient methodologies for the activation of CO₂ is a demanding challenge for organic chemists. Numerous catalytic methods like photocatalytic [6,7], photoelectrochemical [8] and electrochemical [9] techniques have been developed for CO₂ activation. The electrochemical reduction of CO₂ at bare electrode surfaces needs a high overpotential [10]. Heterogeneous or homogeneous electrocatalysts, such as Schiff base complexes, have been used to resolve this problem [11,12]. Moreover, among the possible activators of CO₂, more attention has been paid to superoxide radical anions, O₂^{•-} [13,14]. The O₂^{•-} produced by the electroreduction of O₂ in aprotic solvents activates CO₂ to yield peroxydicarbonate anions, C₂O₆²⁻ [13,14]. Peroxydicarbonate has been used as a carboxylating reagent for synthesis of organic carbamates and carbonates from amines and alcohols, respectively [13–15].

The aim of the present work was to study the effects of ligand structure on the stability of the reduced forms of copper Schiff base complexes by comparing the electrochemical behavior of [*N,N'*-bis

(2-*R*-phenyl-salicylideneaminato)Cu(II)] complexes and [*N,N'*-bis(salicylaldimine)propylenediimino Cu(II)] complex. We also investigated the homogeneous activity of the CuL' complex as a bifunctional electrocatalyst for direct and indirect electrocatalytic activation of CO₂. In each case, the complex exhibited an excellent electrocatalytic behavior for the activation of carbon dioxide. This was along with an increase of the cathodic current as well as a decrease of the over-potential more than 300 mV and 1200 mV in the direct and indirect electrocatalytic activation of CO₂, respectively. It was, indeed, in contrast to what occurs in processes in the absence of the complex.

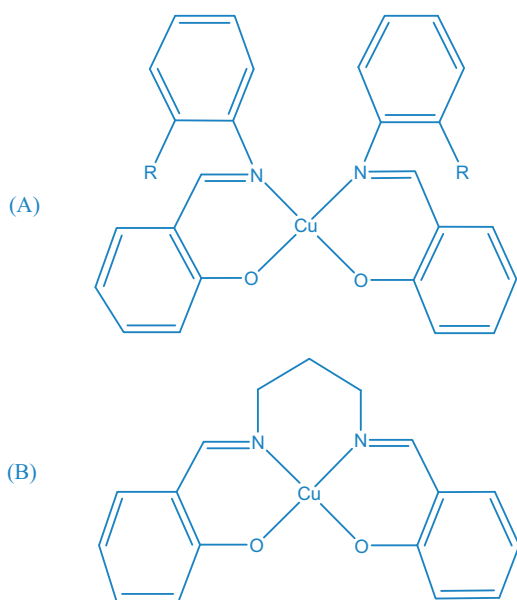
2. Experimental

2.1. Chemicals and apparatus

The [*N,N'*-bis(2-*R*-phenyl-salicylideneaminato)Cu(II)] complex, (CuL₂-Me for *R*=Me, and CuL₂-Cl for *R*=Cl), and [*N,N'*-bis(salicylaldimine)propylenediimino Cu(II)] (CuL') were prepared as previously described [16,17]. The structures of copper(II) complexes are shown in Scheme 1. Briefly, the Schiff base ligand (L) was synthesized through the condensation reaction of salicylaldehyde (10 mmol) and 2-methylaniline for (L-Me) or 2-chloroaniline for (L-Cl) (10 mmol). Then, it was treated in methanol (20 mL) at room temperature for 30 min, thereby an orange powder was obtained with a yield of 72%. The powder was then filtered off and recrystallized in a diethyl ether solution at room temperature [16]. To fabricate CuL₂-R, 2.5 mmol (0.499 g) of copper(II), acetate

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Scheme 1. Structure of (A) $[N,N'$ -bis(2-*R*-phenyl-salicylideneaminato)Cu(II)] (CuL_2-R) and (B) $[N,N'$ -bis(salicylaldimine)propylenediimino Cu(II)] (CuL') complexes.

monohydrate was slowly added to 40.0 mL of a methanol solution containing 5.0 mmol of Schiff base, and the resulting solution was stirred for 1.0 h at room temperature. The resulting brown precipitate was collected by copper(II) filtering and washed with 10.0 mL of methanol. The copper complexes were recrystallized from dichloromethane/acetone (1:1 v/v), through which brown plates like crystals were obtained with a yield of 40%. The corresponding specifications of the product are as follows:

Anal. Calc. for CuL_2-Me , $C_{28}H_{24}CuN_2O_2$: C, 69.48; H, 5.00; N, 5.79. Found: C, 69.57; H, 4.80; N, 5.85%. IR (KBr, cm^{-1}): $\nu_{C=N}$ = 1607, ν_{C-O} = 1326.

Electronic spectra in $CHCl_3$ included d-d, λ_{max} (ϵ) 635 nm ($148 M^{-1} cm^{-1}$). For CuL_2-Cl , green-brown plate-like crystals were obtained with a yield of 45%. The corresponding specifications of the product are as follows:

Anal. Calc. for $C_{26}H_{18}Cl_2CuN_2O_2$: C, 59.50; H, 3.46; N, 5.34. Found: C, 59.37; H, 3.43; N, 5.38%. IR (KBr, cm^{-1}): $\nu_{C=N}$ = 1606, ν_{C-O} = 1326.

Electronic spectra in $CHCl_3$ included d-d, λ_{max} (ϵ) 655 nm ($123 M^{-1} cm^{-1}$). The Schiff base H_2salpn was prepared by a general method [17], involving the condensation reaction between two equivalents of salicylaldehyde and one equivalent of the appropriate diamine. The copper complex was prepared by a general method [18,19], using the reaction between copper acetate and the Schiff base ligand (1:1 ratio) in methanol with a yield of 50%. The corresponding specifications of the product are as follows:

Anal. Calc. for $C_{17}H_{16}CuN_2O_2$: C, 59.38; H, 4.69; N, 8.15. Found: C, 59.12; H, 4.63; N, 8.21.

All the other chemicals were of analytical reagent grades and were purchased from Merck and used without any further purification. The purity of CO₂ and argon (Ar) was 99.995%, and they were used directly.

Cyclic voltammetry was carried out using EG&G PARSTAT 2273 equipped with Power Suite software, in a conventional three-electrode electrochemical cell containing a glassy carbon electrode (GCE) as a working electrode, a Pt wire as a counter electrode and Ag/Ag⁺ (0.01 M AgNO₃ in 0.1 M TBAP acetonitrile solution) as a reference electrode. All the potentials were measured and reported versus the Ag/Ag⁺ (0.01 mol L⁻¹ AgNO₃ in a 0.1 mol L⁻¹ TBAP acetonitrile solution) reference electrode.

3. Results and discussion

3.1. Electrochemistry of the complexes

The voltammograms of 1.0 mmol L⁻¹ of CuL_2-Cl obtained in a DMF solution containing 0.1 mol L⁻¹ TBAP at a glassy carbon electrode in Ar atmosphere at a potential range of 1.1 V to -2.30 V is shown in Fig. 1. In general, the complex exhibits both metal-localized and ligand-localized redox processes [11,20]. On the cathodic potential scan, reduction of the complex proceeds through four reduction peaks located at -0.38 V (peak I), -0.50 V (peak II), -0.73 V (peak III) and -2.00 V (peak IV). During the anodic potential scan, two irreversible oxidations with oxidation peak potentials, 0.22 V (peak V) and 1.00 V (peak VI), appear. Peaks II and III are metal-centered and are related to successive reductions of copper(II) to copper(I) and copper(I) to copper(0), while the other two reduction processes (peaks I and IV) and the irreversible oxidation peak VI are ligand-localized [19,21]. The cyclic voltammogram of the ligand (L-Cl) was also recorded in similar conditions (Fig. S1 of Supporting information). A comparison of Fig. 1 and Fig. S1 indicates that peaks I, IV and VI are ligand-localized redox processes, and peaks II, III and V are metal-localized redox processes. In Fig. 2, voltammograms (a)–(e) show the cyclic voltammograms of CuL_2-Cl in different potential ranges. As it can be seen, when the potential is scanned to more negative than that for peak III (voltammograms (a)–(c)), peak V is observed. The reduction of copper(I) of CuL_2-Cl to copper(0) is responsible for peak III [20,21]. Because the copper(0) complex is unstable, the metal copper is deposited on the electrode surface. The oxidation of the deposited copper to copper(II) occurs on the positive scan (peak V) which has the characteristics of a surface-confined process [22]. On the other hand, when the potential is scanned to -0.6 V (voltammogram (d)), peak V is not observed, but peak II' appears. Also, redox couple II/II' has the characteristics of a diffusion process. This redox couple is related to the redox reaction of the Cu(II)/Cu(I) complex. Disappearance of peak V oxidation signifies the lack of electrodeposited copper on the electrode surface. It means that the reduction of the copper(I) complex to copper(0) has not occurred under these conditions. To ascertain the possible deposition of copper on the electrode surface, controlled potential coulometry was carried out at applied potential of -0.73 V (peak III potential). The appearance of the

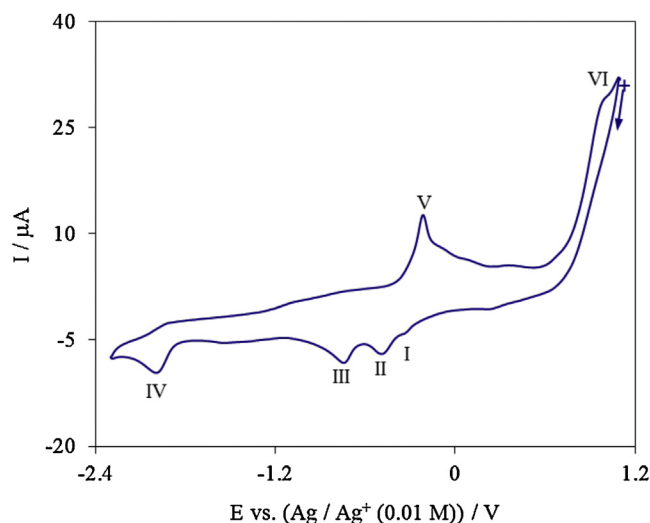


Fig. 1. Cyclic voltammograms of a 1.0 mmol L⁻¹ of CuL_2-Cl complex in DMF (0.1 mol L⁻¹ TBAP) at a glassy carbon electrode and at a scan rate of 100 mV s⁻¹ in an Ar atmosphere.

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