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Salen Ligand Complexes as Electrocatalysts for Direct Electrochemical Reduction of Gaseous Carbon Dioxide to Value Added Products

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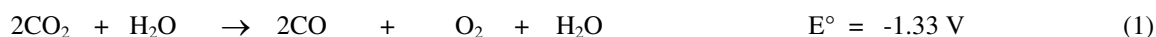
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Abstract CO₂ being linear and centrosymmetric molecule, is very stable and the electrochemical reduction of CO₂ requires energy. Moreover, the CO₂ electroreduction proceeds at significantly higher applied voltage than thermodynamically required. In this concern, salen ligand H₂L^{NO₂}, and its corresponding Ni(II) and Cu(II) complexes are synthesized and being reported for the first time as electrocatalysts for CO₂ electroreduction. Both the metal complexes are active for CO₂ reduction and surprisingly result in formation of C₁ and C₂ hydrocarbons. The complexes are found very efficient to minimize overpotential required for the reaction as compared to their pure metal counterparts. Thus, the present study opens up a new class of metal complexes for the efficient electrochemical reduction of CO₂ having the potential to generate hydrocarbons at lower overpotentials.

Keywords Electrochemical reduction of CO₂; Faradaic efficiency; Hydrocarbons; Metal complex electrocatalysts; Salen ligand

1. Introduction

Utilization of CO₂ for curbing the global warming menace is one of the highly investigated fields in the present scenario. In this respect, the electrocatalytic reduction of CO₂ (ERC) may pave possibly a better way to mitigate and utilize CO₂, along with the generation of high calorific value fuels. Moreover, the use of renewable energy required for the CO₂ reduction can be stored in the form of the fuels.¹⁻⁵ Equations (1-3) represent formation of a few of the high calorific value products using electrochemical reduction of CO₂. The equations show full cell reaction, where 2, 8, and 12 moles of electrons are utilized for the formation of one mole of CO, CH₄, and C₂H₄, respectively, at corresponding standard cell potentials. Thus ERC may be helpful not only for the reduction of CO₂ and generation of the conventional energy resources but also for the storage of renewable energy.





Though the electrochemical reduction of CO_2 offers advantage of the formation of value added products but the process is quite energy intensive. Most of the energy is used up towards conversion of CO_2 by utilizing one-electron to form $\cdot\text{CO}_2^-$ anion radical, which has bent geometry. Generally, metals such as Cu, Ru, Mo, *etc.* have been studied for the ERC process because of their ability to undergo multi-electron reduction of CO_2 forming higher hydrocarbons and/or alcohols.⁶⁻⁸ However, large activation overpotential is required for the formation of such reaction products using metals.⁹ Therefore, metal complexes are being studied in order to reduce the activation overpotential using well designed ligand and central metal atoms.^{2,9,10} Macrocyclic metal complexes, such as Fe porphyrins; Mn, Cu, Zn phthalocyanins; and Ru bipyridines *etc.* have been extensively studied for CO_2 electroreduction.¹¹⁻¹⁷ Most of the systems resulted in the two-electron reduction of CO_2 , forming CO and/or HCOO^- . A few of the workers also reported six and eight-electron reduction mechanism of ERC resulting in CH_3OH and CH_4 formation using Mn, Zn porphyrins; and Cu, Ga and Ti phthalocyanines, respectively.¹⁸⁻²⁰ Thus the synergetics of suitable metal and ligand in metal complex may have greater role in the formation of high calorific value products as well as lowering down the overpotential. In the present study, first time the use of salen ligand metal complex is being reported as the electrocatalyst for direct electrochemical reduction of the gaseous CO_2 .

Salen ligand complexes are well known for their ability to chemically catalyze various reactions.²¹⁻²⁴ Therefore, Gambarotta *et al.* studied the bifunctional salen ligand complex containing nucleophilic cobalt (I) and an alkali cation for CO_2 capture. They have found very encouraging results, where acidic-basic (bifunctional) sites present in the metal complex played a role in binding the CO_2 .²⁵ Infact, this inculcated the idea to bind the CO_2 at the site and simultaneously reduce it at the electrode. Moreover, there is no study on such complexes for CO_2 electroreduction. Hence, the potential of salen complexes needs to be explored in the field of ERC. In this effort, the primary objective of the paper is to evaluate the salen metal complexes for the electrochemical reduction of CO_2 for the formation of value added products. To establish and evaluate the ERC, Ni and Cu were used to form salen metal complex electrocatalysts. Cu is well known to facilitate the formation of hydrocarbons while Ni mostly results in undesired H_2 production with meager formation of CO.²⁶⁻²⁸ Therefore, these metals were chosen to understand the effect of salen metal complex over ERC. It may be noted that the direct use of gaseous CO_2 for the electrochemical reduction of CO_2 (dERC) is being used.²⁹

2. Experimental

2.1 Materials

The 4-nitro-*o*-phenylenediamine was procured from Alfa Aesar. Potassium bicarbonate (KHCO_3), *N,N*-dimethylformamide (DMF), $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were purchased from Loba Chemie. Acetonitrile (CH_3CN), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, triethylamine (Et_3N), ethanol (EtOH) and salicylaldehyde were procured from Merck. CDCl_3 for NMR spectroscopy was purchased from Sigma Aldrich. Pt/C (40wt% Pt) was purchased from ElectroChem, Inc. USA. All the chemicals were used without further purification and de-ionized water was used in

all the experiments unless stated otherwise. Gas diffusion layer from CeTech was used as backing layer for electrocatalyst film to form electrode. Nafion membrane was procured from DuPont, USA.

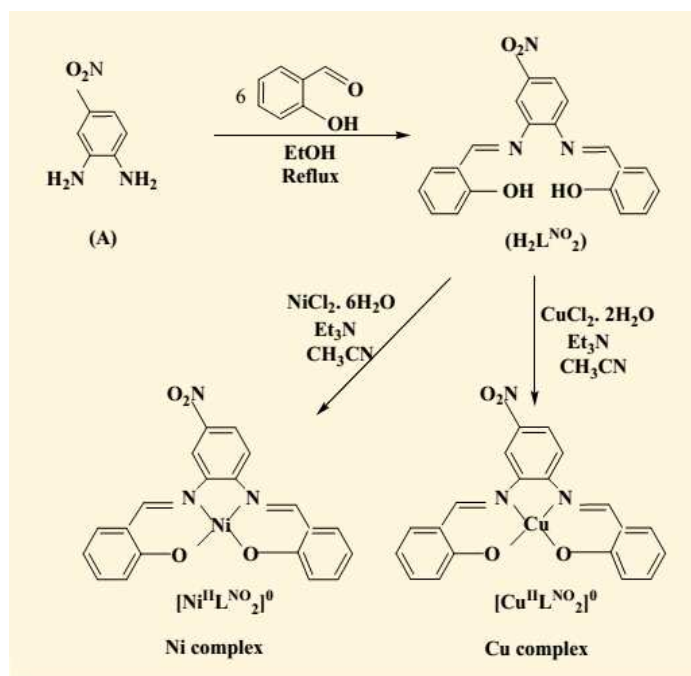
2.2 Method

2.2.1 Characterization techniques

The synthesized ligand and metal complexes were characterized using Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance spectroscopy (NMR), high-resolution mass spectrometry (HRMS), CHN analysis, and electrochemical half-cell studies. FTIR spectra were recorded in the range of 500-4000 cm^{-1} using Perkin Elmer FTIR spectrometer by grinding the sample with KBr (IR grade). The NMR spectrum was recorded at 400 MHz frequency using Varian, Mercury Plus nuclear magnetic resonance spectrometer. To know the mass of the ligand, the spectrum was obtained using Agilent high-resolution mass spectrometer. CHN analysis was carried out in EuroEA elemental analyser. Electrochemical tests (cyclic voltammetry (CV) and chronoamperometry) were performed using potentiostat/galvanostat (CH Instruments Inc.). Product analysis was carried out using gas chromatography (GC) (Nucon 5765).

2.2.2 Synthesis of the salen ligand ($\text{H}_2\text{L}^{\text{NO}_2}$) and corresponding complexes

4-Nitro-*o*-phenylenediamine (**A**) contains a highly electron withdrawing $-\text{NO}_2$ group at the *ortho* position of one of the two amine groups (Scheme 1) and hence, the $-\text{NO}_2$ group reduces the nucleophilic character of the amine group. Therefore, the ligand, $\text{H}_2\text{L}^{\text{NO}_2}$, was synthesized by reacting a large excess (6 equivalents) of salicylaldehyde with **A** in ethanol under refluxing condition. The ligand upon reacting with equivalent amounts of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ / $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in acetonitrile in the presence of Et_3N provided Ni complex/ Cu complex, respectively. The synthesis route of the ligand and the metal complexes is shown in the scheme 1.



Scheme 1. Synthesis route to formation of the ligand and corresponding Ni(II) and Cu(II) complexes (A = 4-Nitro-*o*-phenylenediamine)

2.2.2.1 Synthesis of salen ligand ($\text{H}_2\text{L}^{\text{NO}_2}$)

A suspension of 4-Nitro-*o*-phenylenediamine (1.53 g, 10 mmol) was prepared in ethanol solution (20 mL). Salicylaldehyde (7.33 g, 60 mmol) was added dropwise into the prepared suspension to form a mixture. The resulting mixture was heated to reflux for 20 hours. A yellow precipitate appeared after cooling the mixture at 30°C. The precipitate was filtered, washed thoroughly with EtOH, and finally air dried to get $\text{H}_2\text{L}^{\text{NO}_2}$. Yield: 78%. FTIR (KBr pellet cm^{-1}): 3447, 1615, 1566, 1511, 1478, 1341, 1277, 1194, 1153, 910, 843, 765. ^1H NMR (CDCl_3 , 400 MHz): δ 6.97 (td, $J = 7.6$ Hz, 1.2 Hz, 2H), 7.05 (t, $J = 8.0$ Hz, 2H), 7.33 (d, $J = 8.8$ Hz, 1H), 7.41-7.46 (m, 4H), 8.15 (d, $J = 2.4$ Hz, 1H), 8.18 (dd, $J = 8.8$ Hz, 2.4 Hz, 1H), 8.65 (s, 1H), 8.73 (s, 1H), 12.50 (s, 1H), 12.56 (s, 1H). HRMS (+) m/z for $[\text{C}_{20}\text{H}_{15}\text{N}_3\text{O}_4 + \text{H}]$: calcd, 362.1135; found, 362.1115.

2.2.2.2 Synthesis of metal complexes $[\text{Ni}^{\text{II}}\text{L}^{\text{NO}_2}]$ and $[\text{Cu}^{\text{II}}\text{L}^{\text{NO}_2}]$

In a CH_3CN solution (10 mL) of $\text{H}_2\text{L}^{\text{NO}_2}$ (0.180 g, 0.5 mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.120 g, 0.50 mmol)/ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.090 g, 0.50 mmol) and triethyl amine (0.2 mL) were added and the resulting solution was stirred at 30°C for five hours. During this time the color of the solution changed to reddish-brown (for Ni complex)/yellowish-brown (for Cu complex) with concomitant precipitation of the solid with the said color. Further, the solid was filtered, washed thoroughly with CH_3CN , and air dried.

Ni complex: Yield: 80%. FTIR (KBr pellet cm^{-1}): 3433, 1610, 1576, 1509, 1335, 1279, 1248, 1198, 1155, 914, 836, 768. Anal. calcd for $[\text{C}_{20}\text{H}_{13}\text{N}_3\text{O}_4\text{Ni}]$: %C, 57.55; %H, 3.14; %N, 10.07. Found: %C, 59.46; %H, 3.14; %N, 9.66.

Cu complex: Yield: 82%. FTIR (KBr pellet cm^{-1}): 3320, 1612, 1575, 1509, 1334, 1259, 1189, 1154, 875, 818, 760. Anal. calcd for $[\text{C}_{20}\text{H}_{13}\text{N}_3\text{O}_4\text{Cu}\cdot\text{CH}_3\text{CN}\cdot 0.5\text{H}_2\text{O}]$: %C, 55.93; %H, 3.63; %N, 11.87. Found: %C, 56.04; %H, 3.26; %N, 11.92.

2.2.3 Preparation of electrodes and membrane electrode assembly

Pt/C (40wt% Pt) with nafion dispersion (5wt%) as binder, was used to prepare the anode electrocatalyst ink. The ink was coated over the gas diffusion layer using spraying technique and dried to get the anode. For the cathode (or working electrode), the ink was prepared by dispersing the metal complex electrocatalyst in appropriate solvent along with nafion dispersion. The electrocatalyst ink was then coated over the gas diffusion layer followed by drying. For the preparation of pure metal electrocatalysts (cathode) of Ni and Cu, electroplating was done over the gas diffusion layer using electroplating baths of $\text{NiSO}_4\cdot 6\text{H}_2\text{O}$ and $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ respectively. Suitable additives were added in respective baths to get the smooth deposition of metals over the gas diffusion layer. The electrocatalyst loading for anode and cathode was kept as $0.5 \text{ mg}\cdot\text{cm}^{-2}$ and $2 \text{ mg}\cdot\text{cm}^{-2}$, respectively. The cation exchange membrane (nafion-117) was treated using the standard procedure³⁰ before the experiments. The membrane electrode assembly was prepared by sandwiching the nafion membrane in between anode and cathode at a particular temperature and pressure.

2.2.4 Electrochemical tests

The half-cell studies were conducted in three-electrode cell assembly using Ag/AgCl as reference electrode and Pt wire as counter electrode. The working electrode was prepared using $2 \text{ mg}\cdot\text{cm}^{-2}$ electrocatalyst loading supported over the gas diffusion layer. The cyclic voltammetry test was carried out in aqueous (0.5M KHCO_3) and non-aqueous (dimethylformamide, DMF) electrolytes at the scan rate of $0.01 \text{ V}\cdot\text{s}^{-1}$. In all the half-cell studies, the potential is reported with respect to standard hydrogen electrode (SHE), unless stated otherwise. The full cell studies were carried out in an electrochemical reactor as described elsewhere.^{31,32} The electrode area of $3\times 3 \text{ cm}^2$ was used for both anode and cathode of the electrochemical reactor. The cathode side of the reactor was fed with CO_2 gas (99.995%) with the flow rate of $20 \text{ mL}\cdot\text{min}^{-1}$ adjusted by rotameter. Deionized water was used as proton source at the anode with the flow rate of $1.5 \text{ mL}\cdot\text{min}^{-1}$. The experiment was conducted using chronoamperometry technique (pulse width 5 s) at 8 different electrode potentials and the reaction products were collected at the cathode outlet and analyzed by GC. The electrochemical experiments were carried out at 30°C and at atmospheric pressure.

3. Results and discussion

3.1 Metal complex characterization

The salen ligand and metal complexes were characterized using FTIR spectroscopy along with other characterization techniques as described in section 2.2.2. However, ESI-MS measurement for the complexes was not possible due to insoluble nature of the complexes in the measurement friendly solvents. The infrared spectrum of ligand $\text{H}_2\text{L}^{\text{NO}_2}$ showed a broad band centered at 3447 cm^{-1} due to $\nu(\text{O-H})$ stretching of two $-\text{OH}$ groups. The broadness of the band implied hydrogen bonding in the ligand. The aldamine $\text{C}=\text{N}$ stretch appeared at 1615 cm^{-1} . A sharp band at 1566 cm^{-1} was found because of phenyl asymmetric $\nu(\text{C}=\text{C})$ stretch. The existence of bands at 1511 cm^{-1} and 1341 cm^{-1} consolidated the presence of $-\text{NO}_2$ functional group in the ligand. The phenolic $\nu(\text{C-O})$ band appeared at 1277 cm^{-1} . In Ni and Cu complexes, the aldamine $\text{C}=\text{N}$ stretch shifted slightly to lower value and appeared at 1610 cm^{-1} and 1612 cm^{-1} , respectively. After complexation, asymmetric $\nu(\text{C}=\text{C})$ stretching band for phenyl ring appeared at 1576 cm^{-1} and 1575 cm^{-1} for Ni complex and Cu complex, respectively, and the value was $\sim 10\text{ cm}^{-1}$ higher compared to the value observed in the free ligand. This indicated more aromatic character inside the phenyl rings in the complexes compared to the ligand. Additionally, lower phenolic $\nu(\text{C-O})$ stretching value in the complexes (1248 cm^{-1} in Ni complex and 1259 cm^{-1} in Cu complex) compared to free ligand (1277 cm^{-1}) supported further the higher aromatic character of the phenolate moiety. In the IR spectra of both the complexes, no appreciable changes were observed in 1511 cm^{-1} , and 1341 cm^{-1} stretching bands. This indicated undisturbed and non-interacting nature of the $-\text{NO}_2$ group in both Ni and Cu complexes. Interestingly, in Cu complex a relatively weak and broad band appeared at 3321 cm^{-1} . The band is attributed to $\nu(\text{O-H})$ stretching of H-bonded lattice water. Microanalysis data further supported the presence of lattice water.

3.2 Half-cell studies

To find out the feasibility of the synthesized metal complexes for electrochemical reduction of CO_2 , half-cell studies were carried out. Metal complexes were studied in both aqueous and non-aqueous medium. In aqueous medium, the test was conducted in 0.5M KHCO_3 solution, which was saturated with N_2 or CO_2 gases, to compare the voltammograms in inert and CO_2 environments, respectively. The pH of the saturated solution with N_2 and CO_2 was 8.5 and 7.5, respectively. The cyclic voltammograms (CVs) of the Ni and Cu complexes in the potential range of 0 to -3 V vs. SHE are shown in figure 1. The CVs were recorded in inert gas (N_2) as well as CO_2 environment for both the complexes. It can be seen that significant amount of current density is observed in both the environments. However, the current density in CO_2 saturated system is higher than the corresponding current density in N_2 saturated system for both the complexes. The current density observed in inert atmosphere is due to the reduction of water into H_2 gas. The onset potential (potential at which $0.1\text{ mA}\cdot\text{cm}^{-2}$ current density is observed) was found to be $\sim 1\text{ V}$ for both the complexes. It can be seen that with the increase in the applied voltage beyond onset potential, the current density increases (Figure 1). It can be seen that the current density was found to be more, upto some extent, in CO_2 environment as compared to inert environment for both the complexes. The higher current density in CO_2 saturated environment may signify that electrocatalysts are able to reduce the CO_2 . However, in aqueous medium the increase in current density is not only from the CO_2 reduction but also due to the reduction of water at the cathode, which is evident from the figure 1. Moreover, the different pH level of the saturated solutions also affect the cathodic process as low pH favours the water reduction to hydrogen gas.³³ Therefore, efficacy of the metal

complex electrocatalysts may not be truly ascertained by the above study. It may be noted that the CV was conducted and the products were evaluated using only salen ligand (without metal) also. It was found that only hydrogen gas was evolved, which rules out the possibility that the salen ligands themselves are decomposing under reducing conditions to give the value added products. Hence, CO₂ electroreduction was also carried out in non-aqueous medium to get more information about the electrocatalysts.

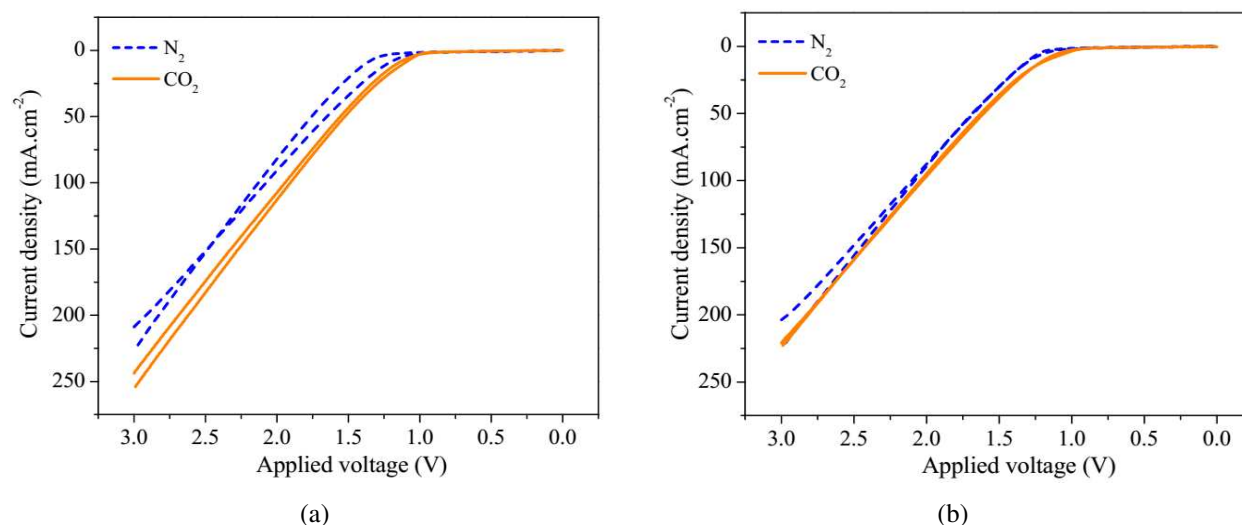


Figure 1. Cyclic voltammograms of Ni complex (a) and Cu complex (b) in N₂ (broken line) and CO₂ (solid line) saturated in aqueous solution

To further confirm the electrocatalytic activity of complexes towards CO₂ reduction, the half-cell tests were conducted in non-aqueous environment (DMF solvent) to avoid any effect due to H⁺ reduction to form H₂ gas.³⁴ The CV scans in non-aqueous environment for both the metal complexes are shown in figure 2. It can be seen that the scan was recorded in absence of CO₂ and thus only charging current could be observed as there is no possibility of electron transfer between the electrolyte and electrode in absence of any redox species (CO₂). Further, CO₂ was bubbled in DMF and the pH was maintained so as to have the same pH when CO₂ was saturated in the aqueous electrolyte.³⁴ Figure 2 shows that the current density increases in the presence of CO₂ because of the transfer of electrons from electrode surface to the dissolved CO₂. This increased current density in CO₂ environment confirms the reduction of CO₂, as there is no other electroactive species present in the medium. Hence, the increase in current density is solely attributed to the CO₂ reduction. It was also seen that, there is no increment in current density after -2.8 V vs. SHE and -2.6 V vs. SHE in CV of Ni complex and Cu complex, respectively. Moreover, on comparing the corresponding current densities in figure 1 and 2, it can be seen that the magnitude of current density is significantly low in case of figure 2. In case of CO₂ saturated aqueous system (Figure 1) a significant amount of current density was due to the reduction of water into hydrogen gas at the cathode apart from the CO₂ reduction. In case of DMF (Figure 2), the CO₂ was bubbled only upto a certain level to maintain the pH instead of CO₂ saturation in the DMF. Moreover, the electroreduction might not be completed due to absence of other reactant to combine with the reduced or activated CO₂. In turn, the low level of CO₂ in the electrolyte along with increased mass transport resistance and

scarcity of co-reactant reduces the current density, which does not increase even with the increase in the applied voltage. Apart from the other reasons, the difference (in the order of 10^3) in electrical conductivities of the media ($\text{mS}\cdot\text{cm}^{-1}$ in case of KHCO_3 , while $\mu\text{S}\cdot\text{cm}^{-1}$ in case of DMF) also affect the performance.³⁴ Therefore, these studies confirm qualitatively the efficacy of the metal complexes, however, can not be used for quantifying the role of the electrocatalysts. Therefore, further study was conducted to evaluate and quantify the products obtained out of the dERC using Ni and Cu complexes.

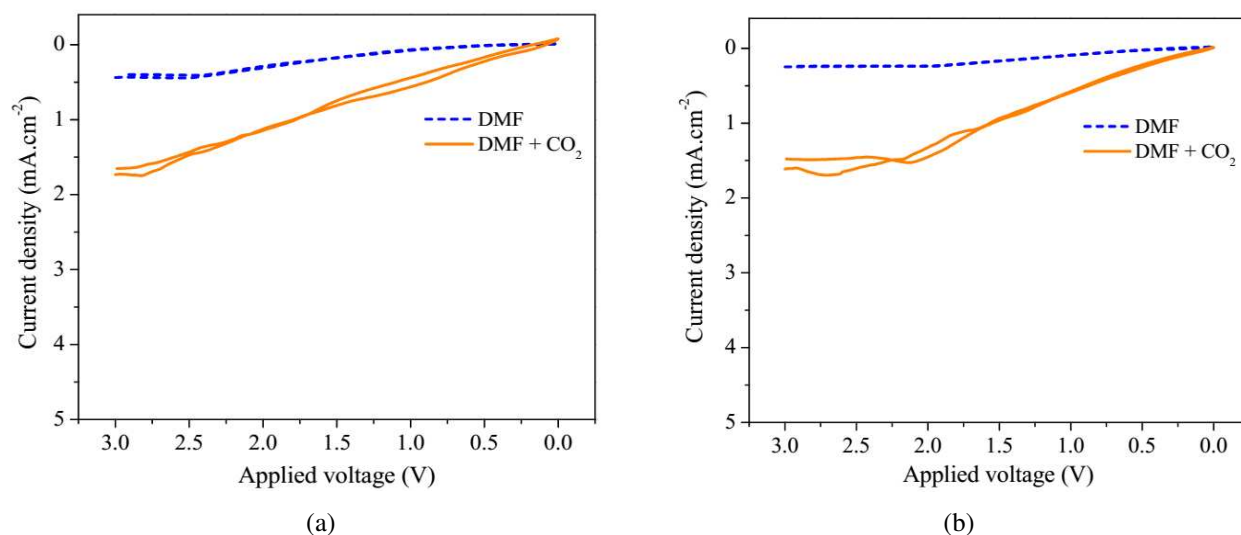


Figure 2. Cyclic voltammograms of Ni complex (a) and Cu complex (b) in absence (broken line) and presence of CO_2 (solid line) in dimethyl formamide

3.3 Electrochemical reduction of CO_2 using metal complexes in electrochemical reactor

Once the activity of the synthesized metal complexes was proved for the electrochemical reduction of CO_2 in preliminary half-cell studies, the full cell studies were attempted for the qualitative and quantitative information regarding the products formed in dERC using the complexes. The reactions were carried out in aqueous solution and above the onset potential range, which is $\sim 1\text{V}$ in all the cases. The products formed were collected at definite time intervals from the cathode outlet and analyzed using gas chromatography. It may be noted that the experiments without the cathode electrocatalyst catalyst (that is with only carbon paper) hardly produce any product.

3.3.1 Effect of applied voltage on current density and Faradaic efficiency towards total CO_2 reduction

For both the metal complex electrocatalysts, the experimental results obtained are presented in figure 3. The figure 3 shows the current density and Faradaic efficiency corresponding to various applied voltages at the terminals of the electrochemical reactor. It can be seen that the current density increases with the increase in the applied voltage for both the complexes. It depicts that with increase in the applied voltage the current density increases, which in turn signifies the increased rate of various electrochemical reactions including H_2 gas generation at the electrode surface.

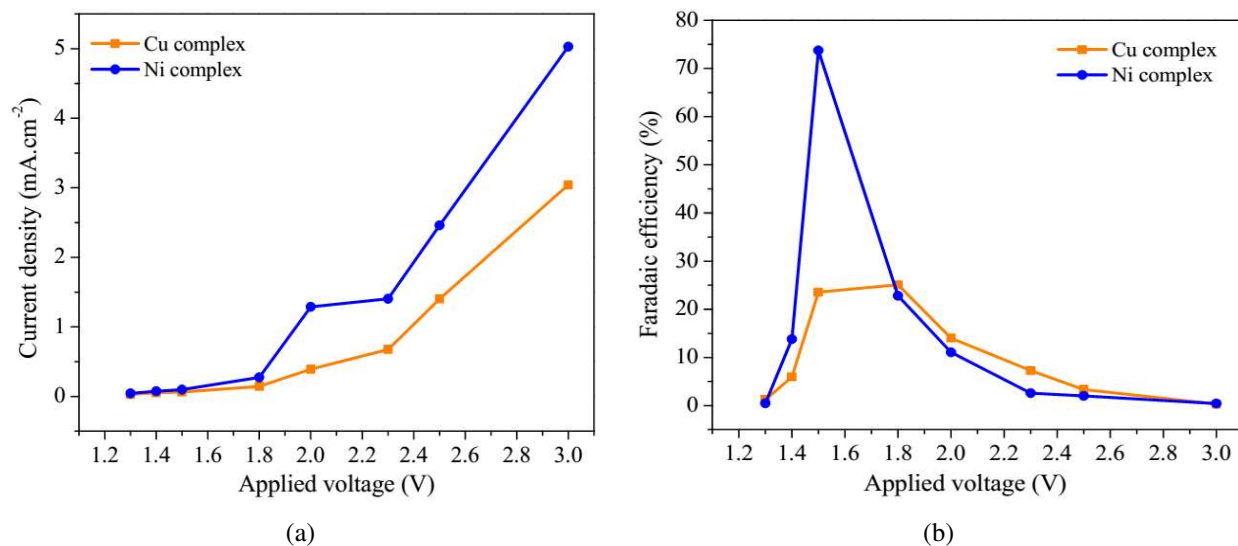


Figure 3. Effect of applied voltage on current density (a) and Faradaic efficiency (b) for dERC using metal complex electrocatalysts

Figure 3 (b) shows the Faradaic efficiency for electrochemical reduction of CO₂ using metal complexes. It can be seen that the Faradaic efficiency for Ni complex is quite high *viz.* 74% at 1.5 V. On further increasing the voltage, the Faradaic efficiency decreases sharply. The Faradaic efficiency for the Cu complex increases initially and attains maxima at 1.8 V and then subsides gradually with the increase in the voltage. The highest Faradaic efficiency of 25% is achieved at 1.8 V for the Cu complex electrocatalyst. It may be noted that the Faradaic efficiency using the complexes is the result of cumulative efficiencies for the formation of various products from electroreduction of CO₂. To determine the energy utilized (Faradaic efficiency) for the various reaction products, it is necessary to quantify the reaction products at the cathode of the electrochemical reactor.

3.3.2 Effect of applied potential on Faradaic efficiency of individual products

To get more insight of the metal complex performance for the formation of various products, the studies were conducted to find the Faradaic efficiencies of individual products of dERC as well as hydrogen production. Figure 4 shows the Faradaic efficiency for the various products formed for dERC using Ni and Cu complexes.

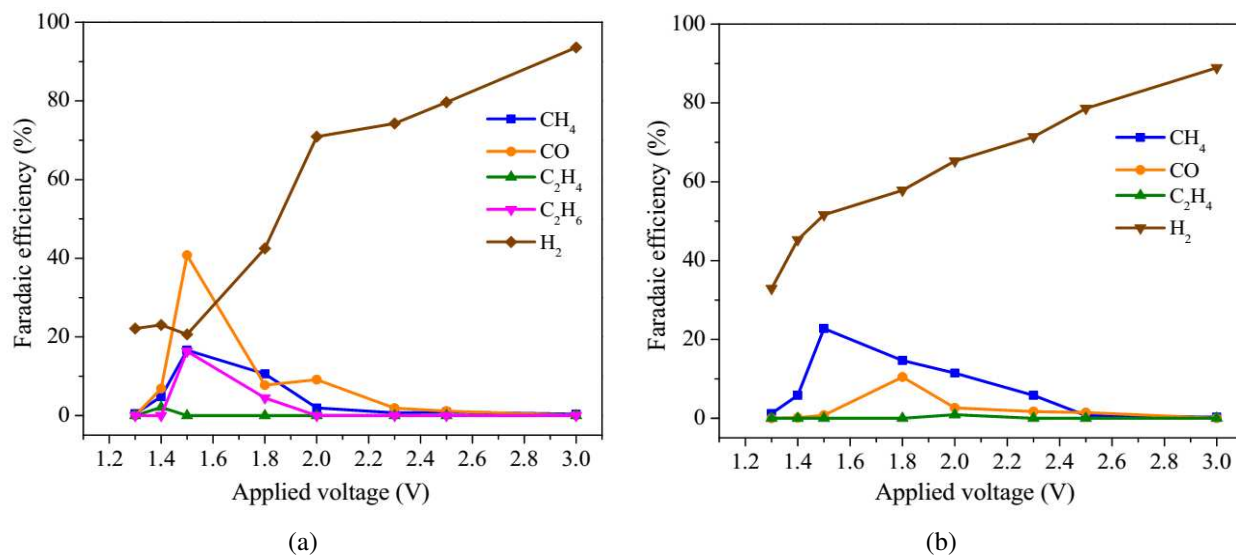


Figure 4. Effect of applied potential on Faradaic efficiency of the products using Ni-complex (a) and Cu-complex (b)

It can be seen in the figure 4 that main products of dERC are hydrocarbons and carbon monoxide using metal complex electrocatalysts. Ni complex resulted in better Faradaic efficiency than Cu complex. In case of Ni complex, Faradaic efficiency for CH₄ and C₂H₆ is considerably high with maximum for CO formation (Figure 4a). It is to be noticed that CO, CH₄ and C₂H₆ show highest Faradaic efficiency at 1.5 V. However, C₂H₄, which was minor, formed at 1.4 V with Faradaic efficiency of 2.1%. In case of Cu complex, CH₄ was the major product along with considerable Faradaic efficiency of CO (Figure 4b). Moreover, C₂H₄ was formed feebly with Faradaic efficiency of 1%. It can be seen that the Faradaic efficiency (23%) for CH₄ is highest at 1.5 V; however, CO attains its maxima at 1.8 V with Faradaic efficiency of 10.5%. Apart from the products resulting from CO₂ reduction, H₂ formation was also found in both the complexes, which approximately compensate for rest of the Faradaic efficiency at any particular voltage.

In order to find the role of the salen ligand in the metal complex, the experiments were also carried out using pure Ni and Cu metal electrocatalysts and compared with the metal complex electrocatalysts. The comparison of Faradaic efficiency of metal complexes with corresponding pure metals is shown in figure 5. Figure 5 shows a few of the very interesting results. It can be seen that the Faradaic efficiency towards the generation of the undesired H₂ gas is reduced significantly using any of the metal complexes as compared to the pure metal electrocatalyst, which in turn increased the Faradaic efficiency towards other useful products. Moreover, the Faradaic efficiency of CO and hydrocarbons were significantly higher for the metal complexes as compared to the pure metal electrocatalysts. Thus the metal complexes show low operating voltage values, and formation of C₂ hydrocarbons as compared to pure metals, where only meagre amount of CH₄ and CO could be formed at high operating voltage. In case of Ni metal, two products were formed with Faradaic efficiency of 1.4% for CO and 1.2% for CH₄. However, in case of Cu metal, the Faradaic efficiency for CH₄ and CO was found to be 4.9% and 0.3%, respectively. C₂ hydrocarbons were

not formed in any of the pure metals and most of the supplied energy was inadvertently used for the H_2 generation. In contrast to this, metal complexes resulted in efficient CO_2 reduction with significantly low Faradaic efficiency towards H_2 generation. It can be said that the ligand has profound impact over the process as it is evident from the performance of Ni and Cu as pure metals and in the complexed form with salen ligand. Thus, drastic change was found in the efficiency of the metals and corresponding metal complexes. Table 1 shows the applied voltage for a few representative reaction products at maximum Faradaic efficiency using the metal (Ni or Cu) and metal complexes. It can be seen that the metal complexes use lower voltage corresponding to their metal counterpart for the product formation at their maximum Faradaic efficiency. It is very interesting and worth to note that the operating voltage of the reaction reduced significantly using the salen ligand metal complex as compared to the pure metal electrocatalyst. The reduction in operating voltage shows the reduction in overpotential of the reactions.

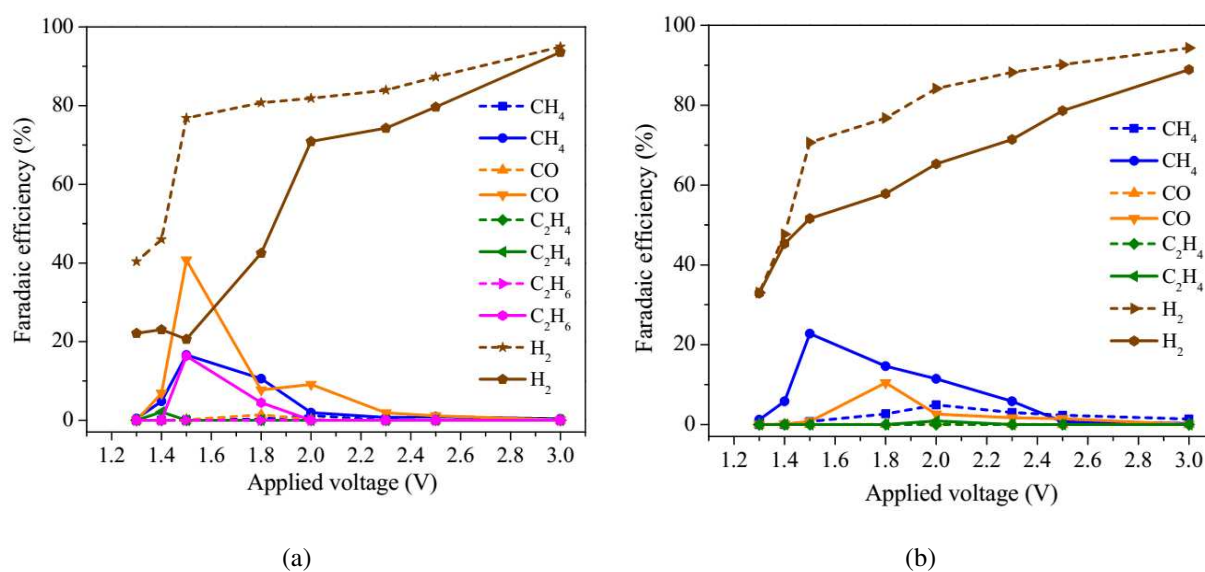


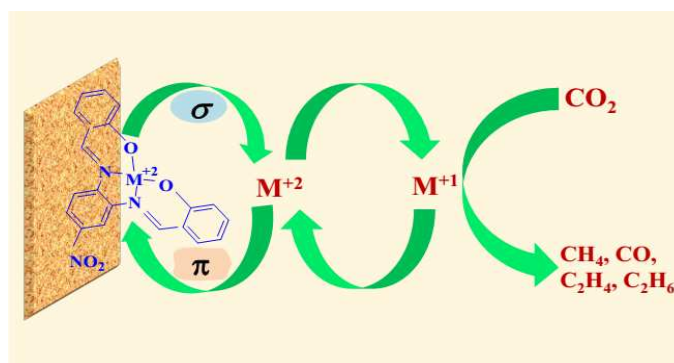
Figure 5. Comparison of Faradaic efficiency of metal complexes (solid line) with corresponding pure metals (broken line); Ni complex vs. Ni metal (a) and Cu complex vs. Cu metal (b)

Table 1. Reduction in operating voltage for a few representative reaction products using the metal (Ni or Cu) and metal complexes

Electrocatalysts	Applied voltage (V) corresponding to maximum Faradaic efficiency of the product		
	CH_4	CO	C_2H_6
Ni	2	1.8	-
Ni-complex	1.5	1.5	1.5
Reduction in operating voltage (V)	0.5	0.3	-
Cu	2	2	-
Cu-complex	1.5	1.8	-

Reduction in operating voltage (V)	0.5	0.2	-
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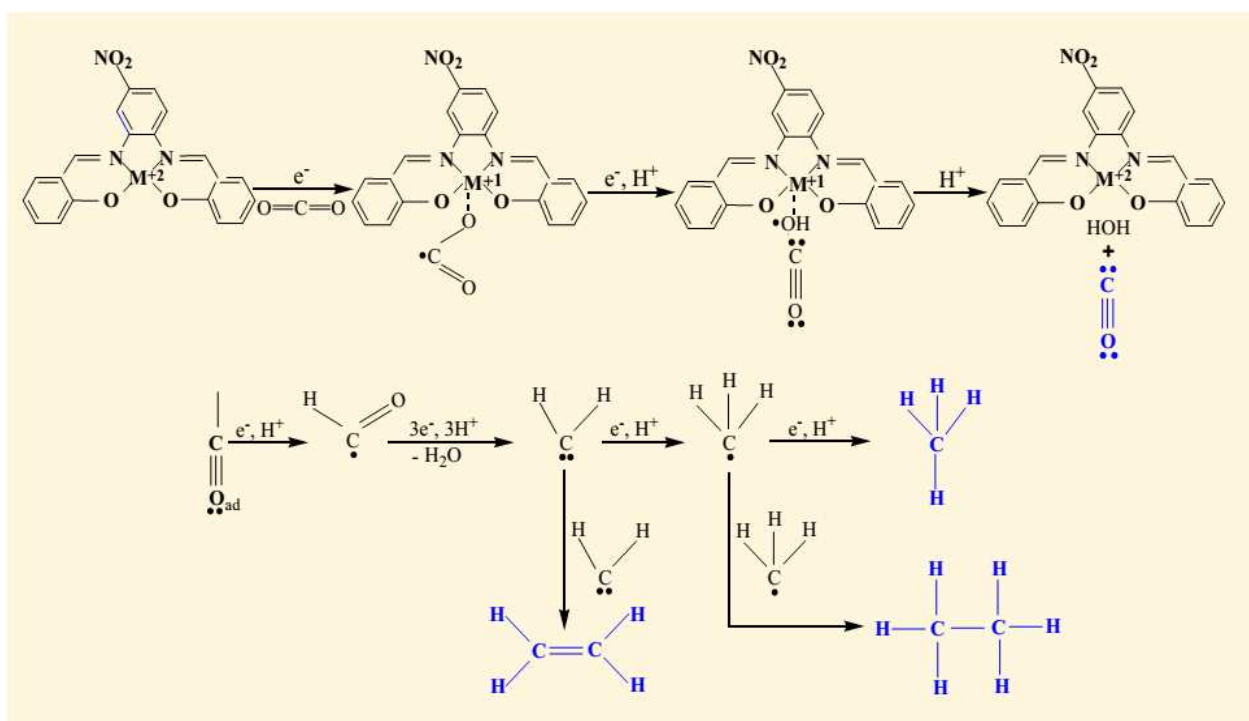
It is evident that both the Ni and Cu complexes were active towards CO₂ reduction and underwent multi-electron reduction of CO₂ resulting in C₁ and C₂ hydrocarbons, which was usually rare in case of other metal complexes. It happened because incorporation of anchoring -NO₂ group in the ligand (H₂L^{NO₂}) backbone provides better interaction of salen complexes to the electrode material and hence, facilitate an efficient electron transfer during the conversion of CO₂ to the products. Additionally, during the conversion process, when Mⁿ⁺ reduces to M⁽ⁿ⁻¹⁾⁺ state (M stands for metal), the decrease in Lewis basicity of the central metal ion due to increase in metal-to-ligand(imine) π-back donation is compensated by two strong σ donations by two phenolate donors as shown in scheme 2. This is due to more aromatic character inside the phenyl rings of the complexes, which was depicted in FTIR spectra. Moreover, the operating voltage required for the reaction was quite low for both the metal complexes as compared to pure metals (Table 1). It is because of the initial reduction of metal complex itself (Mⁿ⁺ to M⁽ⁿ⁻¹⁾⁺), and subsequent reaction with CO₂. Thus, metal complexes act as redox couple, which help to reduce the operating voltage for the CO₂ electroreduction as well as help in multielectron transfer resulting in C₁ and C₂ hydrocarbons.³⁵



Scheme 2. Representation of redox behaviour of salen ligand complex

Overall, Ni complex was found to perform much better than Cu complex, which can be explained in terms of the stability of the Ni(I) and Cu(I) intermediate species. As it is known that the optimum stability or binding of metal-CO₂ bond is crucial for multi-electron reduction during dERC. The strong binding of metal-CO₂ may poison the electrocatalyst, whereas weak bonding may result in higher overpotential for the reaction along with dissociation of product from the reaction site by utilizing only a few electrons. During the CO₂ reduction process, Ni(II) and Cu(II) converts to Ni(I) and Cu(I) species, respectively. Ni(I) being less stable, coordinates with CO₂ yielding stable Ni-CO₂ complex³⁶ thus resulting in effective multi-electron reduction of CO₂ with high efficiency, however, Cu(I) is comparatively more stable and hence does not bind with CO₂ with the same efficacy, which in turn result in lower performance. Based on the products formed, an elementary reaction mechanism is proposed for the formation of hydrocarbons and CO as shown in scheme 3. The scheme 3 shows that initially the metal complexed to the salen

ligand is in +2 state and reduced to +1 state by taking up an electron from the electrode. The addition of CO₂ in the system receives the electron from the reduced metal, which was in +1 state, and binds with it. However, the stability of the system was maintained by the phenolate groups of the ligand. Simultaneously, H⁺ ions were transported through membrane from the anode side to the cathode during the full cell reaction and reacted with the metal complex-CO₂ along with some internal rearrangements in the complex to form either the adsorbed CO (CO_{ad}) or free CO, which escapes from the cathode. The CO_{ad} may further participate in the reaction to form hydrocarbons^{37,38} as shown in the scheme 3. Ultimately, the metal in the complex reverts to its previous oxidation state (+2). This redox behaviour of the salen metal complex is very peculiar and needs further investigation. The intermediate steps are not fully elucidated and is under investigation. Moreover, these metal complexes offer immense opportunity to study and improve for the selective formation of hydrocarbons. Further work needs to be done to get more insights into the detailed reaction mechanism and to understand the salen metal complex.



Scheme 3. Proposed elementary mechanism for the formation of reaction products using salen metal complexes

4. Conclusions

The electrocatalytic property of the salen ligand was unexplored in the field of ERC inspite its ability to bind the CO₂. Hence, the salen ligand and its corresponding Ni and Cu complexes were synthesized and reported for their application as electrocatalyst in direct electrochemical reduction of CO₂ using half-cell and full cell studies. The complexes were found to be quite efficient for the process and resulted in the production of hydrocarbons (C₁ and C₂) and CO. The total Faradaic efficiency was found to be 74% for Ni complex and 25% for Cu complex at 1.5 V

and 1.8 V, respectively. The better performance by the Ni complex as compared to Cu complex was attributed to the low stability of Ni(I) as compared to Cu(I). It was also seen that Ni complex was more selective towards hydrocarbon as compared to Cu complex. Moreover, the Ni-complex showed better efficiency towards CO formation as compared to Cu-complex. The activity of complexes was also compared with the corresponding pure metals to understand the effect of ligand. It was found that redox behaviour of the metal complex is responsible for their better performance and hence the complexes were able to decrease the overpotential upto a great extent. The overpotential using metal-complexes was reduced significantly ranging from 10% to 25% against their pure metal counterparts for formation of different products. Moreover, a reaction pathway was proposed for formation of the various reaction products. It was observed that the formation of hydrocarbons using metal complexes is rather rare and hence these complexes offer immense scope for future research in this field.

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Graphical Abstract