Electrochemistry and Electrocatalytic Activity of Nickel (II) [bis(benzil)(1,2-phenyldiamine)] and Chloro Substituted Nickel (II) [bis(benzil)(4-chloro-1,2-phenyldiamine)] Complexes for CO_2 Reduction.

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Abstract

Increasing emission of CO_2 level in our atmosphere is a serious global issue. Many attempts have been made to mitigate this problem and introduce adaptations. Utilization of CO_2 is a major concern when thinking about adaptations. One way of utilization is coordination of CO_2 to a transition metal center in a macrocyclic complex. The work reported herein describes the synthesis, characterization, electrochemistry and comparison of the electrocatalytic reduction of CO_2 by Nickel (II) [bis(benzil)(1,2- phenyldiamine)] complex and the chloro-substituted Nickel (II) [bis(benzil)(4-Chloro-1,2-phenyldiamine)] complex.

Cyclic voltammetric (CV) studies were carried out in DMF using tetraethylammonium tetraflouroborate as electrolyte, at a glassy carbon working, platinum counter and calomel reference electrodes. The non-chloro substituted nickel (II) complex showed that Ni(II)/Ni(I) redox couple occurred at -1.65 V with ΔE = 0.23 V. Redox couple of the chloro substituted nickel (II) complex appeared at -1.45 V with ΔE = 0.10 V. CV evidence reveal that the reduced forms, Nickel (I) [bis(benzil)(1,2-phenyldiamine)] and Nickel (I) [bis(benzil) (4-chloro-1,2-phenyldiamine)] complexes were able to catalyze CO_2 reduction around -1.63 V and -1.32 V, respectively. During this process, the Nickel (II) [bis(benzil)(1,2-phenyldiamine)] complex showed a new band at -0.58 V and the current intensity of the cathodic wave increased with a shift to the positive potential. The efficiency of the reduction process in terms of i (CO_2) / i (N_2) ratio was 1.70. Similarly, chloro substituted nickel (II) complex showed a new band at -0.52 V and the current intensity of the cathodic wave increased upon passing CO_2. The efficiency ratio was 2.0 for the chloro substituted complex. Both complexes showed regeneration of the original CV when N_2 was passed back into the solution. These observations clearly indicate that chloro substituted macrocyclic complex reduces CO_2 at a significantly lower potential than the non chloro substituted macrocycle. This may be due to the inductive effect of the chlorine attached to benzyl group.

Introduction

The work reported herein, is the synthesis, chemical characterization, electrochemistry and electrocatalytic properties of *Nickel (II) [bis(benzil)(1,2-phenyldiamine)]*[1],(*[Ni($C_{40}H_{28}N_4$)]*) and its 4-chloro-derivative, substituted *Nickel (II) [bis(benzil)(4-Chloro-1,2-phenyldiamine)]*[1], (*[Ni($C_{40}H_{26}N_4Cl_2$)]*) complexes for the reduction of CO_2. Much research has been done aimed at discovering the most efficient catalystsfor conversion of the very inert CO_2 gas into fuels, environmental friendly chemical species or industrial chemicals. The objective of our research was to find an efficient catalyst which reduced CO_2 at a lower potential targetting. heterogeneous catalysts to reduce energy consumption. We now report the synthesis of *[Ni($C_{40}H_{28}N_4$)]* and *[Ni($C_{40}H_{26}N_4Cl_2$)]* complexes and their ability to reduce CO_2 at a potential lower than -2.0 V.

Method and Materials

[Ni($C_{40}H_{28}N_4$)] and *[Ni($C_{40}H_{26}N_4Cl_2$)]* complexes were synthesised according to the literature procedure. The synthetic route of the *[Ni($C_{40}H_{28}N_4$)]*complex is shown in Fig. 1. A similar procedure was used for *[Ni($C_{40}H_{26}N_4Cl_2$)]* complex with 4-chlorophenyldiamine replacing o-phenyldiamine. Cyclic voltammetry (CV) was recorded under N_2 atmosphere. Then, CO_2 gas was passed through the solution for 15 minutes in a closed system. After the solution was saturated with CO_2, while keeping the CO_2 atmosphere just above the solution, CV was recorded. Reversibility of the *[Ni($C_{40}H_{28}N_4$)]* and *[Ni($C_{40}H_{26}N_4Cl_2$)]*

complexes for CO_2 reduction was studied by purging N_2 back into the system and running the CV. X-Ray Fluorescence (XRF) data for *[Ni($C_{40}H_{28}N_4$)]*, *[Ni($C_{40}H_{26}N_4Cl_2$)]* were collected from a 400 MHz Bru kev DRX 400 spectrometer with a 5 mm broadband inverse probe and z-quadients. FT-IR spectra for the synthesized complexes were determined from a FT-IR model 400 spectrometer for dry KBr pellets. Electrocatalytic studies were carried out using an electrochemical workstation (AUTOLAB 204).

Results and Discussion

FT-IR of the *[Ni($C_{40}H_{28}N_4$)]* and *[Ni($C_{40}H_{26}N_4Cl_2$)]* complexes are shown in Fig. 2. The comparisons of the FT-IR data for synthesised and reported complexes are given in Table 1. Observed data are consistent with the reported data. XRF data confirm that *[Ni($C_{40}H_{28}N_4$)]* complex contains 87% of Ni and little amount of Cu (12.91%) as impurities. The *[Ni($C_{40}H_{26}N_4Cl_2$)]* shows that "2% Ni and Cl (98%) have been detected under the detectable limit"(Fig. 3).

The absorption frequencies of Ni (II) complexes along with their assignment are listed in Table 1. The absorption band appeared in the 1465–1495 and 1355–1390 cm^{-1} regions, which are assigned to $\nu_{asym}C_6H_5$ and $\nu_{sym}C_6H_5$, respectively. The mode of coordination is further supported by the presence of the bands at 360–390 cm^{-1} due to ν (Ni←N).

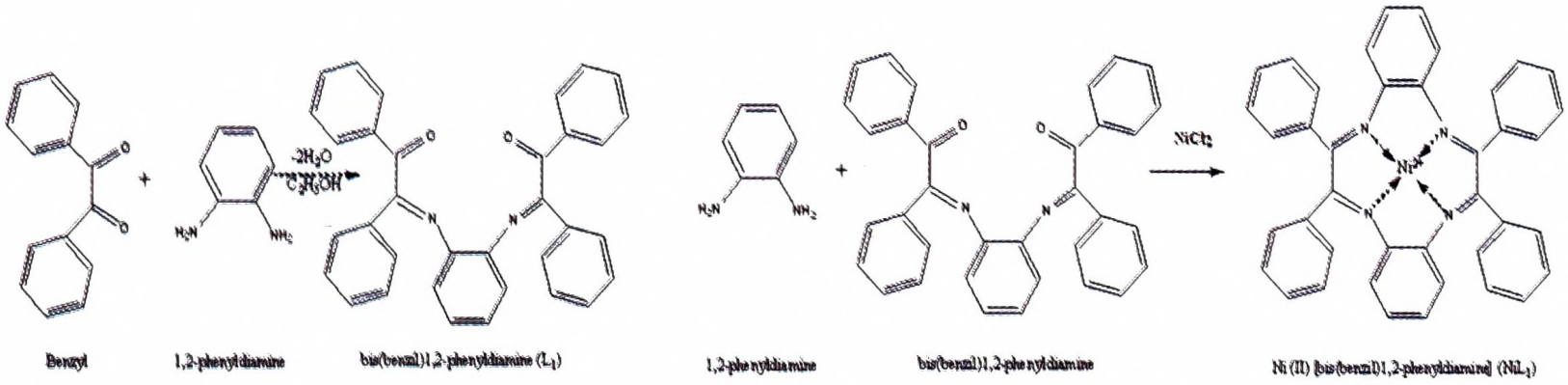

Fig. 1. Synthetic route for the ligand *[bis(ben zil)(1,2-phenyldiamine)]* (L_1) and *Ni (II) [bis(benzil)(1,2-phenyldiamine)]* (NiL_1).

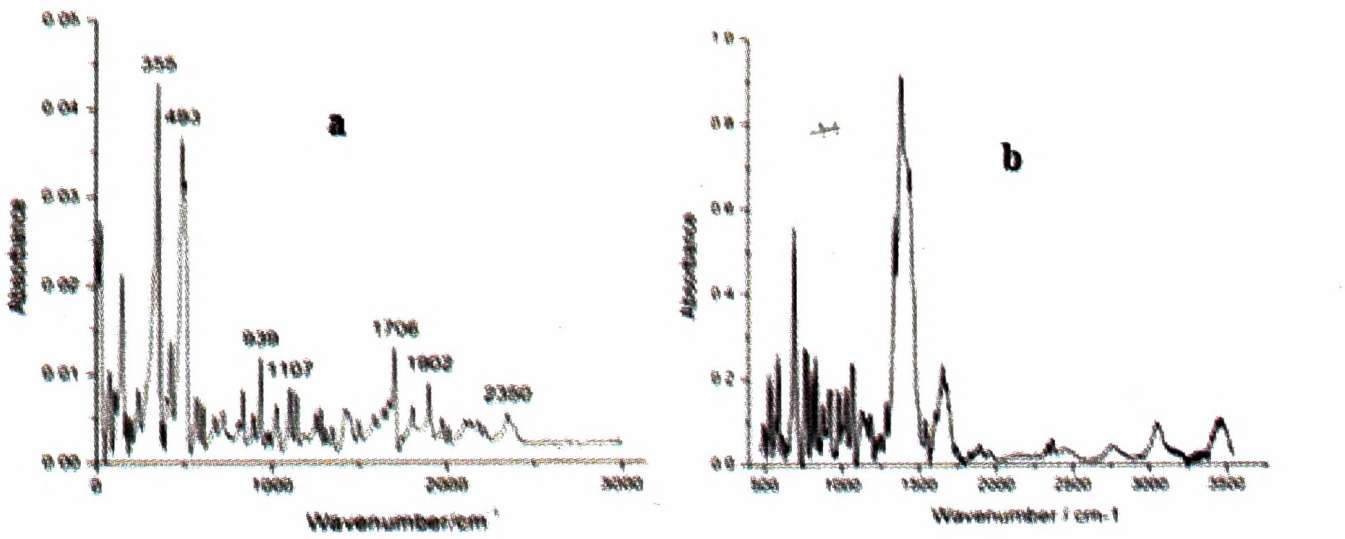

Fig. 2. FT-IR spectra for a) *[Ni ($C_{40}H_{28}N_4$)]* b) *[Ni($C_{40}H_{26}N_4Cl_2$)]* complexes

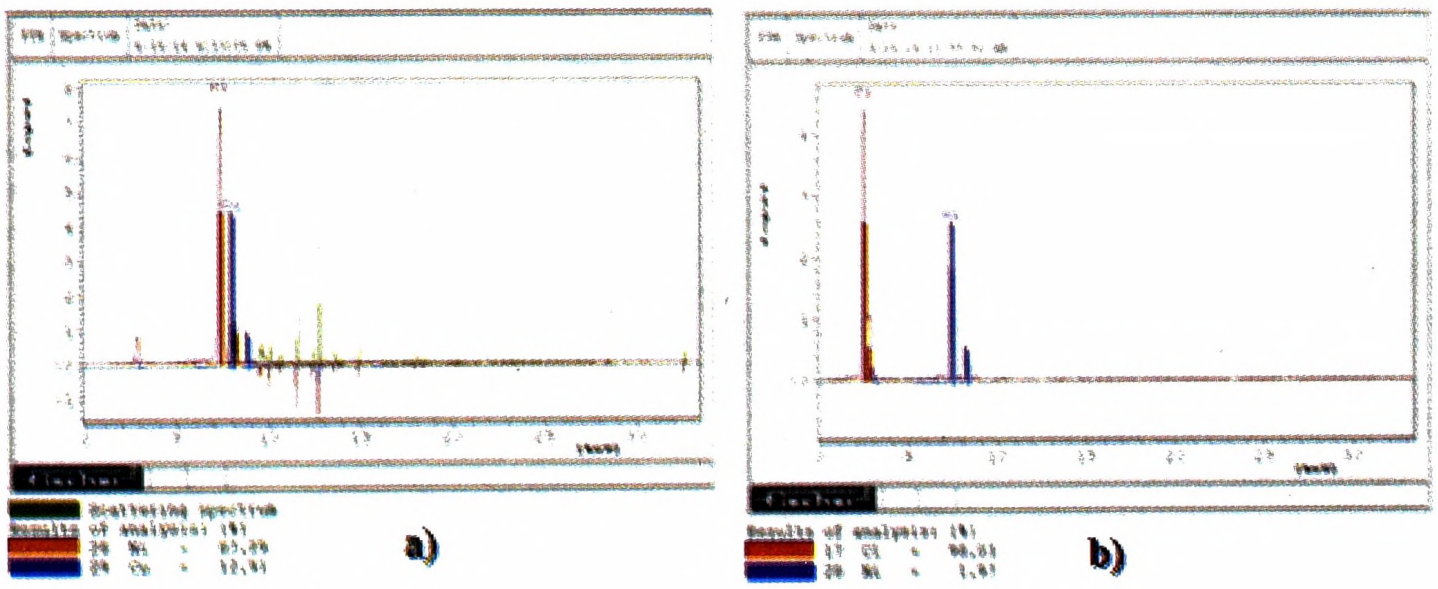

Fig. 3. XRF spectra for a) *[Ni($C_{40}H_{28}N_4$)]* b) *[Ni($C_{40}H_{26}N_4Cl_2$)]* complexes

Compound		Peaks /(cm^{-1})					
		ν (C=N)	**ν (M-N)**	**ν(C=C)**	**ν(C-N)**	**ν(C-H)**	**ν(C-Cl)**
opd-bz-Ni	**Reported**	1617	390	1495	1250	2850	603
	Observed	1706	493	1658	1107	2350	-
cl-opd-bz-Ni	**Reported**	1617	390	1495	1250	2850	603
	Observed	1679	531	1413	1073	2366	695

Table. 1: Reported and observed FT-IR data for the $[Ni(C_{40}H_{28}N_4)]$ and $[Ni(C_{40}H_{26}N_4Cl_2)]$

After fully characterizing the complexes, cyclic voltametric (CV) analyses were carried out in the presence of tetraethylammoniumtetraflouroborate (Et_4NBF_4) electrolyte. The CV for $[Ni(C_{40}H_{28}N_4)]$ complex showed a redox couple at -1.67 V with ΔE= 0.22 V as shown in Fig. 4. Catalytic activity of the complex for the CO_2 reduction was studied at a potential range; from 1 to -2 V. In this potential window, the band at -1.75 V is due to Ni(II) / Ni(I) reduction, the pseudo reversible band at + 1.2 V may be due to Ni(II) / Ni(III) oxidation and the band around -1.1 V may be due to Cu(II) / Cu(I) present in the complex as an impurity. The electrochemical data are given in the Table. 2.

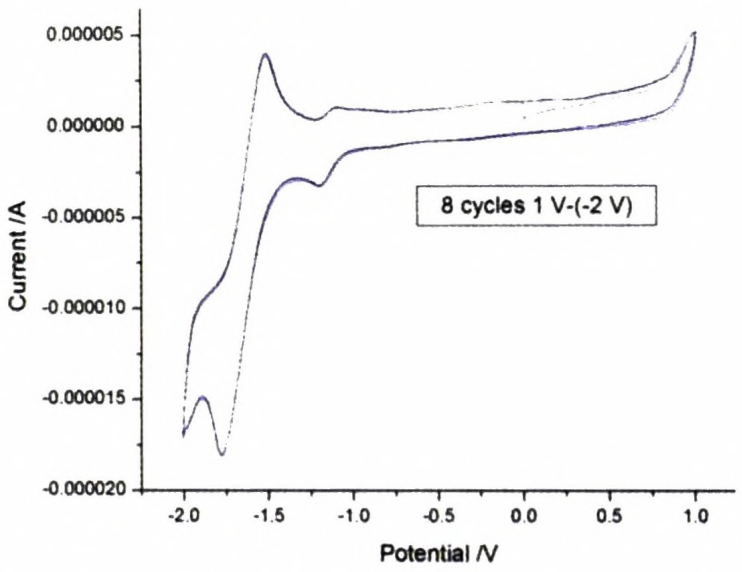

Fig. 4. CV of $[Ni(C_{40}H_{28}N_4)]$ in DMF using glassy carbon (2 mm) working, saturated calomel reference electrode and Pt counter under N_2 and CO_2 in presence of Et_4NBF_4.

It has been shownthat when a compound acts as a catalyst for electrochemical reduction, its CV shows a current gain at the reduction peak while the oxidation peak disappears on passing CO_2. Regeneration of redox peaks occurs on passing N_2 back into the same solution. Literature data suggests that most of the electrocatalyst reduces CO_2 at the original reduction potential. However, a slight positive and negative shift from the original redox potential has also been reported in a very few studies. The electrocatalysts reported in this paper show CO_2 reduction at a lower potential than the original reduction potential. The potential shift can be clearly seen in the Figs 5, 7-8 (dotted line). If these complexes are acting as electrocatalysts, the following mechanism can be proposed for CO_2 reduction (Eqn 1-3).

$$LNi + e \rightarrow LNi \text{ .....-Eq. 1}$$

(Reduction of metal centre)

$$LNi + CO_2 \rightarrow LNi\text{----}CO_2\text{.....Eq. 2}$$

(Co-ordination of CO_2 to reduced Ni (I) center)

$$LNi\text{—}CO_2 \rightarrow LNi + C_2O_4, CO, HCOOH\text{....Eq. 3}$$

(Electrons transfer from Ni (I) to CO_2

In Fig. 5, CV provides evidence for the electro-catalytic reduction of CO_2. On passing CO_2 through the solution, intensity gain at the reduction peak (1.75 V) with a positive shift (1.64 V) is shown by the dotted line. Efficiency in terms of $i(CO_2)$ / $i(N_2)$ ratio was 1.70. On passing N_2 back to the same solution, the original CV reappeared, implying that $[Ni(C_{40}H_{28}N_4)]$ complex is catalytically active. The noticeable feature is that a new oxidation band appears at -0.58 V upon passing CO_2. This feature can be observed in all the reported CO_2 reduction studies. The band may be due to the reduction product formed during the electrolysis such as carbon monoxide and oxalates. The same band is observed for $[Ni(C_{40}H_{26}N_4Cl_2)]$ (Fig. 7) as well.

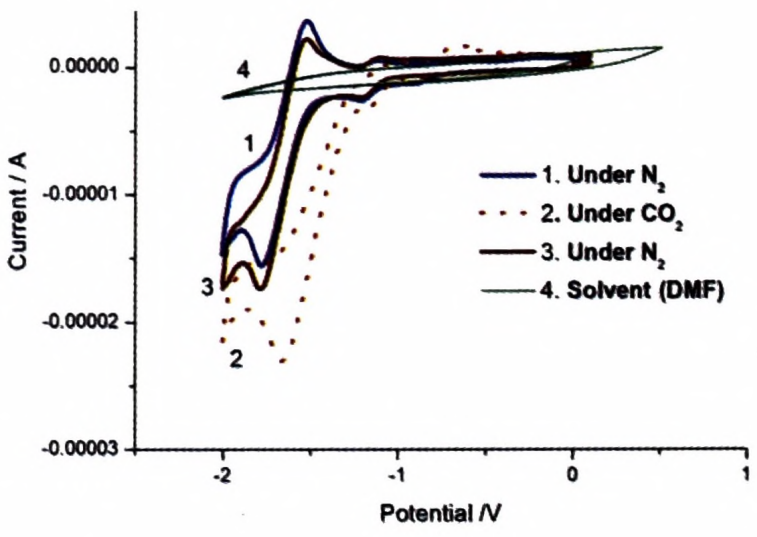

Fig. 5. CV of $[Ni(C_{40}H_{28}N_4)]$ in DMF using glassy carbon (2 mm) working, saturated calomel reference electrode and Pt counter under N_2 and CO_2 in the presence of Et_4NBF_4

Reduction Peak Changes	**Peak potential (V)**	**Peak current (A)**
Under N_2	-1.7564	-6.65E-06
Under CO_2	-1.6365	-1.01E-05
Oxidation peak changes	**Peak potential (V)**	**Peak current (A)**
Under N_2	-1.5308	7.76E-06
Under CO_2	-	-

Table 2: Electrochemical data for *[Ni($C_{40}H_{28}N_4$)]* complex before and after passing CO_2

To check polymerization of *[Ni($C_{40}H_{28}N_4$)]* complex, several cycles were run at the scan rate 0.05 Vs. The graph shows no change in current implying that there was no polymerization as shown in Fig. 6

Similarly, CV analysis was carried out for the synthesized *[Ni($C_{40}H_{26}N_4Cl_2$)]* complex, which showed a redox couple at -1.45 V with ΔE= 0.12 V with Et_4NBF_4 in DMF (10 mL) (Fig. 7).

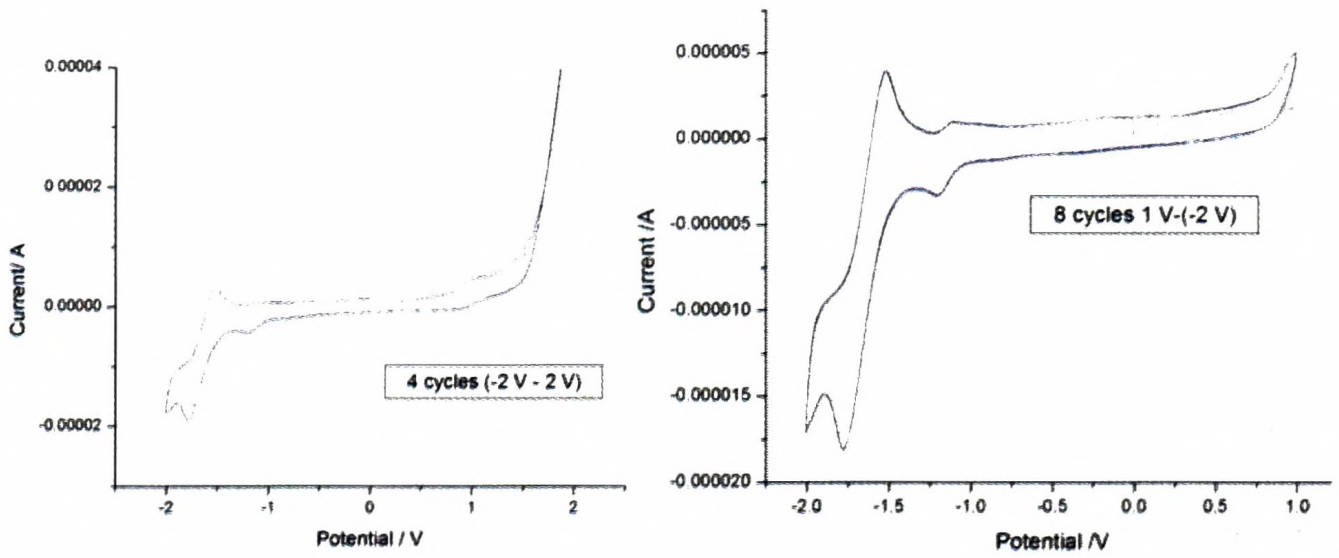

Fig. 6. CVs for the *[Ni($C_{40}H_{28}N_4$)]* under N_2 after running 8, 4 cycles on the Potential range 1 - (-2) V and 2- (-2) V at scan rate 0.05 Vs^{-1}.

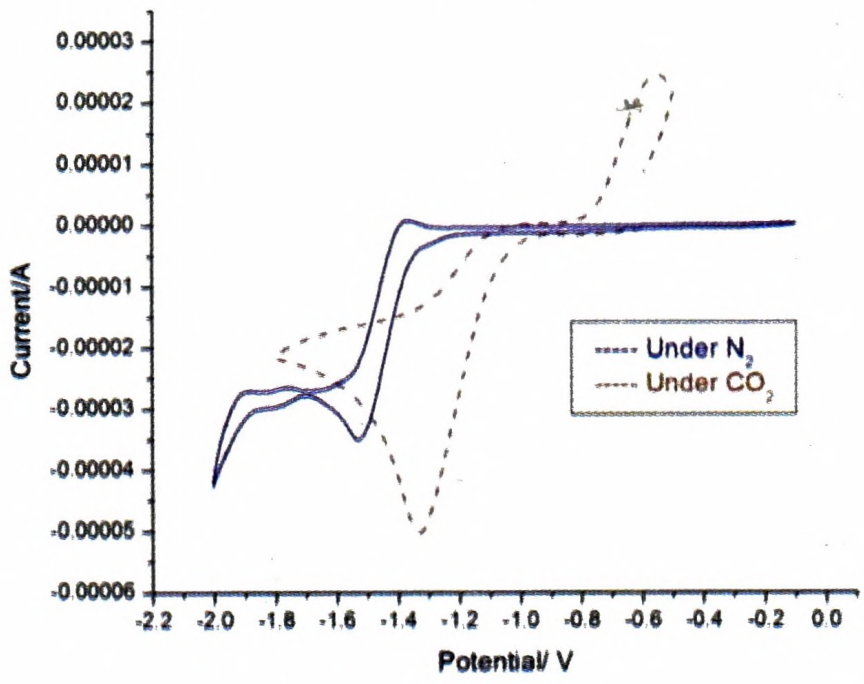

Fig. 7. CV of *[Ni($C_{40}H_{28}N_4Cl_2$)]* in DMF (1 mM) using glassy carbon working (2 mm), calomel reference and Pt counter electrode in the presence of Et_4NBF_4 electrolyte under N_2 and CO_2.

Reduction Peak Changes	**Peak potential (V)**	**Peak current (A)**
Under N_2	-1.5143	-1.95E-5
Under CO_2	-1.3251	-3.96E-5
Oxidation peak changes	**Peak potential (V)**	**Peak current (A)**
Under N_2	-1.3805	-1.92E-5
Under CO_2	-	-

Table. 3. CV data for [Ni($C_{40}H_{26}N_4Cl_2$)] complex, before and after passing CO_2

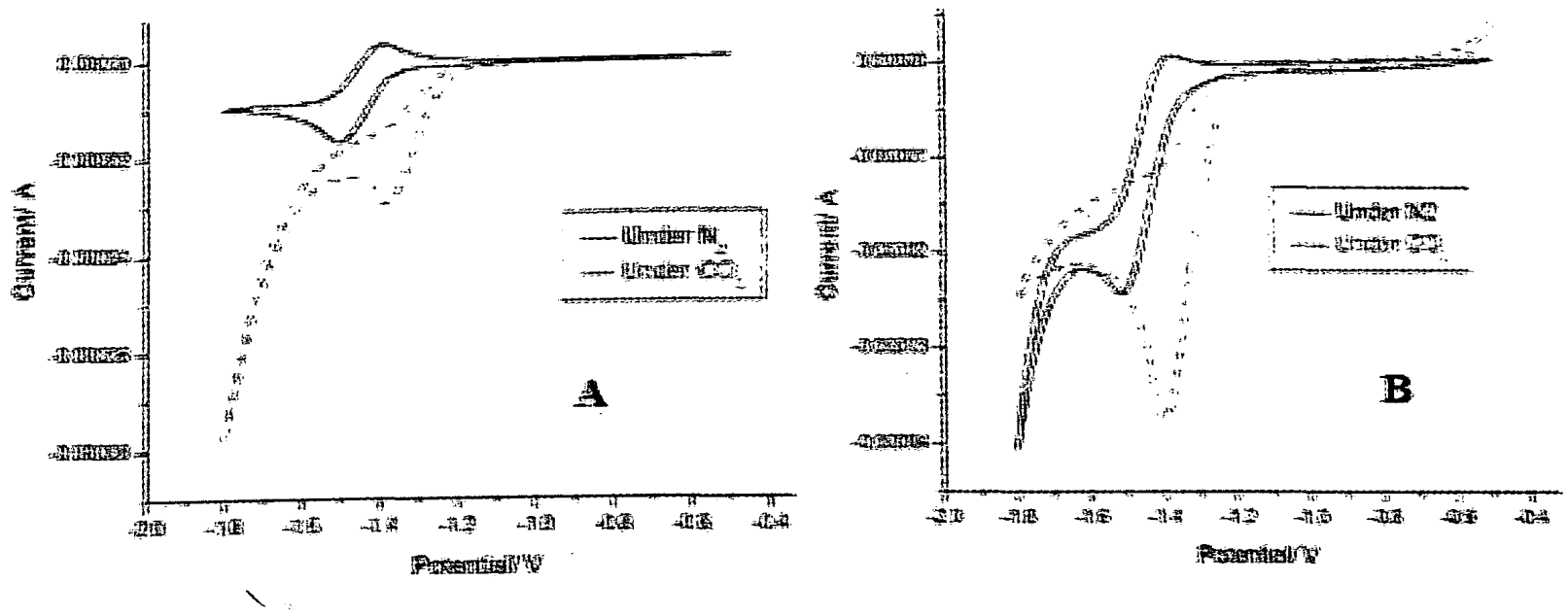

Fig. 8. CV of *[Ni($C_{40}H_{26}N_4Cl_2$)]* in DMF(1 mM) A) using gold (1 mm) , B) platinum (1 mm) working, calomel reference and Pt counter electrode in the presence of Et_4NBF_4electrolyte under N_2 and CO_2.

As described previously, in the presence of Et_4NBF_4, current intensity of the band appeared at -1.51 V increases and shifts towards a positive potential (-1.32 V) as shown in Fig. 7 (dotted line). The efficiency of the reduction process in term of *i* (CO_2) / *i* (N_2) is 2.0. Upon passing N_2 back to the same solution, the original CV reappeared, implying the catalytic activity of *[Ni($C_{40}H_{26}N_4Cl_2$)]* complex. In this study, the CV behaviour of the *[Ni($C_{40}H_{26}N_4Cl_2$)]* complex in the presence of gold (1mm) and platinum (1mm) were also studied and results are shown in the Fig. 8. Efficiency of the catalyst in terms of *i* (CO_2) / *i* (N_2) ratio for gold and platinum electrodes were 1.27, 2.39, respectively.

Efficiency of the CO_2 electocatalytic reduction by these complexes is summarized in Table 4. According to the Table 4, higher efficiency was shown by the chloro substituted *[Ni($C_{40}H_{26}N_4Cl_2$)]* complex which reduced the CO_2 at a lower potential (-1.32 V) than the non chloro *[Ni($C_{40}H_{28}N_4$)]* substituted complex (-1.63 V).

Table 4. Standard potentials and efficiency of CO_2 reduction

Complex in Et_4NBF_4	**Redox potential / V Ni(II)/ Ni(I)**	**Efficiency *i* (CO_2) / *i* (N_2)**
[Ni($C_{40}H_{28}N_4$)]	-1.67	1.7
[Ni($C_{40}H_{26}N_4Cl_2$)]	-1.45	2.0
In Au and Pt working electrodes		
[Ni($C_{40}H_{26}N_4Cl_2$)]-Au	-1.48	1.23
[Ni($C_{40}H_{26}N_4Cl_2$)]-pt	-1.45	2.39

Conclusions

[Ni($C_{40}H_{28}N_4$)] and *[Ni($C_{40}H_{26}N_4Cl_2$)]* were synthesized using a reported procedure. FT-IR and XRF data of the synthesized complexes were consistent with those reported. *[Ni($C_{40}H_{28}N_4$)]* and *[Ni($C_{40}H_{26}N_4Cl_2$)]* complexes electrocatalytically reduce CO_2 in DMF. The maximum catalytic efficiency of *[Ni($C_{40}H_{28}N_4$)]* complex in terms of *i*(CO_2) / *i*(N_2) is 1.70. Similarly, for the chloro substituted *[Ni($C_{40}H_{26}N_4Cl_2$)]* complex, efficiency was 2.0. Electrochemical data clearly indicate that the chloro substituted macrocyclic complex reduces CO_2 at a significantly lower potential than the non chloro substituted macrocycle. This may be due to the inductive effect of the chlorine attached to benzyl group. According to chelation theory, when a halo group is attached to a macroclyclic ring, halogens have non-bonding electrons which can donate electron density through π bonding (resonance donation), and it can ultimately induce electronic density on the central metal ion and decrease the redox potential. The results revealed that when a chloro group is attached to the macrocycle of the complex, the complex can cause electrocatalytic CO_2 reduction at a lower potential.

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