



ANOMALOUS CHEMISTRY OF TRANSITION METAL SHIFT BASE COMPLEXES: SYNTHESIS, ANION BINDING CAPACITY AND CATALYTIC ACTIVITY FOR CO₂ REDUCTION

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Anomalous Properties found on the basic chemistry and electrocatalytic activity towards CO₂ reduction of a series of square planar Ni(II), Cu(II) complexes ($[ML_n]^{2+}$ and $[ML_n]^+$ where M= Cu and Ni) of different shift bases (L_n) are reported. All the complexes show a significant affinity for H⁺ association regardless of the +II charge of the complexes. It seems that such an association is not hindered by the positive charge of the complexes and the ligand (L_n) is susceptible for the protonation. Ni(II) and Cu(II) complexes of L_n show reversible colour changes in the presence of acids and bases containing a coordinating anion. This behavior is nicely reflected in their UV-Visible spectral changes. The broad spectral band that appeared in the visible region for all these complexes due to their d-d electronic transitions decreases its intensity, shows a red shift and grows as a new band at the low energy end of the Visible region on adding HCl into the solutions of each of the complexes. Such behavior is not seen on adding acetic acid in which acetate anion is not a good coordinating anion. The intensity of all the original intense bands at wavelength < 400 nm decreases and a new band appears at the low energy end of UV region on stepwise addition of HCl. Original spectrum reappears on adding NaOH to the acidified solution proving the reversibility of the process. In addition, all the complexes show a significant blue shift in its d-d band on adding anions such as SCN⁻ and Br⁻ successively. This behavior and inferred electrophilicity of the complexes towards the anions is seen on adding these anions to the solutions of the complexes only after acidifying the solutions with HCl. In contrast, $[ML_5]^+$ shows anion association even in the absence of acidic conditions. Anion association to the $[CuL_n]^{2+}$ and $[NiL_n]^{2+}$ complexes, especially for $[ML_5]^+$, is probably largely ionic as in the ion pair at the beginning because the d_z^2 orbital, which has the proper symmetry to be bonded with incoming anion, in both complexes is doubly occupied for the square planar geometries of d^8 and d^9 configurations. If any change in either the geometry or electronic spin state of the square planar $[CuL_n]^{2+}$ and $[NiL_n]^{2+}$ complexes occurs at low pH allowing SOMO, $d_{x^2-y^2}$ to have the proper symmetry to be bonded with an approaching anion, a covalent interaction with $[ML_n]^{2+}$ complexes giving an axial coordination of anions can be expected. ¹H NMR spectroscopic data provides evidence for such a geometry change at low pH. Interaction of all these complexes with CO₂ is always larger than that of their starting metal salts under the same condition. However, spectroscopic and electrochemical data suggest that the incorporation of a different metal ion in the cavity of these macrocyclic ligands alters their catalytic properties very significantly though it does not alter their acid–base properties and anion binding capacities qualitatively. All the Ni²⁺ complexes of L_n show some similarity in their electrochemistry and catalyze the CO₂

reduction at $\sim -2.2 \pm 0.2$ V irrespective of L_n whereas all Cu^{2+} complexes of L_n except $[\text{Cu}L_1]^{2+}$ show some anomalous electrochemistry. $[\text{Cu}L_1]^{2+}$ is the only complex that catalyzes the CO_2 reduction at a significantly lower potential, -1.2 V than that of other $[\text{ML}_n]^{2+}$ complexes studied.

Keywords: CO_2 Reduction, Complexes of shift bases, Transition metal catalysts.

Introduction

Literature reports many studies on square planer transition metal macrocyclic complexes for a variety of purposes including the synthesis of drugs, catalysts, etc.¹⁻³ Among them investigation of the interaction of such systems with small hazardous molecules and ions has received a significant attention in Green Chemistry because global warming caused by increasing emissions of such small molecules like CO_2 has been recognized as a serious environmental problem.⁴⁻⁵ Finding an efficient method for the activation of highly inert CO_2 to get fine chemicals has been received much attention recently. Among the numerous ways of CO_2 activation the coordination of CO_2 to a transition-metal center has been received a significant interest. A naturally available system like Chlorophyll provides an insight for understanding the importance of having a square planer transition metal geometry for CO_2 binding and its conversion in to a $(\text{CH}_2\text{O})_n$ polymer. However, the study of such structurally complicated systems is not simple so that many artificial 14-membered macrocyclic 1,4,8,11-tetraazacyclotetradecane complexes and their derivatives with square planner geometry have been used as the most common systems for CO_2 activation. However, there are only very few systematic studies reported in literature to illustrate the effect of electronic and structural variation of these complexes on their chemistry towards small molecule activation. In other words, the effect of electronic and structural variations of these complexes to optimize the capacity of CO_2 activation has not been properly established. Therefore a systematic study of very simple model systems to determine the effect of their electronic and structural properties on their anomalous chemistry is extremely essential. The major objective of the work reported here is to illustrate the anomalous chemistry of square planar transition metal complexes on their synthesis, acid-base chemistry, anion binding capacity and ability for electrocatalytic reduction of CO_2 . In this regard, the behavior of transition metal shift bases (L_n) in the presence of acids, bases and different anions under aerobic, CO_2 and N_2 atmospheres was monitored both spectroscopically and electrochemically.

Methodology

Chemicals required for the synthesis were purchased from Aldrich, Sigma, Mark and used without further purification. All the complexes shown in the figure 1 below (where $M = \text{Ni}^{2+}$ and Cu^{2+}) were synthesized by using template synthesis.

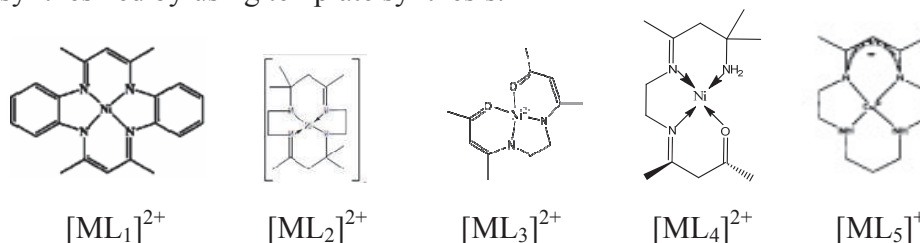


Figure 1.

Literature procedures were modified for the synthesis of the complexes.^{6,8} Complexes synthesized were characterized and further studied by using FTIR, NMR, UV-Visible Spectroscopic, Electrochemical and X-Ray crystallographic techniques. Instrumentation facilities available at the Departments of Chemistry of University Peradeniya (Sri Lanka), Wayne State University (USA) and Monash University (Clayton, Australia) were used.

Results and Discussion

All the attempts made to synthesize analogues 14 membered macrocyclic complex of $[ML_3]^{2+}$ by treating $M(CH_3COO)_2$, acetylacetonate (*acac*) and ethylenediamine (*en*) in 1:2:2 ratio were not successful and only 12 membered $[ML_3]^{2+}$ complex was isolated as the sole product no matter how the stoichiometric ratio of *en* to *acac* was changed. This behavior reflects the unusual stability of 12-membered hemimacrocyclic complex, $[ML_3]^{2+}$. However, the cyclic $[ML_1]^{2+}$ complex is easily formed by treating $M(CH_3COO)_2$, *acac* and diaminobenzene in 1:2:2 ratio though the yield is very poor. The cyclic complexes analogues to $[ML_3]^{2+}$ and $[ML_4]^{2+}$ could not be synthesized by reacting even $M(acac)_2$ with *en* in 1:2 ratio. Presence of acetone, even in very small amount, yields very unusual condensation product that has the structure of $[ML_4]^{2+}$. The easiest way to get 14-membered tetraazamacrocyclic complex is the treatment of *acac* with $[M(2,3,2\text{-tetraamine})]^{2+}$ complex. However, Ni^{2+} complex of $[ML_5]^+$ seems to be the most stable complex among analogues complexes of other first row transition metals.

Both Ni(II) and Cu(II) complexes of $[ML_n]^{2+}$ show a significant affinity for H^+ association (nucleophilicity) regardless of the +II charge of the complexes. It seems that such an association is not hindered by the positive charge of the complexes and the ligand, L_n is susceptible for the protonation. The original colours of all the Ni(II) and Cu(II) complexes of the above ligands, L_n , change with the stepwise addition of dil. HCl to their methanolic solutions. Interestingly, the original colour reappears with the addition of dil. NaOH into the same acidified solutions of the complexes. This behavior is nicely reflected in their UV-Visible spectral changes of $[CuL_3]^{2+}$ and $[NiL_1]^{2+}$ (Figure 2).

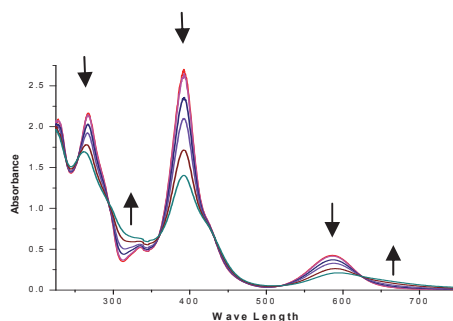


Figure 2. UV-visible spectra on adding HCl (0.1 mol dm^{-3} , $5 \mu\text{l}$ at a time) into a methanolic solution of $[NiL_1][Cl]_2$.

The broad spectral band that appeared in the visible region for all these $[ML_n]^{2+}$ complexes due to their d-d electronic transitions decreases its intensity, shows a red shift and grows as a new band at the low energy end of the Visible region on adding HCl into the solution of each of the complexes. The observed red shift indicates the decrease in CFSE of the complex with the association of Cl^- coming from HCl. The intensity of all the other intense bands at wavelength $< 400 \text{ nm}$ decreases with an appearance of a new band at the low energy end of UV region.

Original spectrum reappears with the addition of NaOH proving the reversibility of the process. These spectral changes with isobestic points imply the existence of a single absorbing species that systematically alters its original geometry without altering its basic skeleton on adding HCl.

In contrast, no significant change in the spectral bands is observed when acetic acid is added successively to the methanolic solution of the complex that is saturated with NaCl. This explains the observed spectral changes are not due to the H^+ association, but due to the Cl^- association.

Further, each $[ML_n]^{2+}$ complex shows a significant blue shift in its d-d band on adding anions such as SCN^- and Br^- successively to the solutions of the complexes acidified with HCl. This implies the electrophilicity of the complexes towards anion association (Figure 3) and an increase CFSE after the association of SCN^- and Br^- .

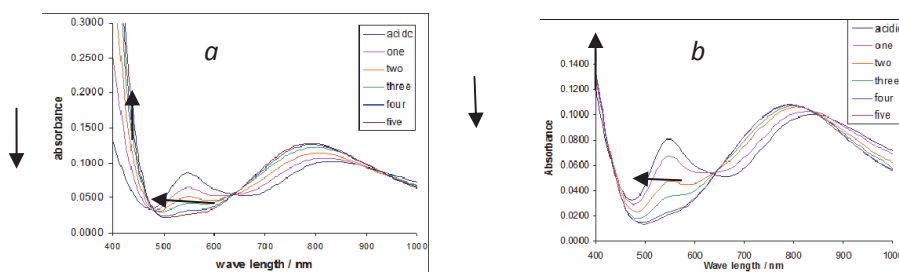


Figure 3. UV-Visible spectra with the stepwise addition ($5 \mu\text{l}$ at a time) of *a.* SCN^- (1.0 moldm^{-3}) *b.* Br^- (1.0 moldm^{-3}) to a methanolic solution of $[CuL_3][ClO_4]$ acidified with HCl.

The important feature is that the anion association was observed only after acidifying the solutions of $[ML_n]^{2+}$ complexes (Figure 4). In contrast, no such pre acidification is required for $[ML_n]^+$ to associate with anions. It can be correlated well with the capacity of axial coordination and the ion pair formation of the different complexes depending on the energy, symmetry and electron occupation of the singly occupied molecular orbital (SOMO) of the metal ion with respect to the axis of incoming anion.

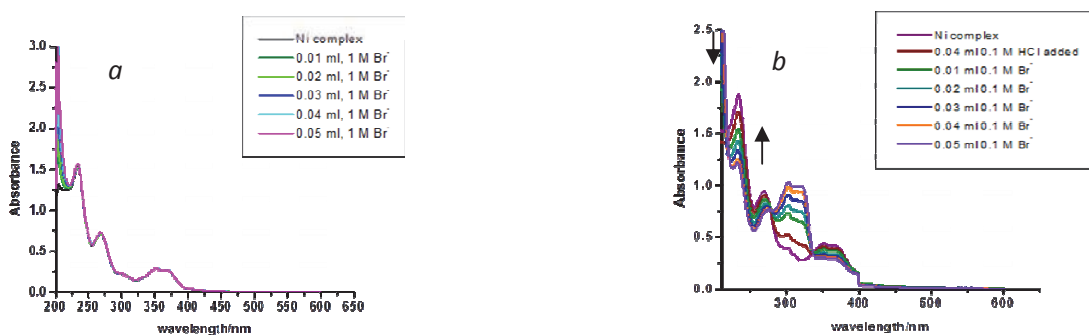
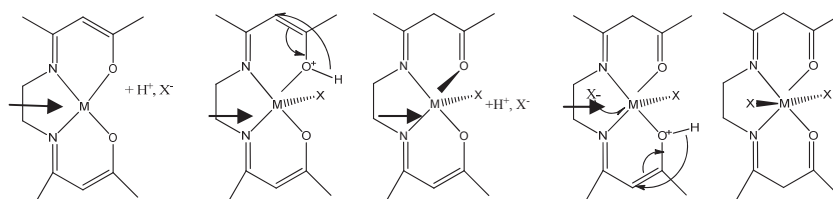


Figure 4. UV-visible spectra with the stepwise addition ($5 \mu\text{l}$ at a time) of Br^- (1.0 moldm^{-3}) to a methanolic solution of $[CuL_3][ClO_4]$ *a.* without prior acidification *b.* acidified with HCl.

Anion association to the Cu^{2+} and Ni^{2+} complexes of L_n is probably largely ionic as in the ion pair at the beginning. Covalent interaction with incoming anions is impossible at the beginning because the SOMO ($d_{x^2-y^2}$) of these complexes is orthogonal to the direction of incoming anion,

and lying along the plane of L_n . Though the symmetry and the direction is significant, the dz^2 orbital in both Ni^{2+} and Cu^{2+} complexes of L_n is doubly occupied in the square planar geometries of d^8 and d^9 configurations and incapable of having any covalent interaction. Though there is no simple basis for a significant covalent bonding interaction between an anion and the metal center, where SOMO is orthogonal to the axis of the approaching anion and the orbital with proper symmetry (dz^2) for the axial coordination is doubly occupied, the UV-Visible spectral shifts with different anions indicate the existence of such an interaction. If any appropriate change in either the geometry or electronic spin state of the complexes occurs after the protonation of L_n aligning the SOMO to the direction of approaching anion, a covalent interaction giving an axial coordination of anions can be expected for the square planar $[ML_n]^{2+}$ complexes. Such an interaction is possible if the geometry of the complex changes to trigonal bipyramidal from square planar due to the rearrangement of the structure after the protonation of either O or N center of L (Scheme I).⁸ H^1 NMR spectroscopic data supports such a change in the presence of an acid, HX (Figure 5a and 5b).



Where $X^- = Cl^-, Br^-, I^-, SCN^-$

Scheme I.

Splitting of the doublet corresponded to CH_3 protons of NiL_3 at ~ 2 ppm in the presence of acids provides evidence for the conversion of magnetically equivalent protons into magnetically nonequivalent protons due to the resultant geometry change of the complex after the protonation of L_n .

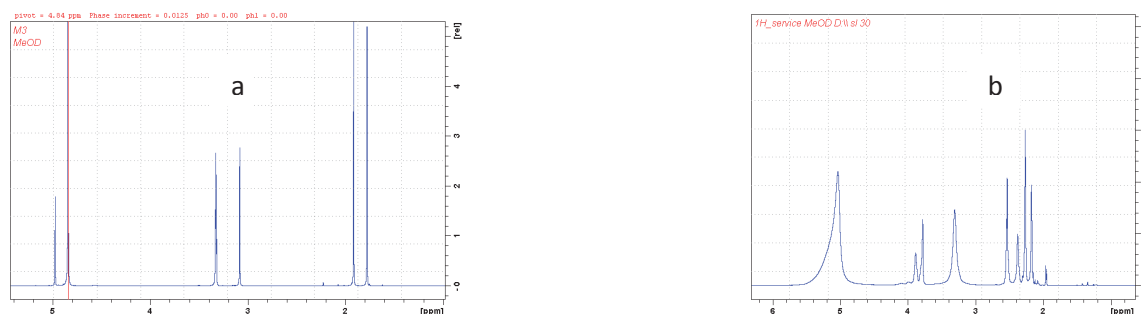


Figure 5. H^1 NMR spectrum of a. NiL_3 in MeOD; b. NiL_3 in the presence of DCl in MeOD.

The amount of CO_2 trapped by all these complexes is always larger than that of their starting metal salts as reflected by the measured area under the curve obtained by plotting CO_2 transmitted vs. time. However, all the $Ni^{(II)}$ complexes of L_n and $Cu^{(II)}$ complex of only L_1 exhibit their capability to act as catalysts for CO_2 reduction.

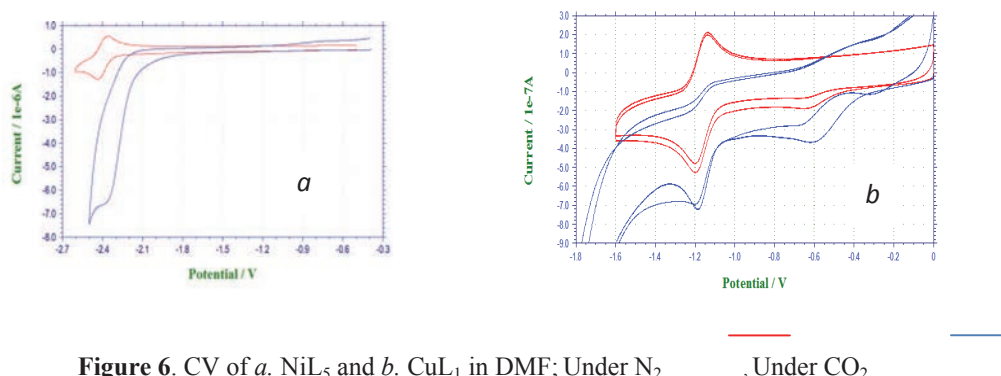


Figure 6. CV of a. NiL₅ and b. CuL₁ in DMF; Under N₂ (red line), Under CO₂ (blue line)

After passing CO₂, the reversible cyclic voltammetric (CV) wave of Ni^{II}/Ni^I redox couple of all Ni²⁺ complexes of L_n becomes irreversible, anodic band disappears and the peak current intensity of the cathodic band increases significantly higher than that (Figure 6) under N₂ atmosphere at a potential $\sim -2.2 \pm 0.2$ V. The original reversible CV wave, corresponded to Ni^{II}/Ni^I redox couple, regenerates after passing N₂ back to the same solution. This behavior together with the significant increase of cathodic peak current in CO₂ compared to that in N₂ atmosphere indicates the catalysis of CO₂ reduction process by these complexes. The observed potentials are not much affected by the different solvents and electrodes. The electrocatalytic reduction potential of all the Ni²⁺ complexes of L_n does not depend on the structure of L_n, but $I_{p,c}(\text{CO}_2)/I_{p,c}(\text{N}_2)$, the current efficiency of the process depends on L_n (Table 1). The complex, [NiL₅]⁺ shows the highest current efficiency compared to the other systems reported here. Among the series of Cu²⁺ complexes of L_n studied, only [CuL₁]²⁺ is stable enough to catalyze the reduction of CO₂ and it occurs at a significantly lower potential (-1.2 V) than all the other complexes studied (Figure 8). All the other Cu²⁺ complexes of L_n show anomalous electrochemistry and they all show only an irreversible CV wave corresponded to Cu^{II}/Cu^I reduction in N₂ atmosphere though the cathodic current intensity increases on passing CO₂. In contrast to all the complexes, both Cu(II) and Ni(II) complexes of L₁ show electropolymerization and the polymeric complexes also show electrocatalysis towards CO₂ reduction.

Table 1. Comparison of the efficiency of the electrocatalysis

Complex	M(II)/M(I) reduction potential in DMF, V using GC electrode	$I_{p,c}(\text{CO}_2)/I_{p,c}(\text{N}_2)$ with respect to GC electrode
[NiL ₁] ²⁺	Three bands in between -1.6 to -2.4	1.6
[CuL ₁] ²⁺	-1.2	1.6
[NiL ₂] ²⁺	-2.4	1.8
[NiL ₃] ²⁺	-2.4	2.1
[NiL ₄] ²⁺	-2.2	1.6
[NiL ₅] ⁺	-2.4	6.5

Conclusion and Significance

All the Ni^(II) complexes of L_n exhibit their capability to act as catalysts for CO₂ reduction at a potential that is few millivolts (~ 100 - 200 mV) lower than the potential required for direct CO₂ reduction. Among the Cu²⁺ complexes of L_n reported here, only [CuL₁]²⁺ shows a reversible CV

wave corresponding to $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ redox couple. Catalytic activity of $[\text{CuL}_1]^{2+}$ occurs at a significantly lower potential than the potential required in the absence of a catalyst. Spectroscopic and electrochemical data suggest that the incorporation of a different metal ion in the cavity of these macrocyclic ligands alters their catalytic properties extremely significantly though it does not alter their acid–base properties and anion binding capacities qualitatively. This provides evidence to confirm that the mode of interaction of $[\text{ML}_n]^{2+}$ complexes with H^+ , anions and a neutral molecule like CO_2 is different. A covalent interaction with the incoming anions occurs only if the geometry of the square planar complex changes to *tbp* upon adding acids and subsequent protonation of the ligand (L_n). Such interaction is possible only with $[\text{ML}_n]^{2+}$ complexes. The anion interaction with the complex, $[\text{ML}_5]^+$ seems to be ion pair type so that the geometry change is not required. Acid binding seems to occur at the ligand, L_n , and it depends on the nature of L_n . CO_2 binding seems to occur at the metal center (M^{2+}) and the reduction of CO_2 after the coordination is more sensitive to the electronic properties of M^{2+} rather than the structural properties of the ligand, L_n . However, the current efficiency for the CO_2 reduction process is sensitive to the L_n and the efficiency is highest for $[\text{NiL}_5]^+$. The absence of a bridged-head proton in L_5 and the inferred low steric hindrance seems to be favorable for binding more CO_2 to $[\text{NiL}_5]^+$. Among all Ni^{2+} complexes of L_n , there is no significant deviation of the potential where $\text{Ni}^{\text{II}}/\text{Ni}^{\text{I}}$ redox wave appears. These data provide evidence for the importance of both metal center and the ligand structure for the efficiency of CO_2 reduction. Concerning the lower potential at which $\text{Cu}^{\text{II}}/\text{Cu}^{\text{I}}$ reduction occurs, future attempts should be made to modify the structure of L_n in relevant Cu^{2+} complexes to open the path for finding the most efficient electrocatalyst for CO_2 reduction.

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References

1. B. Fisher, R.Eisenberg, *J.Am.Chem.Soc.*, **1980**, *102*, 7361.
2. E. Fujita, D.Szalda, C.Curtz, N. Sutin, *J.Am.Chem.Soc.*, **1988**, *110*, 4870.
3. E. Fujita, D.Szalda, C.Curtz, N. Sutin, *J.Am.Chem.Soc.*, **1991**, *113*, 343.
4. K.B.Yatsimirskii, *Russ. Chem. Rev.*, **1990**, *12*, 59.
5. X.Yin, J.R.Moss, *Cood.chem.Rev.*, **1999**, *181*, 27.
6. D.C.Olson, L.Vasilevskis, *Inorg. Chem.*, **1971**, *10*, 463.
7. John J.Martin, Sue C.Cummings, *Inorg.Chem.*, **1973**, *12*, 7, 1477.
8. M.Y. Ugudala-Ganehenege, M. J. Heeg, L. M. Hryhorczuk, L. E.Wegner, J.F. Endicott, *Inorg. Chem.*, **2001**, *40*, 1614.