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Research Article

TEMPLATE SYNTHESIS OF CHLORO AND NITRO SUBSTITUTED PHENOL BASED MACRO CYCLIC CALCIUM (II) COMPLEXES

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Abstract

This paper reports the Synthesis of Chloro and Nitro substituted Phenol based Macro Molecules by Template Synthesis .Effect of various process parameters such as Cation removal and chelating formation and structure has been studied for the Experimental data of macro molecules and characteristic parameters were analyzed by IR, EAS, Molar conductance, TGA and Cyclic Volta metric methods.

Keywords: Synthesis of Chloro and Nitro, Template Synthesis, , EAS, Molar conductance, TGA.

Introduction

Macrocyclic complexes are of great importance due to their resemblance to many naturally occurring macrocycles, such as porphyrins and cobalamines. A number of nitrogen donor macrocyclic derivatives have long been used in analytical, industrial and medical applications.[1-4] Macrocyclic metal complexes of lanthanides, *e.g.*, Gd^{3+}, are used as MRI contrast agents.[5] Macrocyclic metal chelating agents are useful for detecting tumor lesions.[6] The chemistry of macrocyclic complexes is also important due to their use as dyes and pigments[7]as well as NMR shift reagents.[4] Furthermore, some macrocyclic complexes have been found to exhibit potential antibacterial activities.[8]

A macrocycle is a cyclic macromolecule or a macromolecular cyclic portion of a molecule. In the chemical literature, organic chemists may consider any molecule containing a ring of nine or more atoms to be a macrocycle. Prompted by these facts, Schiff base ligands are considered as “privileged ligands” because they are easily prepared by the condensation between aldehydes and amines. Schiff base ligands are able to coordinate many different metal ions and to stabilize them in various oxidation states. Structure activity relationship of Schiff base compounds are studied due to their antitumor, antimicrobial and antiviral activities.[9-11]

In recent years, because of new interesting applications found in the field of pesticides and medicine, the metal complexes with tridentate O, N, N types of alternative structures have attracted the attention of chemists. Various metal complexes with bi-and tridentate Schiff bases containing nitrogen and oxygen donor atoms play important role in biological systems.[12-14] Schiff base complexes incorporating phenolic group as chelating moieties in the ligand are considered as models for executing important biological Reactions and mimic the catalytic activities of metalloenzymes.[15]

Macrocyclic Schiff bases are very important molecules in biological systems. They have wide range of applications in bioinorganic, coordination and catalysis field. They have some interesting properties and biological functions such as being models for metalloproteins and oxygen carrier systems, in catalyzing organic oxidation ion reaction. These ligands found to be very versatile due to their capability of forming stable complexes.[16]

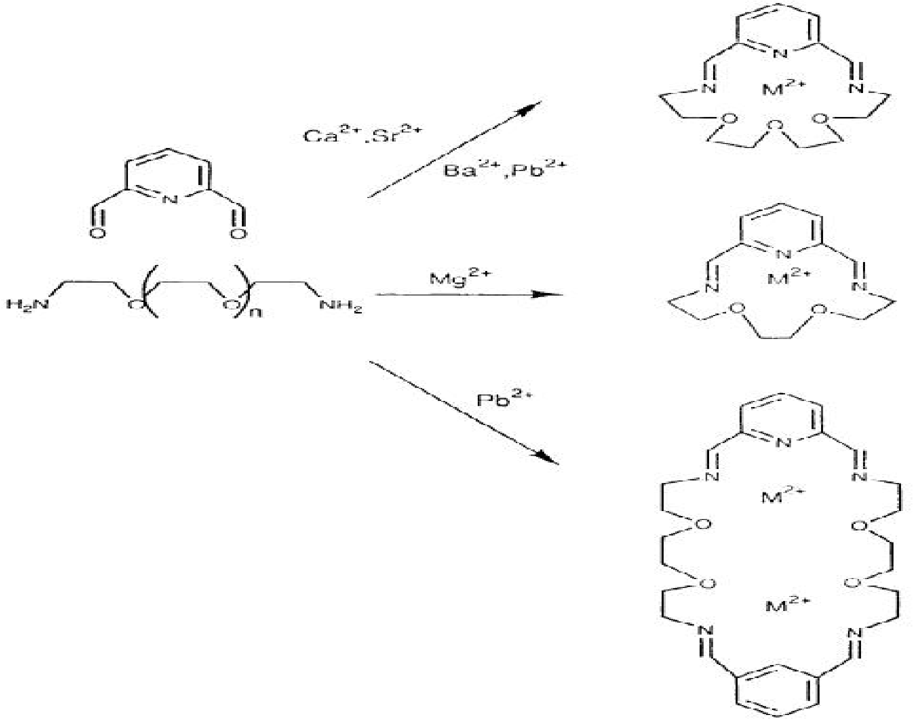
Template effect

Ideally, a macrocyclic complex is formed by adding the required metal ion to a preformed ligand. However, the synthesis of the required macrocycle often results in a low yield of the desired product with side reactions such as polymerization predominating. In order to circumvent this problem, the ring-closure step in the synthesis may be carried out under conditions of “high dilution”, or “rigid groups” may be introduced to restrict rotation and internal entropy losses in the open-chain precursor and so facilitate cyclization. One effective method for the synthesis of macrocyclic complexes involves an *in situ* approach wherein the presence of a metal ion in the cyclization reaction markedly increases the yield of the cyclic product. The metal ion plays an important role in directing the steric course of the reaction; this has been termed the metal template effect.[22]

The size of the cation used as a template has proved to be of importance in directing the synthetic pathway in the Schiff base systems **(Scheme 2).** Of the alkaline earth cations only magnesium generates the pentadentate [1 + l] macrocycle but it is ineffective in generating the hexadentate [1 + l] macrocycle which is readily synthesized in the presence of the larger cations like calcium, strontium, barium and lead (II) ion. These cations, however, generate the [2 + 2] macrocycle derived from the components giving the [1 + 1] macrocycle with magnesium.[23]

The similarity in ionic radii between the alkaline earth metal cations and the lanthanide(III) cations suggested that the latter should also be efficient tern plating devices, and this has proven to be the case.

The actinides, with their high ionic radii and/or unusual coordination geometry, can produce and stabilize expanded macrocyclic ligands as in the preparation of “superphthalocyanines”.[24] With certain precursors (i.e. 2,6-diacetylpyridine and 1,3-diamino-2-hydroxypropane), [3 + 3] and [4 + 4] macrocyclic complexes have been synthesized. For the [2 + 2] ligands, the head and the lateral units can be varied with the consequent formation of macrocycles with different donor atoms and/or different cavity sizes.[25]



Scheme 1

Materials and Methods

Reagents

2,6-Diformyl-4-methyl phenol was synthesized by the method described by Gagne et al.[121] Calcium (II) chloride dehydrate (AR, E. Merck) and copper(II) nitrate (AR, E. Merck) were used as such. O-Phenylene diamine (AR, E. Merck), 4-Nitro-1,2-phenylenediamine (AR, Sigma Aldrich) and 4-chloro-1,2-phenylenediamine (AR, Sigma Aldrich) were purchased and used.

Solvents

Aceto nitrile (AR, Avra Synthesis), toluene (AR, E. Merck), diethyl ether (AR, Avra Synthesis) and di methyl form amide (AR, E. Merck) were used as such. Absolute ethanol was obtained by distillation of rectified spirit over lime. Distilled water was used throughout the study.

Template Synthesis of Macro cyclic Complexes

Synthesis of $[Ca_2(L1)(H_2O)Cl]Cl$

To a hot solution of 2,6-diformyl-4-methylphenol (0.164 g, 1 m mol) in acetonitrile was added Calcium (II) chloride dehydrate (0.170 g, 1 mmol) in acetonitrile. To the above clear solution, was added a solution of o-phenylenediamine (0.108 g, 1 mmol) in acetonitrile drop by drop and then refluxed for 3 h. The precipitate formed was filtered through G-4 sintered crucible and then washed with diethyl ether and dried over anhydrous calcium chloride. The yield was 40%.

Synthesis of $[Ca_2(L1)(H_2O)(NO_3)]NO_3$

To a hot solution of 2,6-diformyl-4-methylphenol (0.164 g, 1 mmol) in acetonitrile was added Calcium (II) nitrate hexahydrate (0.241 g, 1 mmol) in acetonitrile. This clear solution was added a solution of o-phenylenediamine (0.108 g, 1 mmol) in acetonitrile drop by drop and then refluxed for 3 h. The brown precipitate formed was filtered through G-4 sintered crucible and then washed with diethyl ether and dried over anhydrous calcium chloride. The yield was 42%.

Physical measurements

Infrared Spectra

The infrared spectra of all the complexes were recorded on a Perkin Elmer FT-IR Spectrometer in the range of 4000 – 400 cm^{-1} using KBr pellets.

UV-Visible Spectra

UV-Visible spectra of all the complexes were recorded on Perkin Elmer Lambda 3B UV-Visible Spectrophotometer in the range 200-900 nm. The spectra of the complexes were recorded in DMF at 25°C using matched pair of Teflon stoppered quartz cell of path length 1 cm.

Molar Conductivity Measurements

The molar conductance of the Ca(II) complexes were measured using 10^{-3} M solution of DMF at 25^{o}C using an Elico CM-180 Conductivity meter and Elico type CC-03 Conductivity cell of cell constant 1.05 cm^{-1}.

Cyclic voltammetry

The cyclic Volta metric studies of the complexes were carried out on EG&G PAR potentiostat/galvanostat electrochemical analyzer. Cyclic voltammograms were recorded for Calcium (II) complexes in 10^{-3} M solution in DMF, containing 0.1 M tetraethyl ammonium per chlorate in an inert atmosphere at 25^{o}C. The standard three electrode configuration consisting of a glassy carbon disc working electrode, a platinum wire auxiliary electrode and Ag/Ag^{+} reference electrode was used.

TG-DTA study

The TGA and DTA measurement of all the complexes were carried out using DTG-60 Thermal analyzers in the temperature range of RT to 800 °C.

Template synthesis of complexes

The Calcium (II) complexes of the 18-membered tetraza phenolic macro cyclic legends (H_2L1), (H_2L2) and (H_2L3), are synthesized by the Schiff's base condensation of 2,6-diformyl-4-methylphenol and o-phenylenediamine, nitro-o-phenylenediamine, or chloro-o-phenylenediamine, respectively in the presence of Ca(II) chloride dihydrate or Ca(II) nitrate hexa hydrate as templates in 1:1:1 mole ratio in acetonitrile. The Calcium (II) complexes were obtained as brown or dark brown precipitates. They are highly soluble in DMF and DMSO and insoluble in ethanol, acetonitrile, chloroform and diethyl ether. The yields of the complexes are reasonably good.

Characterization of the Macro cyclic Complexes

The Ca (II) complexes of H_2L1, H_2L2 and H_3L3 are characterized by IR, UV and molar conductivity measurements.

IR Spectra

The infra red spectrum of $[Ca_2(L1)(H_2O)Cl]Cl$ shows absorbance at 1618 cm^{-1} which is due to C=N stretching and at 3400 cm^{-1} due to OH stretching. The strong absorption at 1547 cm^{-1} is due to C=C stretching vibration of the aromatic ring. The weak absorption at 1263 cm^{-1} is due to C-O stretching. For the complex, $[Ca_2(L1)(H_2O)(NO_3)]NO_3$, shows absorbances at 1588 and 3436 cm^{-1} are due to C=N and OH stretching. The absorbance at 1384 cm^{-1} is attributed to N-O stretching in the complex. The complex, $[Ca_2(L2)(H_2O)Cl]Cl$ shows the absorbance at 1592 cm^{-1} due to C=N stretching and the strong absorption at 3392 cm^{-1} is due to OH stretching.

For the complex [Ca_2(L2)(H_2O)(NO_3)]NO_3 the absorbance at 1588 cm^{-1} is due to C=N stretching and at 3410 cm^{-1} is due to OH stretching. A strong absorbance in nitrate complexes at 1349 cm^{-1} is attributed to N-O stretching. The chloride complex [Ca_2(L3)(H_2O)Cl]Cl shows an intense absorbance at 1618 cm^{-1} which is due to C=N stretching and another strong absorbance at 3421 cm^{-1} is due to OH stretching. The nitrate complex of ligand L3, [Ca_2(L3)(H_2O)(NO_3)]NO_3, shows absorbance due to C=N stretching at 1538 cm^{-1} and the OH stretching at 3421 cm^{-1}. The absorbance at 1384 cm^{-1} is due to the N=O of ionic nitrate.

The IR spectra of all the complexes clearly show absorbances due to all characteristic functional groups like imines, nitrate, chloro groups present in the macro cyclic complexes and the nitrate salt is giving an additional absorbance at the 1384 cm^{-1} range. This range confirms that there will be a free N-O stretching in the complexes as compared to the other anionic complexes. The IR spectra of all copper (II) complexes are shown in Figures **1** and **2** and the IR spectral data are presented in **Table 1.**

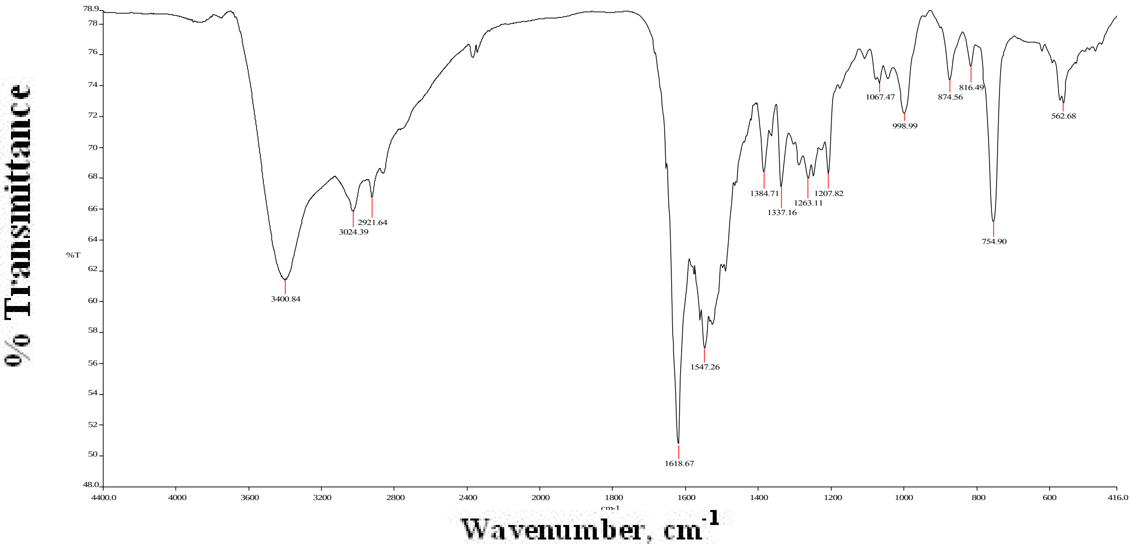


Figure 1. IR spectrum of [Ca_2(L1)(H_2O)Cl]Cl

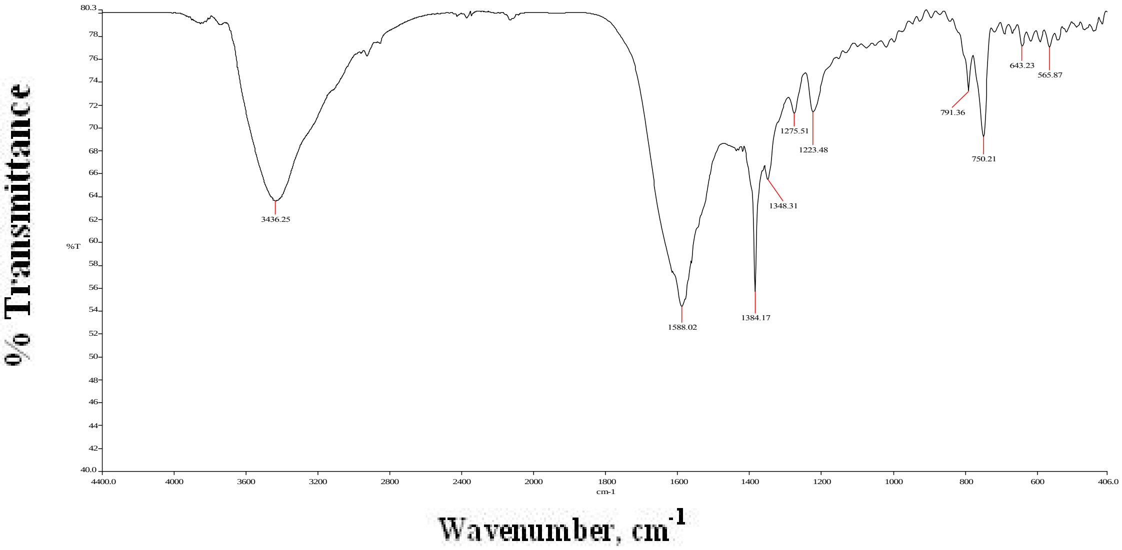


Figure 2. IR spectrum of [Ca_2(L1)(H_2O)(NO_3)]NO_3

Table1. Infrared spectral data of the Ca(II) complexes of H_2L1, H_2L2 and H_3L3.

Complexes	Assignments						
	ν(O-H)	ν(C-H)	ν(C=N)	ν(C=C)	ν(C-O)	ν(N=O)	δ(O-H)
$[Ca_2(L1)(H_2O)Cl]Cl$	3400	3024	1618	1547	1263	-	754
$[Ca_2(L1)(H_2O)(NO_3)]NO_3$	3436	3012	1588	1570	1275	1384	750

Electronic Absorption Spectra

The electronic absorption spectra of all the Calcium (II) complexes were recorded using10^{-4} M solutions in DMF. In the case of $[Ca_2 (L1) (H_2O)Cl]Cl$, a peak at 266 nm is due to π→π* transition and the peak at 344 nm is due to n→ π* transition and a peak at 436 nm is due to charge transfer transition. The peak at 529 nm is due to d-d transition**.** The electronic absorption spectrum of $[Ca_2 (L1) (H_2O)Cl]Cl$ is shown in Figure 3.

The electronic absorption spectrum of $[Ca_2 (L1) (H_2O)(NO_3)]NO_3$ shows peaks at 266, 323 and 396 nm due to π→π*, n→ π* and charge transfer transition and a peak at 481 nm is due to d-d transition. The electronic absorption spectrum of $[Ca_2 (L1) (H_2O)(NO_3)]NO_3$ is shown in Figure 4.

Table 2. Electronic absorption spectral data and molar conductance data of Calcium (II) complexes

Complexes	Assignments						
	π→π*	n→π*	CT	d-d	Λo $\Omega^{-1}cm^2 mol^{-1}$	Electrolytic Nature	% of metal
$[Ca_2(L1)(H_2O)Cl]Cl$	266	344	436	529	54.8	1:1	18.40
$[Ca_2(L1)(H_2O)(NO_3)]NO_3$	266	323	396	481	14.3	1:1	17.23

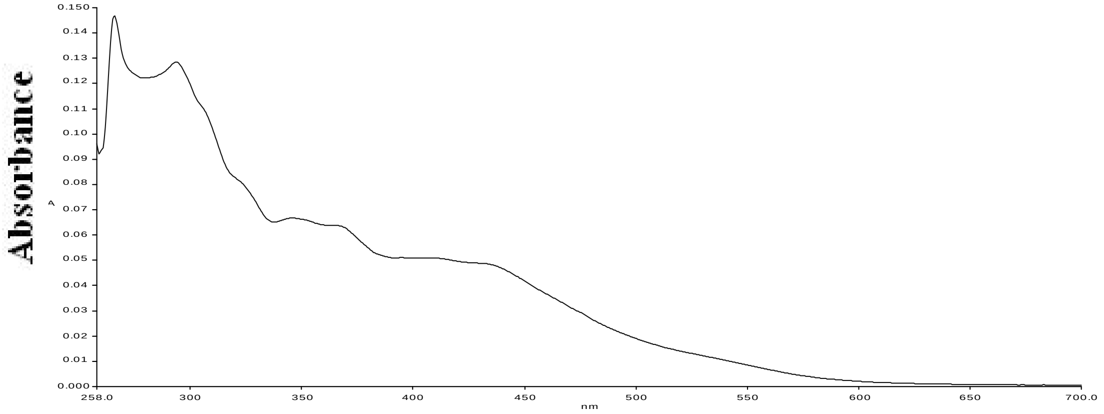


Figure 3. The electronic absorption spectrum of $[Ca_2 (L1)(H_2O)Cl]Cl$

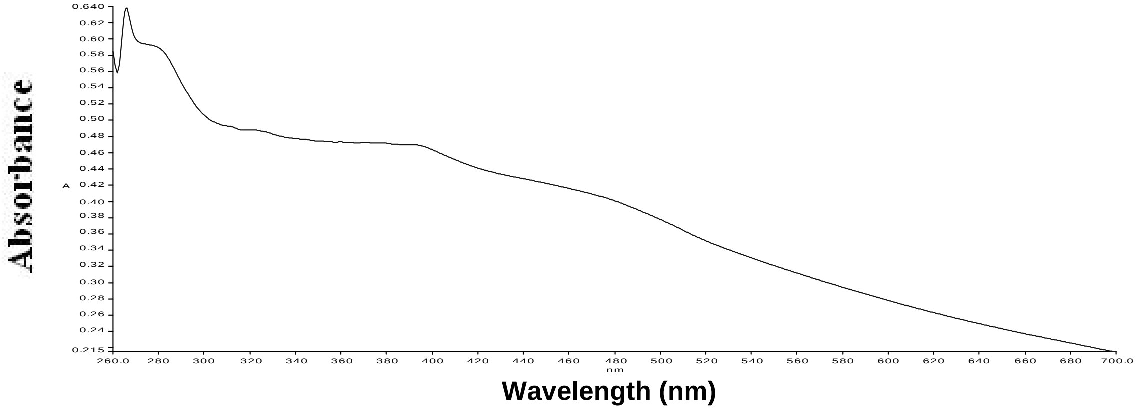


Figure 4. The electronic absorption spectrum of $[Ca_2 (L1) (H_2O) (NO_3)] NO_3$

Molar conductivity measurements

The molar conductance of the Ca (II) complexes was measured using 10^{-3} M solution in DMF. The molar conductance values of Ca(II) complexes are 54.8,14.3,56.3,20.2,79,27 ohm^{-1} cm^{2} mol^{-1}which suggest that they correspond to 1:1 electrolytes. Hence, the molecular composition of Ca(II) complexes of ligands H_2L1,H_2L2, are assigned as $[Ca_2(L1)(H_2O)Cl]Cl$,
$[Ca_2(L1)(H_2O)(NO_3)]NO_3$, respectively.

Thermo gravimetric analysis

The TG/DTA study of copper chloride complexes of H_2L1, H_2L2 and H_2L3 was studied in inert atmosphere in thermal range 30 ˚C to 800 ˚C. The TGA pattern of $[Cu_2 (L1) (H_2O)Cl]Cl$ shows the continuous mass loss from 50 ˚C up to 300 ˚C accounting for a mass loss of 6%. In the temperature range 300 ˚C to 540 ˚C there is a mass loss of 10% accounting to loss of two chloride ions. From 540 ˚C up to 800 ˚C the ligand is lost. However the decomposition is not complete up to 800 ˚C. The DTA pattern shows two endothermic peaks at 360 ˚C for the loss of ionic HCl and at 479 ˚C for the loss of coordinated Cl^- as HCl.

The TGA pattern of $[Ca_2 (L2) (H_2O)Cl]Cl$ shows a loss of water molecule at around 100 ˚C. Loss of chlorides takes place at around 319 ˚C and 348 ˚C. The macrocycle is lost in the temperature range 500 ˚C to 800 ˚C but the decomposition is only partial. The DTA pattern of $[Ca_2 (L2) (H_2O)Cl]Cl$ shows two endothermic peaks at 320 ˚C and 384 ˚C for the loss of two chloride ions as HCl.

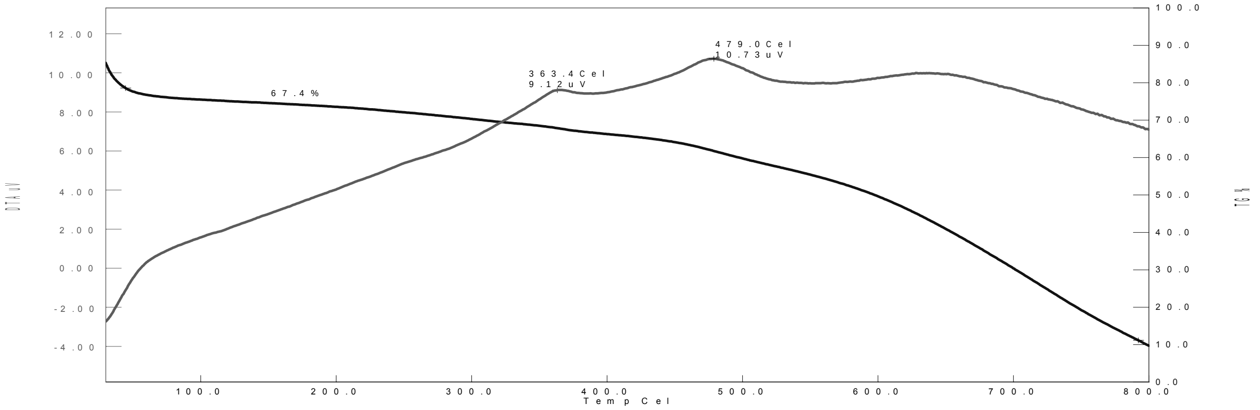


Figure 5. TG-DTA pattern of $[Ca_2(L1)(H_2O)Cl]Cl$

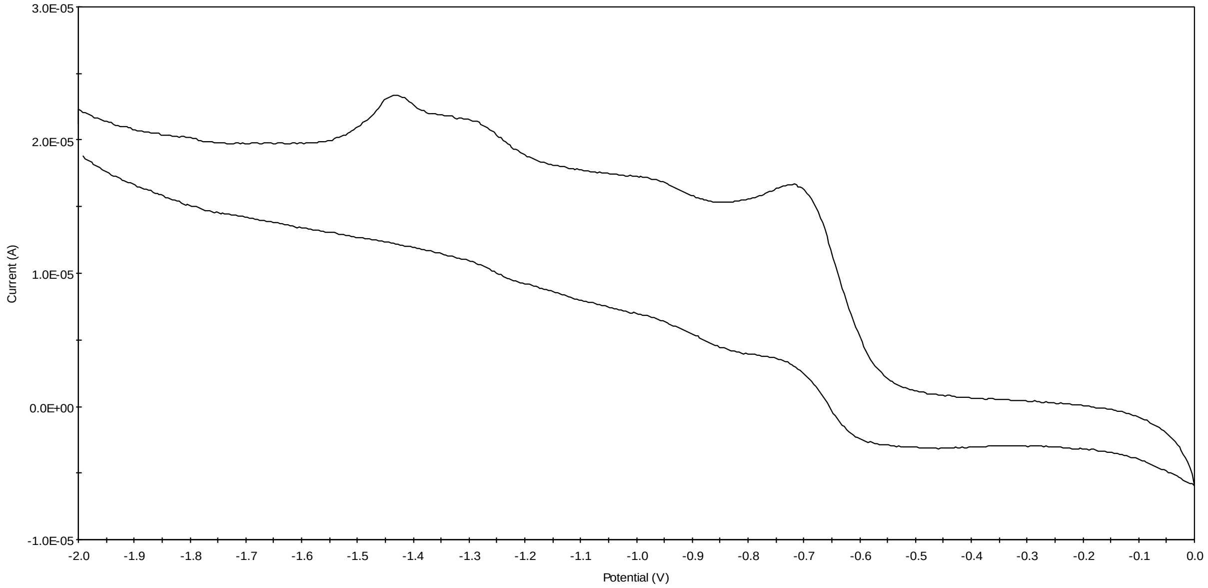


Figure 6. TG-DTA pattern of $[Ca_2(L1)(H_2O)(NO_3)]NO_3$

Cyclic voltammetry

The cyclic Volta gram of Ca(II) complexes of H_2L1, H_2L2 and H_2L3 were recorded using 10^{-3} M solution in DMF. Tetra ethyl ammonium bromide was used as a supporting electrolyte and scan rate was fixed at100 mV/sec. The cyclic Volta gram of $[Cu_2(L1)(H_2O)Cl]Cl$ consists of two cathodic peaks at -0.66 and -1.3 V. and two anodic peaks at -1.1 and -0.56 V. The red ox couple of Ca(II)/Ca(I) takes place at $E_{1/2}$ = -0.61 V. the ΔEp of the reaction is 100 mV and the ip_a/ip_c is 0.45 V. This shows that the reaction is highly irreversible. The legend centered reduction takes place at $E_{1/2}$ of -1.2 V and this process is also highly irreversible.

The cyclic voltammogram of $[Ca_2(L1)(H_2O)(NO_3)]NO_3$ shows the cathodic and anodic peak maxima for Ca(II)/Ca(I) redox couple at -0.71 and -0.60 V. The $E_{1/2}$ of the reaction is -0.65 V and the ΔEp value is 110 mV with the ip_a/ip_c 0.4 V suggesting highly irreversible process. The legend centered red ox reaction takes place at $E_{1/2}$ of -0.85, -1.25 and -1.35 V. Compared to the chloride complex, the nitrate complex shows additional redox systems for nitrate group which confirms the presence of nitrate groups inside the compounds.

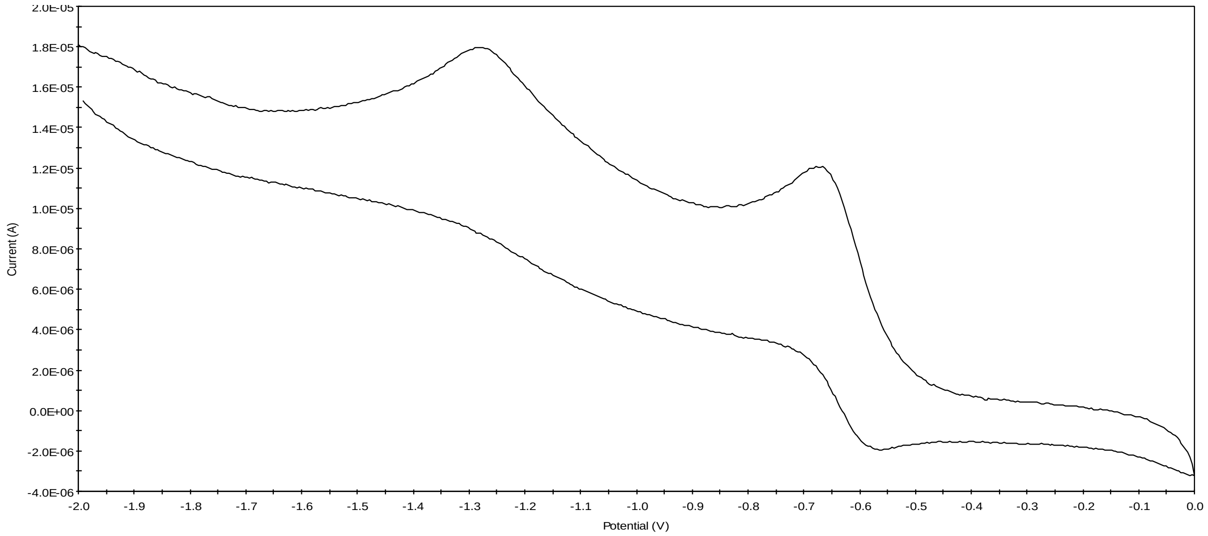


Figure 7. Cyclic voltammogram of $[Ca_2(L1)(H_2O)Cl]Cl$ in DMF with Et_4NBr at the scanning rate of 100 mV/s

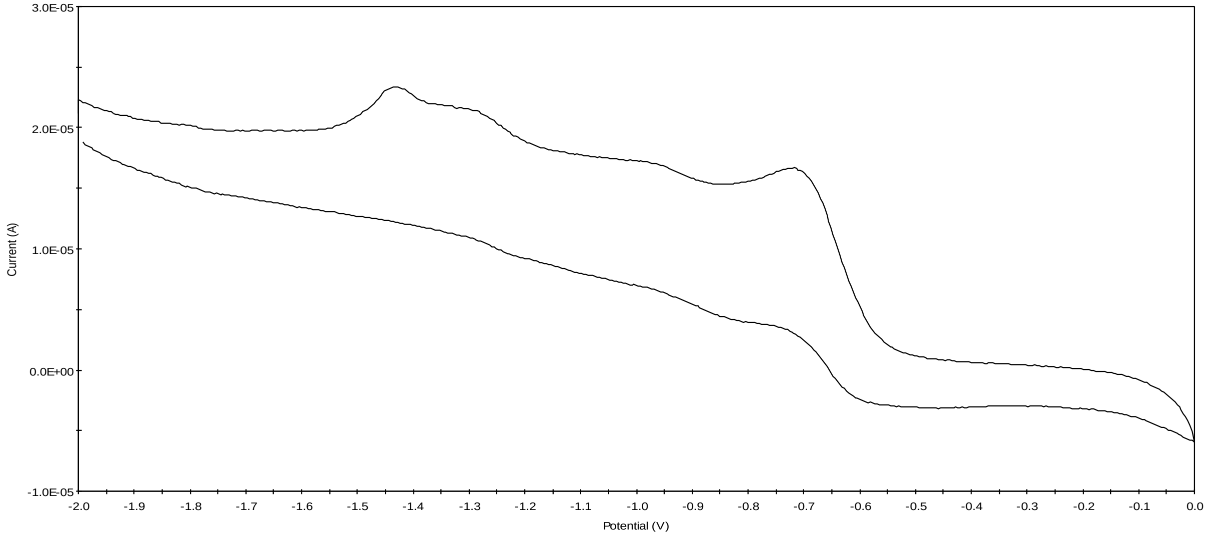


Figure 8. Cyclic voltammogram of $[Ca_2(L1)(H_2O)(NO_3)]NO_3$ in DMF with Et_4NBr at the scanning rate of 100 mV/s

Summary and Conclusion

Summary

The Calcium (II) complexes of H_2L1, and H_2L2, are prepared by template method using 2,6-diformyl-4-methylphenol and 1,2-diaminobenzene, 4-nitro-1,2-diaminobenzene or 4-chloro-1,2-diaminobenzene with suitable Calcium chloride or Calcium nitrate salts in 1:1:1 mole ratio in acetonitrile. The complexes are obtained in reasonably good yield. They are stable both in the solid state and in the solution.

The IR spectrum of the complexes show peaks corresponding to ν(O-H), ν(C=N) and aromatic ν(C-H) at around 3324, 1588 and 3028 cm^{-1}, respectively. The free nitrate for the nitrate complexes are observed at 1384 cm^{-1}. The ν(O-H) observed at 3324 cm^{-1} may be due to coordinated water molecule. The UV visible spectrum of the complexes show peaks corresponding to $\pi\rightarrow\pi^*$, $n\rightarrow\pi^*$, CT transition and $d\rightarrow d$ transition at around 266, 340, 400 and 450 nm, respectively.

The luminescence spectra of the complexes show ligand centered emission. The methyl substituted complexes show intense emission at 530 nm. The chloro substituted complexes show less emission whereas nitro substituted complexes show poor emission. The excitation maxima in all the complexes were observed either at 280, 360 and/or 420 nm. In common, all the chloride complexes show increase in intensity of emission whereas nitrate complexes show less intense emission. This may be due to the electronic effect of the electron withdrawing groups like chloro and nitro which suppresses the emission of the ligand either by extended conjugation or by quenching process.

Cyclic voltammogram of the copper complexes of H_2L1, H_2L2, and H_2L3 show both metal and ligand centered redox reactions. The metal centered redox reaction takes place at the $E_{½}$ of around -0.6 V and the ligand centered redox reaction for methyl takes place at on -1.4V, for nitro at -1.1V and for chloro at -1.0 V. The nitro complexes show additional redox couple in all the three types of ligands at around -1.3 and -1.2 V, respectively. All the redox reactions are highly irreversible as the ΔEp values are more than 100 and ipa/ipc is less than 1. This may be due to the ligand or the metal ion, after reduction from stable complexes, they are reluctant to undergo oxidation.

Conclusion

Chloro and nitro substituted macrocyclic complexes are prepared successfully with Calcium chloride and Calcium nitrate salts. The complexes are very stable. The luminescence and cyclic voltammogram of these complexes show interesting results that these complexes, if fine tuned, could well be used as suitable energy converter or electron transfer agents that they may find application in solar energy conversion. If these complexes are appended suitably with water soluble groups or water soluble anions may make them suitable candidates for metal extraction and as fluorescent emitters.

References

1. Constable E. C., *Coordination Chemistry of Macrocyclic Compounds*, Oxford University Press, Oxford, **1999**;
2. Gloe K., Ed., *Current Trends and Future Perspectives*, Springer, Berlin, **2005**
3. Singh D. P., Kumar R., Malik V., Tyagi P., *Transition Met. Chem*. *32***, 2007,**1051
4. Singh D. P., Kumar R., Malik V., Tyagi P., *J. Enzym. Inhib. Med. Chem*. *22***, 2007**, 177
5. Watson A. D., Rockladge S. M., in *Magnetic Resonance Imaging of the Body*, C. B. Higgins, Ed., Raven Press, New York, **1992.**
6. Kosmos C., Snook D.,. Gooden C. S, Courtenay-Luck N. S., McCall M. J., Meares C. F., Epenetos A. A., *Cancer Res. 52***, 1992**, 904
7. Seto J., Tamura S., Asai N., Kishii N., Kijima Y., Matsuzawa N., *Pure Appl. Chem. 68*, **1996**, 1429
8. Singh D. P., Kumar R., Tyagi P., *Transition Met. Chem*. *31*, **2006**, 970
9. Ren, S., Wang, R., Komatsu, K., Bonaz-Krause, P., Zyrianov, Y., McKenna, C. E., Csipke, C., Tokes, Z.A., Lien, E. J., *J. Med. Chem., 45*, **2002,** 410.
10. Panneerselvam, P., Nair, R. R., Vijayalakshmi, G., Subramanian, E. H., Sridhar, S. K., *Eur. J. Med. Chem*., *40*, **2005,** 225.
11. Vicini, P., Geronikaki, A., Incerti, M., Busonera, B., Poni, G., Cabrasc, C. A., Collac, P. L., *Bioorg. Med. Chem*., *11*, **2003,**4785.
12. Kasumov, V. T., Ozalp-Yaman, S., Tas, E., *Spectrochim. Acta A*, *62*, **2005,**716.
13. Frausto da Silva J., Williams, R., "*The Biological Chemistry of the Elements*", Clarendon Press, Oxford, **1991**.
14. Kaim, W., Schwederski, B., "*Bioinorganic chemistry: Inorganic elements in the chemistry of life*", Wiley, New York, **1996**.
15. Khandar A. A., Hosseini-Yazdi, S. A., Zarei, S. A., Rabie, U. M., *Inorg. Chim. Acta., 358*, **2005,** 3211.