Synthesis, Spectroscopic and Electrochemical Studies of Cobalt(II) and Nickel(II) Macrocyclic Complexes Derived from Oxalodihydrazide and Aldehydes/Propanone

H.C. Rai*, Priyanka, Annapurna Sharma†, Meera Sharma‡ and Sarita Kumari
Department of Chemistry, B.R.A. Bihar University, Muzaffarpur-842 001, India
E-mail: hcrai@rediffmail.com

Synthesis of 14-membered macrocyclic complexes of cobalt(II) and nickel(II) of the type [M(mac[1-3])] are reported. The complexes have been characterized on the basis of analytical, metal conductivity, magnetic susceptibilities, infrared, electronic, spectral data and electrochemical studies. Infrared spectral data show that the ligands behave in a diabasic tetradentate manner in all the complexes. Electronic spectral data and magnetic moment value are indicative of square planar geometry. The nickel complexes were red or orange to yellow in colour, whereas cobalt(II) complexes were chocolate brown in colour. High dilute conditions were maintained to dispense with polymerization reaction. The thermodynamic parameters $E_{1/2}$ are found within the range -1.34 to -1.50 V.

Key Words: Co(II), Ni(II) complexes, Macrocyclic ligands, Electrochemical studies.

INTRODUCTION

Use of macrocycles in chelation therapy, for conducting artificial nanoscale machinery such as rotaxanes, as chemical sensors, in mimicry of cellular receptors and in light emitting organic diodes has given an impetus to the research interest in the field[1-10]. Consequently, in the present communication the synthesis and characterization of a series of 14-membered macrocycles of cobalt(II) and nickel(II) are reported.

EXPERIMENTAL

All the chemicals used were of analR and GR grade. Solvents were used as such. The ligand oxalodihydrazide was prepared by following literature procedure[11]. Diethyl oxalate was of common grade and was distilled before use. Hydrazine hydrate, nickel(II) chloride hexahydrate and cobalt(II) acetate tetrahydrate were of BDH quality. Nicke(II), acetate tetrahydrate was prepared by dissolving the carbonate in acetic acid of BDH quality followed by crystallization.

---

†Department of Chemistry, Government Polytechnic, Muzaffarpur-842 002, India.
‡Department of Chemistry, Dr. J. M. College, Muzaffarpur-842 001, India.

Metal and nitrogen contents were estimated by standard procedure[12]. Carbon and hydrogen were estimated by semi-micro combustion method in a MLW micro elementary CHN analyzer. Molar conductances at room temperature were measured in 10^{-3} M dioxane solution using a Toshniwal conductivity bridge. Room temperature, magnetic susceptibility measurement of solid complex was made by the Gouy method with mercury tetraisothiocynatocobaltate(II) as calibrant. The elemental analytical data, colour, conductivity data, molecular weight and electronic spectral data have been shown in Table-1. The infrared spectra (KBr) were recorded on a Perkin-Elmer 398 spectrophotometer and important bands have been shown in Table-2. Electronic spectra were recorded on a Cary-2390 spectrophotometer and bands have been shown in Table-3. The molecular weight of the complexes were determined by Rast's method.

TABLE-1
ANALYTICAL, COLOUR, MAGNETIC MOMENT AND MOLAR
CONDUCTIVITY DATA FOR NICKEL(II) AND COBALT(II)
MACROCYCLIC COMPLEXES OF THE TYPE [M(mac$^{1-3}$)]

Compound	m.w.	Elemental analysis (%): Found (calcd.)				μ_{eff} (BM)	Ω^{-1} cm^2 mol^{-1}
		M	C	H	N		
[Co(mac^1)]	317	18.51 (18.61)	22.65 (22.71)	3.80 (3.13)	33.27 (33.33)	2.20	3
[Co(mac^2)]	345	16.98 (17.10)	22.75 (22.82)	4.35 (4.41)	32.38 (32.46)	2.37	4
[Co(mac^3)]	369	15.93 (15.98)	32.07 (32.15)	4.81 (4.87)	30. 27 (30.35)	2.65	5
[Ni(mac^1)]	317	18.56 (18.61)	22.67 (22.71)	3.10 (3.15)	35.25 (25.33)	0	3
[Ni(mac^2)]	345	17.00 (17.10)	27.75 (27.82)	4.35 (4.41)	32.40 (32.46)	0	4
[Ni(mac^3)]	369	15.92 (15.98)	32.25 (32.32)	4.80 (4.87)	30.30 (30.35)	0	3

TABLE-2
IMPORTANT INFRARED BANDS SPECTRAL DATA OF OXALODIHYDRAZIDE
PRECURSORS [M(OXALODIHYDRAZIDE)$_2$(CH$_3$COO)$_2$ AND [M(mac$^{1-3}$)]

AAOB	[Ni(AAOB)$_2$(AC)$_2$]	[Ni(mac^1)]	[Ni(mac^2)]	[Ni(mac^3)]	[Co(mac^1)]	[Co(mac^2)]	[Co(mac^3)]	Assignments
3230	3350	3380	3385	3375	3300	3305	3310	ν(N-H)
3150	3155	–	–	–	–	–	–	–
3014	3015	3200	3205	3210	3150	3155	3160	ν_s(NH)
1690	1685	1650	1655	1645	1645	1640	1650	ν_{one}(NH)
1620	1675	1540	1545	1550	1545	1540	1530	Amide I
1530	1535	1200	1205	1205	1210	1195	1205	+ - NH$_2$
1284	1260	1220	1120	1120	1120	1120	1120	Amide-III vibration
1120	1120	1050	1055	1050	1050	1055	1045	ν(C-N)
–	460	465	465	470	460	465	460	ν(M-N)

TABLE-3
ELECTRONIC SPECTRAL BANDS (cm⁻¹) OF THE MACROCYCLIC
NICKEL(II) AND COBALT(II) COMPLEXES OF THE TYPE [M(mac$^{1-3}$)]

Complexes	L. F. Bands	C. T. Band	μ_{eff} (BM)
[Ni(mac^1)]	20,000 25,000	28,000	Diamagnetic
[Ni(mac^2)]	20,800 25,200	28,000	Diamagnetic
[Ni(mac^3)]	19,300 22,500	27,000	Diamagnetic
[Co(mac^1)]	19,000	25,000	2.19
[Co(mac^2)]	19,500	24,800	2.37
[Co(mac^3)]	19,600	25,600	2.65

A manual set-up was used for taking polarograms. The temperature was controlled by a Haake type thermometer. The dropping mercury electrode had these characteristics: m = 1.9 mg/s as t = 3.5 s in open circuit. Height of the mercury column was 50 cm. The data has been shown in Table-4. A representative polarogram has been shown in Fig. 1 and log plots in Fig. 2.
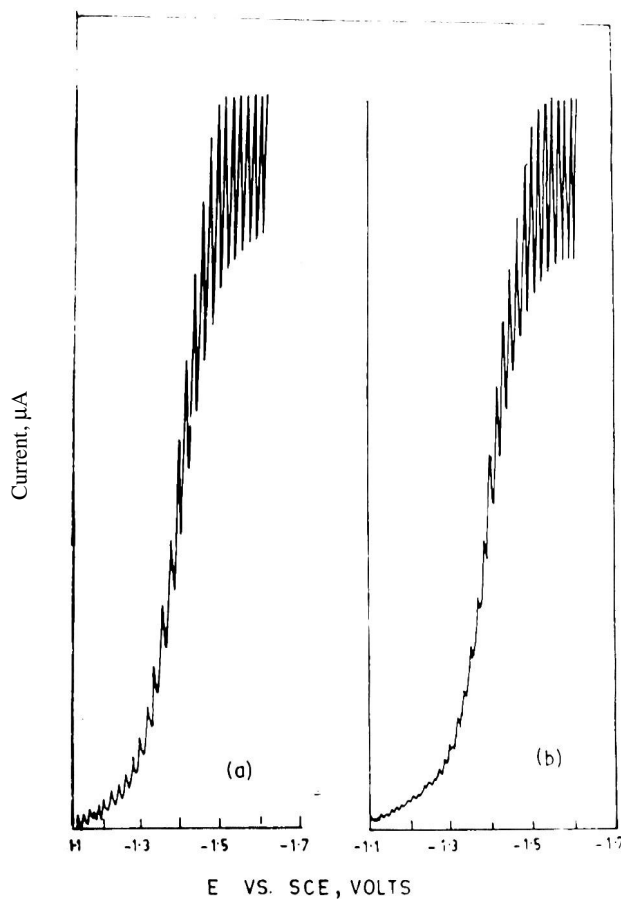

Fig. 1. Polarograms of (a) Ni(mac^3) (b) Co(mac^2)

TABLE-4
POLAROGRAPHIC DATA FOR THE MACROCYCLIC COMPLEXES OF
NICKEL(II) AND COBALT(II) OF THE TYPE [M(mac$^{1-3}$)]

Complexes	Ni(II)	Co(II)
[M(mac^1)]	-1.48 (59)	-1.43 (65)
[M(mac^2)]	-1.42 (66)	-1.42 (61)
[M(mac^3)]	-1.50 (60)	-1.35 (63)

Figures outside the parenthesis indicate $E_{1/2}$ values in volt and those inside the parenthesis are the slope values of the log plots in millivolt.
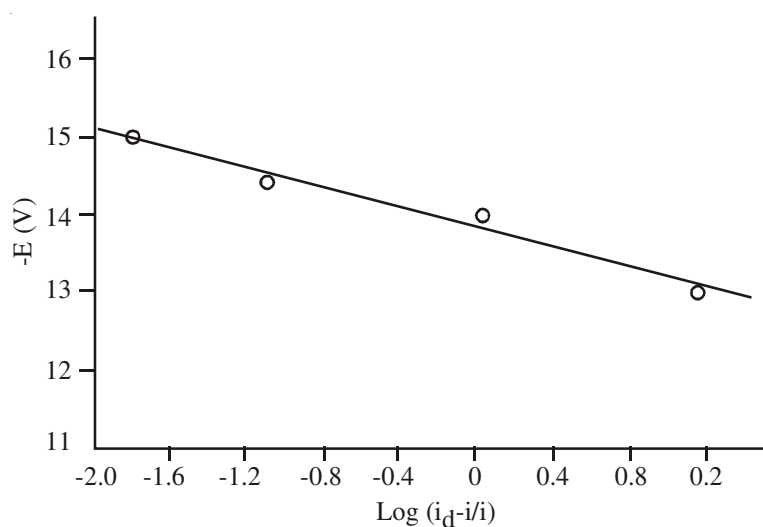

Fig. 2. log plots of Ni(mac^1)

The complexes were prepared by refluxing the components namely metal salts, oxalodihydrazide and aldehydes/propanone in aquous alcoholic solution for several hours when the products were obtained in crystalline state in the forms of inner complex salts. The complexes have been prepared by macrocyclization reaction as shown in **Scheme-I**. All the six complexes were prepared under similar condition.

7,7,14,14-Tetramethyl-3,4,10,11-tetraoxo-1,2,5,6,8,9,12,13-octaaza cyclotetradecanatonicke(II) [Ni(mac^3)]: About 2.4 g (0.02 mol) of oxalodihydrazide was dissolved in 200 mL of hot water. A solution of nickel(II) chloride hexahydrate (2.4 g, 0.01 mol) in 100 mL of water was added to oxalodihydrazide solution. A greenish blue solution was formed and it was refluxed. About 1.4 mL of acetone was added dropwise to the refluxing mixture. The reflux was continued for a day. The colour of reaction mixture gradually deepened and a red compound separated out. It was washed with warm water and then with ethanol. It was dried in vacuum and analyzed.

The preparation of cobalt(II) complexes were carried out in an inert atmosphere of nitrogen.
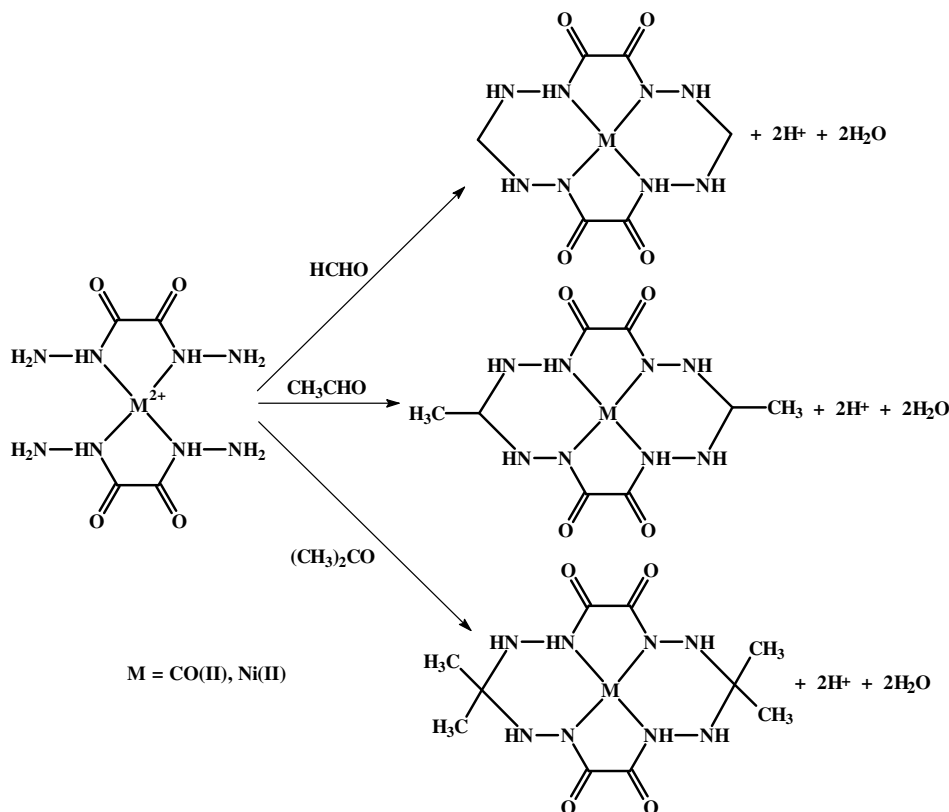
Scheme-I

RESULTS AND DISCUSSION

Infrared spectra of the ligand oxalodihydrazide and the precursor metal complexes of the type [M(oxalodihydrazide)$_2$(OAc)$_2$] have been recorded in the range 4000-400 cm^{-1} region in order to establish macrocyclization and the mode of bonding of the macrocyclic ligands with metal ions.

In the high frequency region 3500-3000 cm^{-1} oxalodihydrazide exhibits a group of three bands near 3290, 3150 and 3014 cm^{-1}. The vibrational spectra of precursor metal complexes of the type [M(oxalodihydrazide)$_2$X$_2$] also exhibit similar features consisting of three bands. However, the highest energy band is found to shift to a higher energy region for the precursors and appears near 3350 cm^{-1}. Taking into account the spectral features of the free ligand, the precursors and the macrocyclic complexes, we are led to assign the highest energy band to secondary amide N-H stretching vibrations and the following pair of bands to asymmetric and symmetric stretching vibrations of the terminal NH$_2$ groups.

The profiles of the spectra of the macrocycles are different from the spectra of oxalodihydrazide and the precursor complexes and manifest the macrocyclization

reaction involving the terminal -NH$_2$ groups and the carbonyl functions of formaldehyde, acetaldehyde and acetone (**Scheme-I**). These macrocycles exhibit two sharp bands of medium intensity one in the region 3400-3300 cm^{-1} and the other in the region 3260-3100 cm^{-1}, while the former arises due to the originally present amide N-H stereochemistry vibrations, the latter band originates due to the stretching vibrations of the newly generated (N-H) groups on macrocyclization.

In the fingerprint region oxalodihydrazide, the precursors and the macrocyclic complexes exhibit profusion of bands which are clearly discernible and can be unambiguously assigned. The free ligand and the precursor complexes exhibit a group of three bands in the region 1700-1500 cm^{-1} which are located in the vicinity of 1680, 1620 and 1530 cm^{-1} and have been assigned to amide I band, the deformation mode of vibrations of the terminal-NH$_2$ groups and amide II vibrations, respectively. In sharp contrast the vibrational spectra of all the macrocyclic complexes exhibit only two bands in the region 1680-1500 cm^{-1} which possess characteristic features and assign amide I and amide II vibrations. These vibrations are observed in the neighbourhood of 1650 and 1540 cm^{-1}, respectively. It is natural to expect the disappearance of NH$_2$ scissoring mode of vibrations in the macrocycles since the NH$_2$ groups are involved in macrocyclization reaction.

The amide III band observed near 1284 cm^{-1} in oxalodihydrazide is appreciably affected in the precursor complexes as well as in the macrocycles and shifts to lower frequency region and appears near 1200 and 1260 cm^{-1}, respectively.

Besides the amide III band, oxalodihydrazide and the precursor complexes exhibit another strong and sharp band near 1120 cm^{-1} which is attributed to (C-N) stretching vibrations. On the other hand, the macrocycles exhibit a pair of (C-N) stretching vibrations nearly of equal intensity and sharpness, one near 1120 cm^{-1} and another near 1050 cm^{-1}. This feature demonstrates the introduction of additional (C-N) groups during macrocyclization and is consistent with macrocyclic structure (Fig. 3).
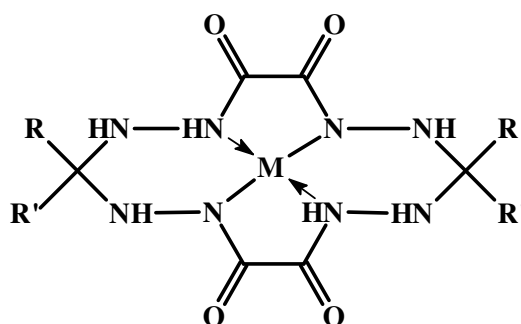
M = Co(II), Ni(II); for mac^1, R = R' = H; for mac^2,
R = H, R' = CH$_3$ and for mac^3, R = R' = CH$_3$

Fig. 3

Apart from these structurally important bands, the macrocyclic complexes exhibits a number of bands due to skeletal vibrations in the range 900-600 cm^{-1}. The deformation mode of vibrations of -CH$_3$ and CH$_2$ groups also appear in their appropriate energy regions.

A sharp band of medium intensity observed in the range 470-460 cm^{-1} in the spectra of the macrocylces as well as precursors has been assigned[13,14] to ν(M-N). This band is significantly absent in the spectrum of oxalodihydrazide.

The important feature of the infrared spectra are, on the whole, self consistent with the macrocyclic structure elucidated in Fig. 3. The metal ion is quadratically bonded to the amidic nitrogen atoms and a pair of protons of the macrocyclic ligand have been lost giving inner complex macrocyclic salts.

Electronic spectra and magnetic properties: The nickel(II) macrocyclic complexes [Ni(mac$^{1-3}$)] are diamagnetic and their electronic spectra show two intense bands one in the region 19000 to 21000 and another near 27000 cm^{-1}. The transitions are assigned to $^1A_{2g}\rightarrow^1A_{1g}$ and $^1B_{1g}\rightarrow^1A_{1g}$ under a square planar environment having NiN$_4$ chromophore. The higher energy band is, however, more intense and the intensity is believed to arise due to metal$\rightarrow$ligand π^* charge transfer transitions[15].

The cobalt(II) complexes are of low spin type and are found to possess magnetic moments in the range 2.2 to 2.7 BM. Electronic spectra of the complexes are similar and most of them exhibit two transitions near 20,000 and 25000 cm^{-1}, respectively. The lower energy band has been assigned to the transition $^2A_{1g}$ ground term to one of the higher energy term $^2A_{2g}$ or ^2E_g, the split components of the orbitally triplets $^2T_{1g}$ term. The higher energy band is more intense and indicates its origin due to metal$\rightarrow$ligand (π^*) charge transfer transition[16].

Molar conductivity measured in DMF solution lies in the range 2-5 Ω^{-1} cm^2 mol^{-1} and indicate the macrocyclic complexes to be non-electrolytic in nature.

Electrochemical studies: Electrochemicl studies of the macrocyclic complexes have been persued involving polarography along with their synthesis. Polarograms yield informations about the types of reducible species in solution, the composition and stability of complexes and the number of electrons participating in redox processes.

They are used to study the kinetics of electrochemical transformations and to find the various steps involved in electrochemical reactions. A careful analysis of polarographic behaviour and comparison with similar complexes provides informations which are helpful in drawing conclusions about the molecular orbitals involved in the electron transfer as well as the oxidation states of atoms.

All the polarographic measurements were carried out in deoxygenated DMF-water (90:10) medium. Potassium perchlorate at an ionic strength of 0.1 M was used as supporting electrolyte. Triton-X-100 solution (0.002 %) was used as suppressor. saturated calomel electrode was used as the reference electrode.

The redox process of all the complexes are diffusion controlled at the dropping mercury electrode (d.m.e.) as revealed by the linear plots of i$_d$ *vs.* $\sqrt{h_{eff}}$ and i$_d$ *vs.* concentration which pass through the origin.

The reduction process for all these complexes are either reversible or quasi-reversible as evidenced by the magnitude of the slope of the plots or E *vs.* $\log\{(i_d-i)/i\}$. Polarographic data are presented in Table-3. A representative polarogram is shown in Fig. 2 and log plots in Fig. 3. The polarogram of all the complexes show a redox wave and wave is well defined. The redox process is observed to involve transfer of one electron.

REFERENCES

1. M.P. Suh and S. Kang, *J. Korean Chem. Soc.*, **23**, 417 (1979),
2. M.P. Suh, Ph.D. Thesis, The University of Chicago (1976).
3. S. Chandra, L.K. Gupta and Sangeetika, *Synth. React. Inorg. Metal. Org. Chem.*, **34**, 1591 (2004).
4. S. Chandra and L.K. Gupta, *Spectrochim. Acta*, **60A**, 1563 (2004).
5. S. Chandra and A. Gautam, *J. Indian Chem. Soc.*, **85**, 980 (2008).
6. R.R. Jha and N. Sahu, *Asian J. Chem.*, **20**, 6301 (2008).
7. H.C. Rai and B. Sahoo, *J. Indian Chem Soc.*, **53**, 646 (1976).
8. H.C. Rai, M. Kumar, M.K. Roy and K.K. Sharma, *Asian J. Phys.*, **6**, 459 (1997).
9. H.C. Rai and B.K. Rai, *Asian J. Phys.*, **12**, 133 (2003).
10. H.C. Rai, J. Tiwary and R. Kumari, *Indian J. Chem.*, **27A**, 1054 (1988).
11. B.S. Furniss, A.J. Hannaford, P.W.G. Smith and A. Tatchell, Vogel's Textbook of Practical Organic Chemistry, ELBS/ Longman, England, p. 1125 (1978).
12. A.I. Vogel, A Textbook of Quantitative Chemical Analysis, Revised by J. Bessett, R.C. Denney, J.H. Jeffery and J. Mendham, ELSB, London, edn. 5 (1996).
13. L. Mitu, N. Raman and A. Kriza, *Asian J. Chem.*, **21**, 5751 (2009).
14. K. Nakamoto, Infrared and Raman Spectra of Inorganic Compounds, John Wiley and Sons, New York (1979).
15. A.B.P. Lever, Inorganic Electronic, Spectroscopy, Elsevier, Amsterdam, p. 343 (1968).
16. B.N. Figgis and R.S. Nyholm, *J. Chem. Soc.*, 12 (1954).