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Spectroscopic studies, cyclic voltammetry and synthesis of nickel(II) complexes with N_4, N_2O_2 and N_4S_2 donor macrocyclic ligands

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Abstract

Nickel(II) complexes of the general composition $Ni(L)X_2$ (where X = SCN, NO_3 and $1/2SO_4$ and ligands = L^1 L^2 and L^3) have been synthesized and characterized by elemental analyses, magnetic moments, IR, ^1H NMR, ^{13}C NMR and electronic spectral studies. Nickel(II) ions, such as nitrates, thiocyantes and sulphates were found to act as templates for the cyclic condensations [1 + 1] and [2 + 2] of $NH_2—C_6H_4—O—CH_2—CH_2—O—C_6H_4—NH_2$, $NH_2—(CH_2)_2—NH_2$ and $NH_2—CH(CH_3)—CH_2—NH_2$ with $C_6H_5—CO—CO—C_6H_5$, $C_6H_5—CO—CH_2—CO—C_6H_5$ and $(COOH—CH_2—CH_2)_2S$.

All the complexes show magnetic moments corresponding to two unpaired electrons except $[Ni(L^1)](NO_3)_2$ and $[Ni(L^2)](NO_3)_2$ complexes which are diamagnetic. Electronic spectroscopy was used to analyse the differences between the paramagnetic and diamagnetic forms. Electrochemical properties have been studied extensively for Ni(III/II) and Ni(II/I) couples. The equilibrium between the paramagnetic and diamagnetic forms and the nickel(III/II) couple are strongly dependent on the electrolyte. It has been observed that the sulphate group coordinated selectively on the apical position of the nickel(II) centers of the compounds. The structural and electrochemical studies suggest that cooperative effects, involving coordination of sulphate to one nickel center, is responsible for the recognition of this anion. Various ligand field parameters have been calculated and discussed.

Keywords: Macrocyclic ligands; Nickel(II); Mass spectroscopy; ^1H NMR; ^{13}C NMR; Electronic; IR; Cyclic voltammetry

1. Introduction

Molecules possessing O, N and S donor sites are important in the development of coordination chemistry as well in the bio-mimetic chemistry of a number of metals, particularly in transition metals [1–3]. It is known from many reports that nickel(II) complexes of macrocyclic ligands can act as versatile supramolecular receptors for globular guests like carborane, C_{60}, C_{70} and S_8 [4–6]. A rapidly emerging area of chemical interest in resent year is in the synthesis of nickel(II) complexes derived from such macrocyclic ligands which contain polydentate coordination modes. These coordination sites lead to the formation of homo and heteroploynuclear complexes [7,8]. This opens opportunity to design the macrocyclic ligands containing additional donor atoms such as N_2O_2, N_4, or S_2N_4 in the chain. A variety of possible applications, including crystal engineering, the preparation and stabilization of anionic metal complexes, as well as cooperatively and selectivity of anion binding have been described with macrocyclic ligands complexes. In a series of recent papers, the synthetic and characterization aspects of a number of transition metal complexes of different donor atoms have been reported [9,10]. The electrochemical properties have also been studied extensively for Ni(III)/Ni(II) and Ni(II)/Ni(I) couples which were affected by coordination sites and donor environments. This paper gives an insight about the preparation, spectral, characterization and cyclic voltammetry studies of some N_4, N_2O_2,

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or N_4S_2 donor macrocyclic ligands and their nickel(II) complexes.

2. Experimental

All chemicals used were of AR grade and were purchased from Sigma Chemical Co., U.S.A., E. Merck, Germany or Sarabhai Merck Company, India. Ethanol used was of analytical grade procured from S.D. Fine Chemicals Pvt. Ltd. It was dried by storing over clean, dried sodium wire, refluxed for 30 min and distilled using a double-walled condenser at 78 °C.

3. Synthesis of the ligands

3.1. Synthesis of diamines

1,2-Di(*o*-aminophenoxy)ethane diamine was prepared by the method reported [1].

3.2. Preparation of macrocyclic ligands

(L^1) (2,3-diphenyl-1,4-diaza-7,10-dioxa-5,6:11,12-dibenzocyclododoca-1,3-diene[N_2O_2]) was prepared by method earlier reported [1] and ligand L^2 (2,4,9,11-tetraphenyl-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tertaene [N_4]) is prepared by the method as given below.

An ethanolic solution (25 ml) of 1,2-diaminoethane (0.001 mol, 0.06 g) was added to an ethanolic solution (25 ml) of dibenzoylmethane (0.001 mol, 0.224 g) in the presence of 1 ml concentrated HCl. The resulting solution was boiled under reflux for 3–6 h. On cooling, light yellowish crystals separated out, which were filtered, washed with ethanol and dried under vacuum over P_4O_{10}.

Ligand L^3 (8,17-dimethyl-1,7,10,16-tetraaza-4,13-dithacyclooctadeca-2,6,11,15-teraone[N_4S_2]).

To an ethanolic solution (25 ml) of thiodiglycolic acid (0.002 mol, 0.30 g), an ethanolic solution (25 ml) of 1,2-diaminopropane (0.002 mol, 0.15 g) in absolute ethanol (25 ml) was added drop-wise. The resulting solution was refluxed on water bath with constant stirring at a temperature of 75 °C. The solution was then concentrated to half of its volume under reduced pressure and kept for two days at room temperature. Light yellowish crystals separated out. The resulting solution was filtered, washed with ethanol and dried under vacuum over P_4O_{10}.

3.3. Characterization of macrocyclic ligands

The bands corresponding to $-NH_2$ and >CO groups are not observed in the IR spectra of L^1 and L^2. It indicates that the condensation takes place between the 1,2-di(*o*-aminophenoxy)ethane or 1,2-diaminoethane and benzyl or dibenzoylmethane. A sharp band at 1599–1595 cm^{-1} (Fig. 1) due to the C=N group is observed [11,12], which indicates that the ligands are macrocyclic in nature.

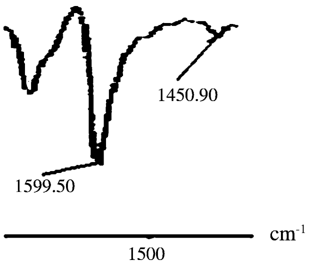


Fig. 1. IR spectrum of macrocyclic ligand (L^1).

^1H NMR: ($CDCl_3$) δ: 7.32 (10H, m), 6.81 (2H, d, $J = 7.2$), 7.1 (2H, m), 6.6 (2H, m), 7.0 (2H, d, $J = 7.4$), 3.20 (4H, m, $-O-CH_2^-$). ^{13}C NMR: 121.90, 122.15, 122.25, 123.07, (C_6H_4); 128.20, 128.30, 128.4, 130.07–136.09 (C_6H_5); 147.20, 147.30 (*o*-C_6H_4); 157.30, 155.50 (C=N); 60.46–64.50 (CH_2). Mass spectrum of ligand shows a peak at 417 corresponding to molecular ion ($M^+ + 1$). Mass spectrum, EIMS *m/z* (%) 417 (M^+, 100) for ligand (L^1) (Fig. 2).

^1H NMR: ($CDCl_3$) δ: 7.2–7.3 (20H, m), 7.1 (8H, m), 7.0 (4H, m); ^{13}C NMR: 121.94, 122.10, 122.30, 123.10, (C_6H_4); 128.22, 128.35, 128.96, 130.07, 136.90 (C_6H_5); 147.15, 147.32 (*o*-C_6H_4); 155.60, 156.48, 156.60, 156.90 (C=N); 63.60, 64.60–66.65 (CH_2) (Fig. 3). Mass spectrum of ligand shows a peak at 523 corresponding molecular ion ($M^+ + 1$). Mass spectrum, EIMS *m/z* (%) 523 (M^+, 100) for ligand (L^2).

The bands corresponding to free $-COOH$ and $-NH_2$ groups are not observed in the IR spectrum of L^3. It confirms complete condensation [7] between thiodiglycolic acid and 1,2-diaminopropane. Some new bands appear at 1680, 1620, 1520 and 1325 cm^{-1} corresponding new groups. A single, sharp band also observed in the region 3340–3380 cm^{-1} which may be assigned to ν(N–H). It indicates secondary moderate-intensity absorptions in amino group [8].

^1H NMR: ($CDCl_3$) δ: 14.31 (4H, s), 4.54 (2H, m), 2.8 (8H, s), 1.5 (4H, m), 0.51 (6H, d, $J = 4.7$ Hz); ^{13}C NMR: 13.50, 13.62 (CH_3) 60.45, 61.40, 62.40, 63.90, 66.60, 67.65

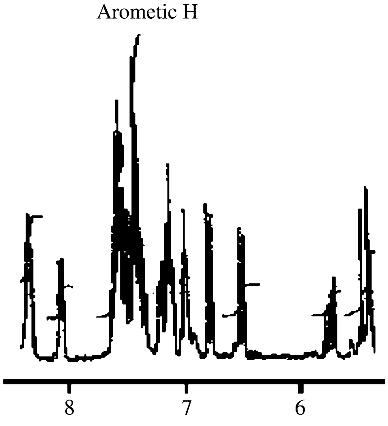


Fig. 2. ^1H NMR spectrum of macrocyclic ligand (L^2).

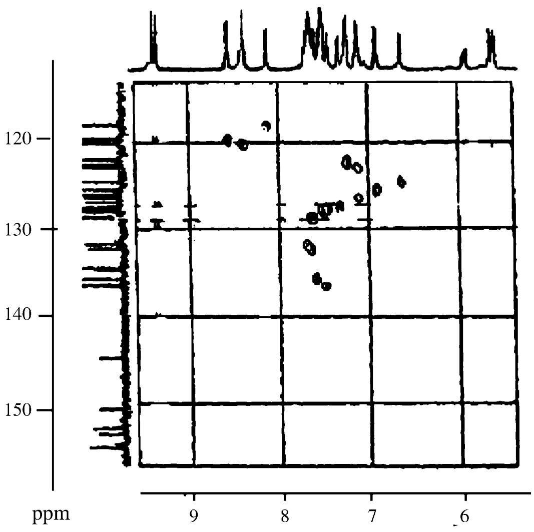


Fig. 3. ^{13}C NMR spectrum of macrocyclic ligand (L^2).

($-CH_2-$) 67.85, 67.90 ($-CH-$); 168.50, 169.90, 170.55, 170.60 (C=O). Mass spectrum of ligand shows a peak at 377 corresponding molecular ion ($M^+ + 1$). Mass spectrum, EIMS *m*/*z* (%) 375 (M^+, 70) for ligand (L^3) (Fig. 4). Suggested structures of macrocyclic ligands are given in Fig. 5.

3.4. Preparation of the complexes

A general method is used for the preparation of the complexes. To a hot (90–95 °C) aqueous ethanolic solution (25 ml) of the $NiX_2 \cdot xH_2O$ (where X = NCS, NO_3 and SO_4) (0.001 mol) and a hot ethanolic solution (25 ml) of the respective ligand (0.001 mol) was added. The mixture was refluxed for about 6–5 h at 75–80 °C. On cooling to 6 °C, the complexes were separated out. They were filtered, washed with 98% ethanol and dried over P_4O_{10}.

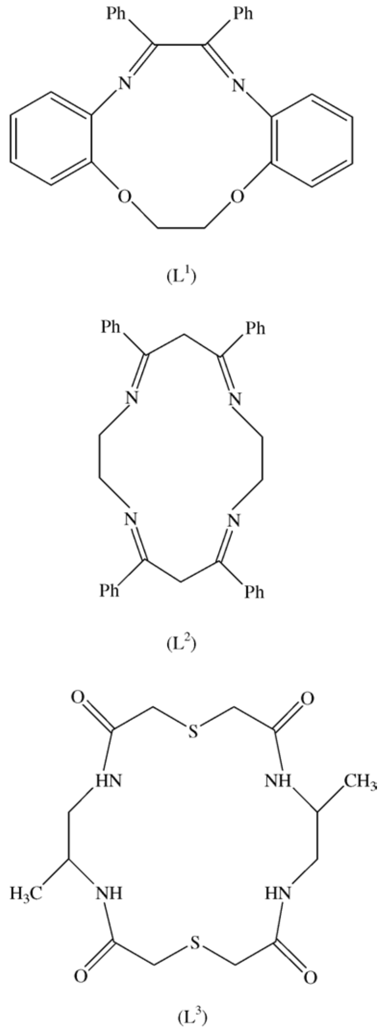


Fig. 5. Suggested structures of macrocyclic ligands.

4. Physical measurements

The magnetic susceptibilities were measured on a Gouy balance using $Hg[Co(NCS)_4]$ as a calibrant. Infrared spectra of the complexes were recorded on a Perkin-Elmer FTIR 1710 automatic recording spectrophotometer in KBr. Electronic spectra of the complexes were recorded on a DMR-21 automatic recording spectrophotometer in DMF solution. Conductance measurements in nitromethane were carried out on a Leeds Northup Model 4995 conductivity bridge. Anal-

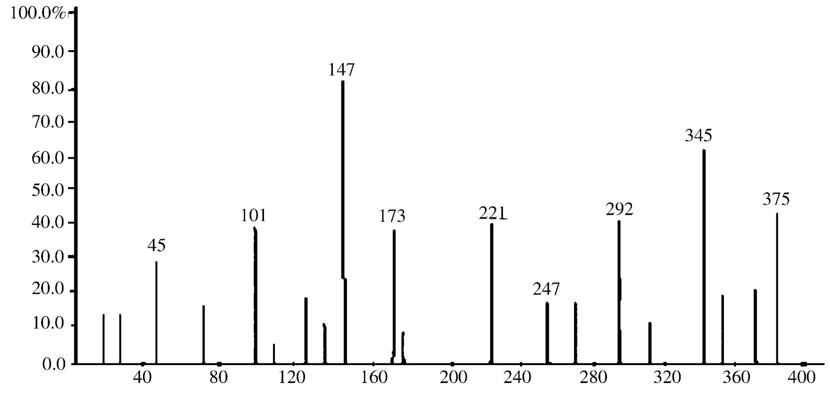


Fig. 4. Mass spectrum of macrocyclic ligand (L^3).

Table 1
Analytical data of nickel(II) complexes

Complexes	Yield (%)	mp (°C)	Molar conductance (Ω^{-1} cm^2 mol^{-1})	Colour	Elemental analysis calculated (found) %			
					Ni	C	H	N
L_1 $C_{28}H_{22}N_2O_2$	40	190	–	White	–	80.0 (79.5)	5.3 (5.0)	6.6 (6.1)
$[Ni(L_1)(NCS)_2]$, $NiC_{30}H_{22}N_4O_2S_2$	45	232	18.0	Light Blue	9.89 (9.80)	60.73 (60.7)	3.74 (3.70)	9.44 (9.40)
$[Ni(L_1)](NO_3)_2$, $NiC_{28}H_{22}N_4O_8$	50	219	165	Light Blue	9.77 (9.72)	55.9 (55.80)	3.69 (3.60)	9.32 (9.30)
$[Ni(L_1)SO_4]$, $NiC_{28}H_{22}N_2O_6S$	65	222	06	Light Blue	10.24 (10.10)	58.67 (58.50)	3.87 (3.60)	4.89 (4.75)
L_2 $C_{36}H_{36}N_4$	55	186	–	White	–	82.4 (82.0)	6.92 (6.50)	10.68 (10.16)
$[Ni(L_2)(NCS)_2]$, $NiC_{38}H_{22}N_6S_2$	58	240	12.0	Sky Blue	8.56 (8.50)	66.59 (66.30)	3.24 (3.16)	12.26 (12.10)
$[Ni(L_2)](NO_3)_2$, $NiC_{36}H_{22}N_6O_6$	61	265	195	Sky Blue	8.47 (8.41)	62.37 (62.23)	3.20 (3.00)	12.12 (12.0)
$[Ni(L_2)SO_4]$, $NiC_{36}H_{22}N_4O_4S$	63	242	12.0	Green	8.82 (8.75)	64.99 (64.50)	3.33 (3.20)	8.42 (8.32)
L_3 $C_{14}H_{24}N_4O_4S_2$	52	189		White	–	44.66 (44.0)	6.43 (5.90)	14.88 (14.20)
$[Ni(L_3)(NCS)_2]$, $NiC_{16}H_{24}N_6O_4S_4$	57	210	180	Light Blue	10.65 (9.99)	34.85 (34.65)	4.39 (4.26)	15.24 (15.0)
$[Ni(L_3)](NO_3)_2$, $NiC_{14}H_{22}N_6O_{10}S_2$	68	215	195	Sky Blue	10.50 (1025)	30.07 (29.80)	4.33 (4.23)	15.03 (14.90)
$[Ni(L_3)SO_4]$, $NiC_{14}H_{22}N_4O_8S_3$	61	217	80	Light Blue	11.05 (10.90)	31.65 (31.61)	4.55 (3.44)	10.55 (1024)

yses of carbon and hydrogen were performed at the Microanalytical Laboratory of the Central Drug Research Institute, Lucknow, India. The nitrogen contents of the complexes were determined using Kjeldahl's method. The ^{1}H NMR and ^{13}C NMR spectra of the macrocyclic ligands were recorded on Bruker Avance 300 spectrophotometer at 100 kHz modulation and higher frequency also at room temperature. The voltammograms and the simultaneous current intensity-time plots for electrolysis were registered in a x-y Houston-Ommigraphic 2000 recorder. The values of E_F for reversible or quasi-reversible redox transformations were calculated as the midpoints between the anodic and cathodic peaks. The distances between peaks (ΔE) were used as the parameters for the characterization of the reversibility of the electrochemical transformation.

5. Result and discussion

5.1. Nickel(II) complexes with the ligand L^1 (2,3-diphenyl-1,4-diaza-7,10-dioxa-5,6:11,12-dibenzocyclododoca-1,3-diene[N_2O_2]) and L^2(2,4,9,11-tetraiphenyl-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tertaene[N_4])

All the nickel(II) complexes with these ligands have the composition $[Ni(L)X_2]$ (X = SCN and 1/2SO$_4$) and $[Ni(L)](NO_3)_2$ (where L = ligands L^1 and L^2). The magnetic moments of the complexes at room temperature (300 K) lie in the range 2.90–2.98 B.M. [13] corresponding to two unpaired electrons, except for $[Ni(L^1)](NO_3)_2$ and $[Ni(L^2)](NO_3)_2$ which are diamagnetic in nature. The molar conductance measurements lie in the range of 6–18 Ω^{-1} cm^2 mol^{-1} for all the complexes expect for $[Ni(L^1)](NO_3)_2$ and $[Ni(L^2)](NO_3)_2$ which show molar conductance in the range of 165–195 Ω^{-1} cm^2 mol^{-1} (Table 1) corresponding to a 1:2 electrolyte [14].

5.1.1. Thiocyanato complexes

Both the nickel(II) thiocyanato complexes with ligands L^1 and L^2 have the composition Ni(L^{1}or L^2)(NCS)$_2$ (Table 1). The ν(C=N) bands in the infrared spectra of $[Ni(L^1)(NCS)_2]$ and $[Ni(L^2)(NCS)_2]$ appeared at 1597 and 1601 cm^{-1}, respectively [10]. They also show a ν(CN) band at 2087 and 2089 cm^{-1}, respectively (Figs. 6 and 7) corresponding to coordinated NCS group.

Electronic spectra of $[Ni(L^1)(NCS)_2]$ and $[Ni(L^2)(NCS)_2]$ display [11] bands at 14,285–14,290, 16,000–16,994 and 30,258–32,250 cm^{-1}. These bands may be assigned to the following transitions $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3), in order of increasing energy,

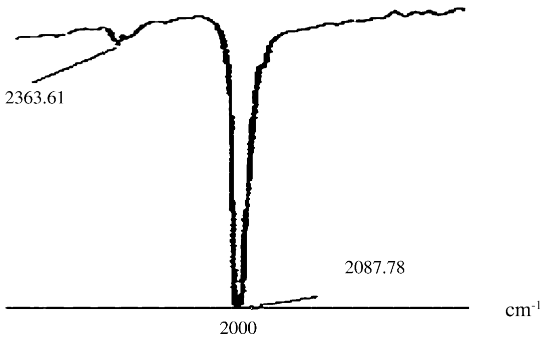


Fig. 6. IR spectrum of $[Ni(L^1)(NCS)_2]$.

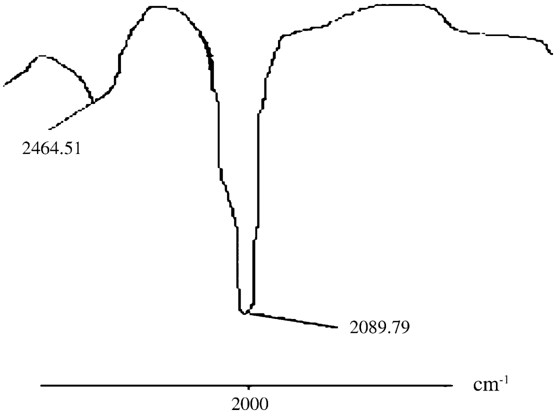


Fig. 7. IR spectrum of $[Ni(L^2)(NCS)_2]$.

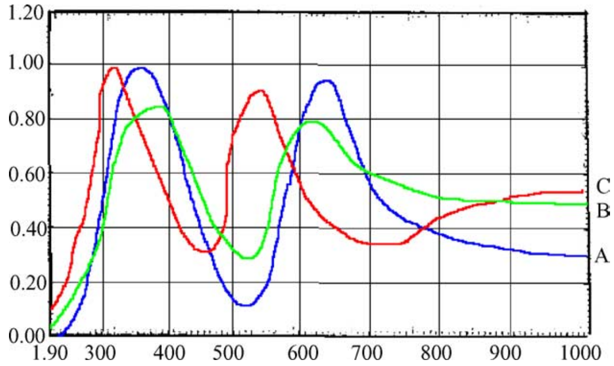


Fig. 8. UV spectrum of A and B are [Ni(L^{1}and L^2)(NCS)$_2$] and C is [Ni(L^1)](NO$_3$)$_2$.

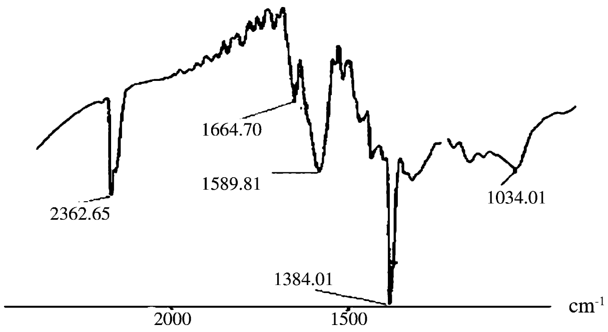


Fig. 10. IR spectrum of [Ni(L^1)](NO$_3$)$_2$.

respectively, characteristic of an octahedral geometry [15] (Fig. 8).

On the basis of above studies, a six-coordinated octahedral geometry may be suggested for these thiocyanato complexes. Suggested structures of the complexes are given below (Fig. 9).

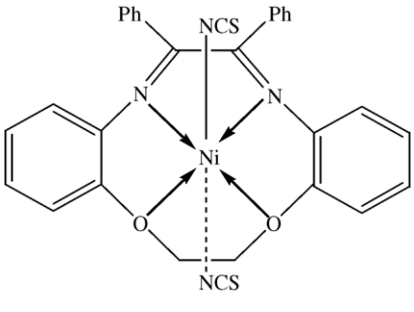
5.1.2. Nitrate complexes

Both the nickel(II) nitrate complexes with ligands L^1 and L^2 have the composition Ni(L^{1}or L^2) (NO$_3$)$_2$ (Table 1).The ν(C=N) bands in the infrared spectra of [Ni(L^1)](NO$_3$)$_2$ and [Ni(L^2)](NO$_3$)$_2$ appear at 1590 and 1594 cm^{-1}, respectively [14] and also show bands at 1384 and 1385 cm^{-1} (Fig. 10) corresponding to an un-coordinated nitrate group. Further, the complexes have diamagnetic character (no unpaired electrons) in the solid as well as in benzene solution. This suggests a square-planar geometry around nickel(II) [17].

The electronic spectra of these complexes display three well-defined bands in the range of 18,115–19,200, 22,540–23,540 and 26,240–27,450 cm^{-1} these may be assigned, to $^1A_{1g} \rightarrow {}^1A_{2g}$ (ν_1), $^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2) and $^1A_{1g} \rightarrow {}^1E_g$ (ν_3) transitions, respectively characteristic to square-planar geometry. The first two bands are purely *d–d* transitions, whereas ν_3 obviously is enveloped by strong charge transfer [15]. On the basis of above studies, four-coordinate square-planar geometry may be suggested for [Ni(L^1)](NO$_3$)$_2$ and [Ni(L^2)](NO$_3$)$_2$. Suggested structures of the complexes are given below (Fig. 11).

5.1.3. Sulphate complexes

Both the nickel(II) sulphate complexes with ligands L^1 and L^2 have the composition [Ni(L^1)SO$_4$] and [Ni(L^2)SO$_4$]



(L^1) complex

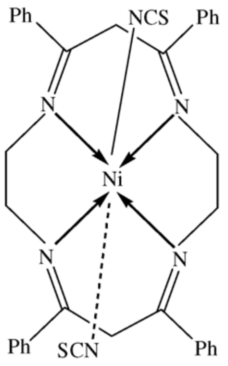
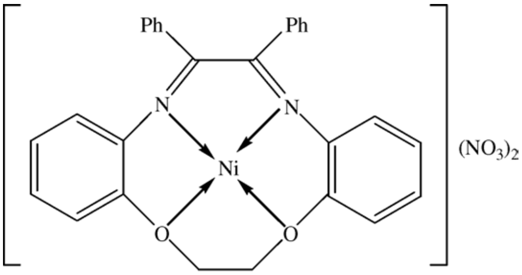


Fig. 9. Suggested structure of [Ni(L^{1}or L^2)(NCS)$_2$].



(L^1) complex

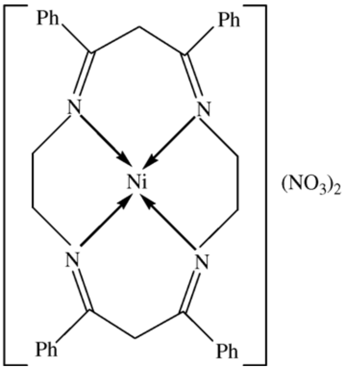


Fig. 11. Suggested structures of [Ni(L^{1}or L^2)] (NO$_3$)$_2$.

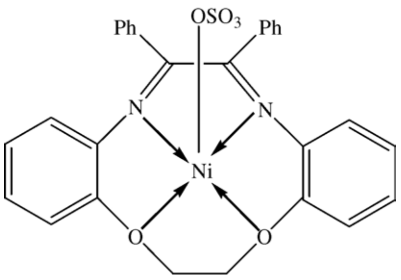


Fig. 12. Suggested structure of $[Ni(L^1)](SO_4)$.

(Table 1). The ν(C=N) bands in the infrared spectra of $[Ni(L^1)SO_4]$ and $[Ni(L^2)SO_4]$ appeared at 1590 and 1594 cm^{-1}, respectively [8]. These complexes also show bands at 940 (ν_1), 1050 (ν_2) and 1150 (ν_3) cm^{-1} and 942 (ν_1), 1055 (ν_2) and 1160 (ν_3) cm^{-1} corresponds to the unidentate sulphate group [14].

The electronic spectra of the complexes show two absorption bands at 10,425 and 12,475 cm^{-1} these may be assigned to $^3E \rightarrow {}^3A_2$ (F) (ν_1) and $^3E \rightarrow {}^3B_2$ (F) (ν_2) transition, respectively corresponding to a five-coordinate square-pyramidal geometry [17]. Suggested structures of the complexes are given below (Figs. 12 and 13).

5.2. Nickel(II) complexes with the ligand L^3 (8,17-dimethyl-1,7,10,16-tetraaza-4,13-dithiacyclooctadeca-2,6,11,15-teraone[N_4S_2])

All the complexes have the composition $Ni(L^3)X_2$ ($X = NO_3$ or NCS) and $Ni(L^3)SO_4$ (Table 1). The magnetic moments of the complexes lie in the range of 2.90–3.01 B.M. corresponding to two unpaired electrons.

The molar conductance of $Ni[(L^3)]X_2$ ($X = NO_3$ or NCS) in nitrobenzene was found in the range 180–195 $\Omega^{-1}\,cm^{-1}\,mol^{-1}$ which indicates that the complexes are 1:2 electrolyte and may be formulated as $[Ni(L^3)]X_2$ ($X = NO_3$ and SCN). But the molar conductivity measurement of $Ni[(L^3)]SO_4$ in nitrobenzene was found 80 $\Omega^{-1}\,cm^{-1}\,mol^{-1}$ which indicates that the complex is 1:1electrolyte and may be formulated as $[Ni(L^3)]SO_4$. A single, sharp bands in the IR region 3375–3340 cm^{-1} may be assigned to ν(N–H) which indicates secondary moderate-intensity absorptions in amino group shifted to lower side as comparative to the macrocyclic ligand [8,16].

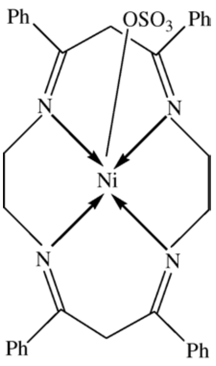


Fig. 13. Suggested structure of $[Ni(L^2)](SO_4)$.

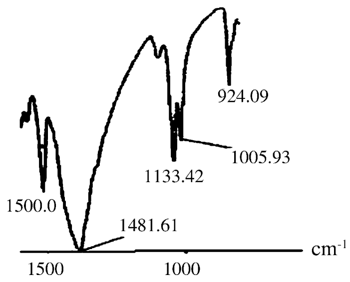


Fig. 14. IR spectrum of $[Ni(L^3)](SO_4)$.

5.2.1. Thiocyanate complex

On the basis elemental analysis this complex has the composition $[NiL^3](NCS)_2$ (Table 1). IR spectrum shows ν(CN) absorptions at 2020 cm^{-1} indicating un-coordinated NCS group [14]. The electronic spectrum of this complex exhibits three strong bands at 11,111 (ν_1), 15,384 (ν_2) and 27,777 (ν_3) cm^{-1}, [17]. These bands may be assigned to $^3B_{1g} \rightarrow {}^3E_g$ (ν_1) and $^1B_{1g} \rightarrow {}^3B_{2g}$ (ν_2) and $^3B_{1g} \rightarrow {}^3A_{2g}$ (ν_3) transition, respectively (Fig. 15) on the basis of symmetry arguments [18–20].

5.2.2. Nitrate complex

On the basis elemental analysis this nitrate complex has the composition $[Ni(L^3)](NO_3)_2$. IR spectrum shows ν(CN) absorptions at 1385 cm^{-1} corresponding to un-coordinate nitrate group [14]. The electronic spectrum of this complex exhibits three strong bands at 11,000 (ν_1), 15,258 (ν_2) and 26,766 (ν_3) cm^{-1}, [17]. These bands may be assigned to $^3B_{1g} \rightarrow {}^3E_g$ (ν_1) and $^1B_{1g} \rightarrow {}^3B_{2g}$ (ν_2) and $^3B_{1g} \rightarrow {}^3A_{2g}$ (ν_3) transition, respectively (Fig. 15) on the basis of symmetry arguments [18–20].

5.2.3. Sulphate complex

On the basis elemental analysis this sulphate complex has the composition $[Ni(L^3)]SO_4$. IR spectrum shows absorption at 1133 (ν_2) and 1005 (ν_1) cm^{-1} (Fig. 14) indicating un-coordinated nature of sulphate group [14]. The electronic spectrum of this complex exhibits three strong bands at 10,526 (ν_1), 14,285 (ν_2) and 25,000 (ν_3) cm^{-1}, [17]. These bands may be assigned to $^3B_{1g} \rightarrow {}^3E_g$ (ν_1) and $^1B_{1g} \rightarrow {}^3B_{2g}$ (ν_2) and $^3B_{1g} \rightarrow {}^3A_{2g}$ (ν_3) transition, respectively (Fig. 15) on the basis of symmetry arguments. Suggested structures of the complexes are given below (Fig. 16) [18–20].

6. Ligands field parameter

Lever [17] has devised normalized spherical harmonic Hamiltonian parameters applicable to molecules of D_{4h} symmetry. The values of ligand field parameters Dt (540–300),

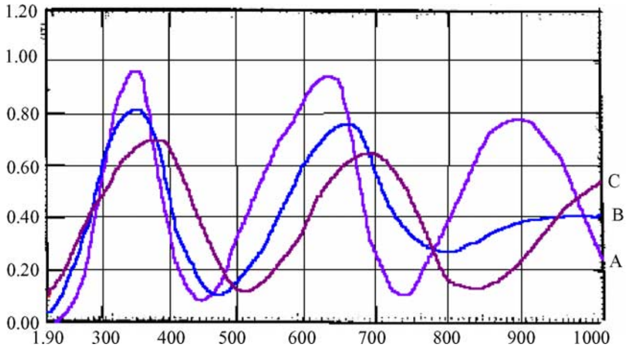


Fig. 15. UV spectrum of $[Ni(L^3)]X_2$ X = CI, NCS and SO_4.

Dq^z (645–610), Dq^{xy} (1245–1232), and McClure's [21] parameters (δt_{2g} (1011–310) and δe_g) are calculated. σ-bonding along the *xy*-plane is strong. It is related to the negative sign of the $\delta\sigma$ (723–127) values. But the $\delta\pi$ (575–190) values are positive in our result. It indicates that the π-bonding effect is relatively more important along the axial direction than σ-bonding.

7. Cyclic voltammetry

Perhaps as a consequence of the complicated nature of these reductions, we observed minimal catalytic activity for the one-electron reduction of the nickel(II) complex. The electrochemical behaviour of the nickel(II) complexes was studied in acetonitrile solution. The reduction potential observed for nickel(II) complexes have a slight difference comparatively non-complex nickel(II) ion.

Cyclic voltammetry spectra show that the oxidation and reduction potentials of the nickel(II) complexes of all ligands lie in the range = +0.040 to +0.045 (V) and −1.60 to −1.70 (V) quasi-reversible redox process, assigned to the Ni(III)/Ni(II) couple was observed (Figs. 17–20). E_F [16] (binding constant) = 1.085 V (ΔE = 86 mV). An irreversible process where E_{cat} = −1.48 V is attributed to the Ni(II)/Ni(I) couple [22] which indicates two electron electrochemical redox behaviour.

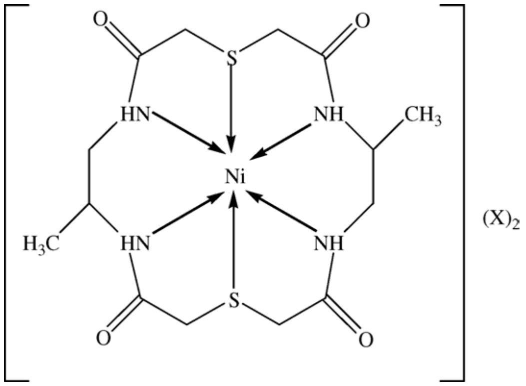


Fig. 16. Suggested structure of $[Ni(L^3)X]X$, where X = SCN, NO_3 and $1/2SO_4$.

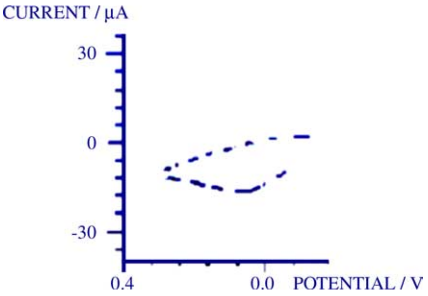


Fig. 17. Cyclic voltammogram $[Ni(L^1)(NCS)_2]$ in the anodic region.

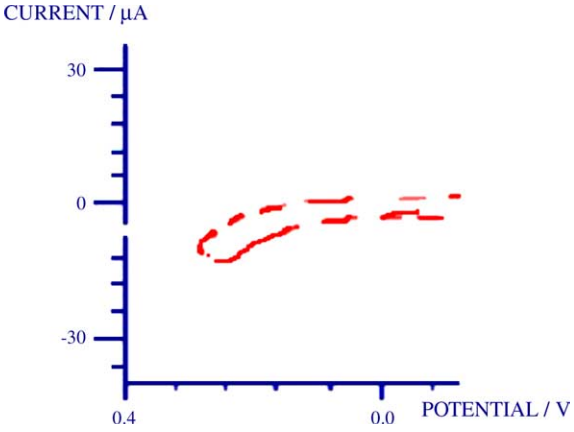


Fig. 18. Cyclic voltammogram $[Ni(L^2)(NCS)_2]$ in the anodic region.

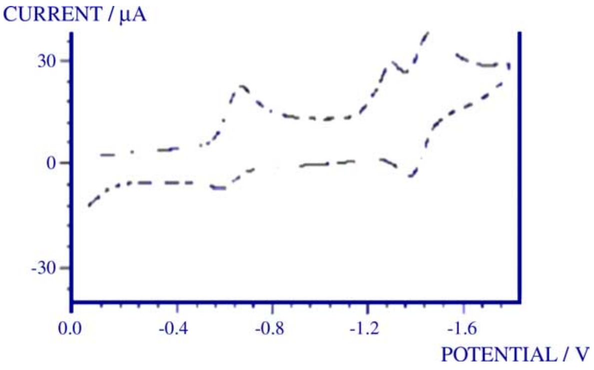


Fig. 19. Cyclic voltammogram $[Ni(L^1)(NCS)_2]$ in the cathodic region.

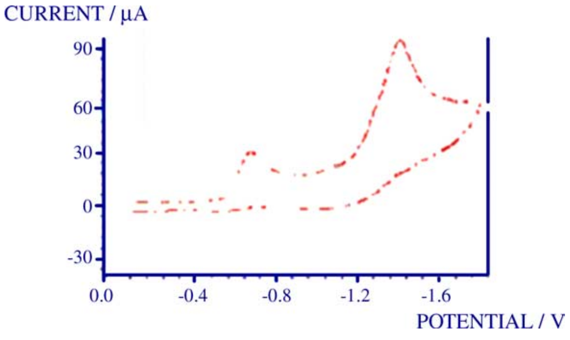


Fig. 20. Cyclic voltammogram $[Ni(L^2)(NCS)_2]$ in the cathodic region.

According to Nernst equation, the greater the difference between the values of the reduction potential of the metal complexes comparatively to the metal ions, the higher is the complexation constant. It can be determine that the more negative the potential is, the greater the constant. It may be assumed that the ligand forms stable complexes with nickel(II) comparatively other metal salts. During cyclic voltammetry studies, it is find out that the oxidation and the reduction potential of the nickel(II) complex is corresponding more negative that for square planar complexes of nickel(II). This fact can be attributed to the coordination of the axial groups of the macrocyclic nickel(II) are coordinated to the metal ion. The E_F values for the single quasi-reversible redox transformation of the nickel(II) complexes are strongly anion dependent and decrease in the order $SCN > NO_3 > SO_4$. This sequence is typical for Ni(III)/Ni(II) couples of azamacrocyclic ligands and reflects the increasing stabilization of nickel(III) by electrostatic effects [23,24].

8. Conclusion

The size of cavity and different donor atoms in the macrocyclic ligands affected the stability of complexes, which can be easily explained by comparing between the values of crystal field splitting energy. The redox properties and stability of the complexes towards oxidation wave explored by cyclic voltammetry are related to the electron withdrawing or releasing ability of the substituents of macrocyclic ligands moiety. Proposed structures of the ligands and their nickel(II) complexes have been given. It is find out that the geometry of the complexes is depended on the number of coordination sites of the ligands and different anion. All the complexes are showing diamagnetic character comparatively other anions in L^1 ad L^2. Magnetic moment data are supported by the infrared information about the diamagnetic nickel(II) complexes which show uncoordinated behaviour of nitrate group.

The detailed information about the geometrical arrangements of atoms in a cyclic environment has been discussed on the basis of ^{1}H NMR and ^{13}C NMR data. The cyclic voltammetry of the complexes showed that the nickel(II) complexes undergo one-electron reduction and oxidation to from the corresponding nickel(I) and nickel(III). These kinds of different oxidizing compounds may be found being used as one electron redox reagent since the former is a strong reducing agent and the latter is strong oxidizing agent. All the complexes in present study show kinetic property due to the chemical reaction coupled between two charges transfer processes in which irreversible first order chemical reaction is interposed between two successive one-electron transfers. The E_F values of the complexes are strongly anion dependent. Ligands field parameters are also calculated and their values in our result help to explain the stereochemistry of the complexes.

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