Available online at www.sciencedirect.com

SCIENCE DIRECT®

Spectrochimica Acta Part A 62 (2005) 1050–1057

SPECTROCHIMICA
ACTA
PART A

www.elsevier.com/locate/saa

Spectral studies, cyclic voltammetry and synthesis of cobalt(II) and ruthenium(III) complexes with symmetric and asymmetric ring containing membered N_2S_2, N_4, and N_5 donor macrocyclic ligands

Sulekh Chandra*, Rajiv Kumar

Department of Chemistry, Zakir Husain College (Delhi University), J.L. Nehru Marg, New Delhi 110002, India

Received 9 December 2004; received in revised form 21 March 2005; accepted 14 April 2005

Abstract

Reaction of divalent cobalt(II) and trivalent ruthenium(III) salts (NO_3, SCN and SO_4) with macrocyclic ligands L^1, L^2 and L^3 having N_2S_2, N_4 and N_5 core, have been designed and carry out. All these three macrocyclic ligands and their complexes were obtained in pure form. Their structures were investigated by using microanalytical analyses, IR, mass, magnetic moments, electronic and EPR spectral studies. The redox properties of the complexes were also examined by cyclic voltammetry. An interesting feature of complexes is that the relatively large rings of macrocyclic ligands prevent the macrocyclic rings from approaching the metal center as closely as they would, if they were not constrained. So the Ru–N distances are longer than expected due to ring size. Electrochemical studies show that the macrocyclic ligand L^1 is more effective electron donors to ruthenium than of L^2 and L^3.

Electronic spectral properties also show that the sulphur donor atom of L^1 weakens the ligand field with respect to ligand-to-metal charge-transfer band. However it is expected that second-row transition metal–ligand bonds tend to be weaker than third-row transition metal–ligand bonds. There are well-established examples of reactions in which decreased of reactivity down a triad of transition metals is not observed. These novelties are usually attributed to π-bonding effects for ligands such as carbon monoxide, solvent effects, or a change in mechanism.

Keywords: Macrocyclic ligands; Mass spectroscopy; Cobalt(II); Ruthenium(III); IR; UV; Cyclic voltammetry

1. Introduction

The rational design and synthesis of macrocyclic ligands systems, capable of accommodating metal centers in close proximity and their spatial arrangement is an effective area of research [1]. Indeed, macrocyclic ligands and their complexes in which donor atoms can be tuned via variation functionality in the ligand structure, also find application as models for important metallobiosities [2], as catalysts [3] and in the investigation of the mutual influence of proximal metal centers on the electronic, magnetic and redox properties of such systems [4]. This may represent a very promising new synthetic approach to design the macrocyclic ligands whose metal binding sites are extremely effective in terms of cavity size, geometrical requirements, coordination number, and nature of the donor atoms to selectively form complexes. In fact, by changing the nature of macrocyclic frameworks symmetrically or asymmetrically introduced with in the macrocyclic structure, selectively could be reach in the binding properties of the two different donating atoms. An important role is of course played by the flexibility of the large ligand ring. These aspects were addressed in a symmetric manner by developing three types of ligands, in which these ligands are tetradentate, and pentadentate, having either N_2S_2, N_4, and N_5 core. In the present process, the reaction product in each case was isolated, purified and characterized. In this paper, we report the preparation and characterization of cobalt(II) and ruthenium(III) complexes with multidentate ligands having N_2S_2, N_4, and N_5 core. The geometry of the present complexes is highly affected from a number of

---

* Corresponding author. Tel.: +91 1 234276530; fax:+91 1 234276530.
E-mail addresses: schandra_00@yahoo.com (S. Chandra), chemistry_rajiv@hotmail.com (R. Kumar).

1386-1425/$ – see front matter
doi:10.1016/j.saa.2005.04.002

Table 1
Analytical data of cobalt(II) complexes

Complexes	Empirical formula	Yield (%)	m.p. (°C)	Molar conductance (Ω^{-1} cm^2 mol^{-1})	Color	Elemental analysis calculated (found) (%)			
						Co	C	H	N
$CO(L^1)(NCS)_2$	$COC_{31}H_{24}N_4S_4$	36	211	11.0	Brown	9.21 (9.14)	58.20 (58.10)	3.78 (3.60)	8.76 (8.74)
$CO(L^2)(NCS)_2$	$COC_{38}H_{36}N_6S_2$	49	205	17.0	Reddish	8.42 (8.40)	65.22 (65.02)	5.19 (5.10)	12.01 (11.85)
$CO(L^3)(NCS)_2$	$COC_{20}H_{25}N_7S_2$	57	221	95.0	Light red	12.11 (12.0)	49.37 (49.30)	5.18 (5.09)	20.15 (20.0)
$CO(L^1)(NO_3)_2$	$COC_{29}H_{24}N_4S_2O_6$	51	240	195	Light red	9.10 (8.90)	53.79 (53.42)	3.74 (3.65)	8.65 (8.32)
$CO(L^2)(NO_3)_2$	$COC_{36}H_{36}N_6O_6$	55	231	190	Reddish brown	8.33 (8.16)	61.10 (61.0)	5.13 (5.02)	11.88 (11.23)
$CO(L^3)(NO_3)_2$	$COC_{18}H_{25}N_7S_2O_6$	44	250	185	Red	10.55 (10.10)	38.71 (38.50)	4.51 (4.25)	17.56 (17.26)
$CO(L^1)SO_4$	$COC_{29}H_{24}N_2S_3O_4$	39	247	12.0	Blackish red	9.51 (9.20)	56.21 (56.02)	3.90 (3.75)	4.52 (4.25)
$CO(L^2)SO_4$	$COC_{36}H_{36}N_4SO_4$	58	237	19.0	Light red	8.67 (8.12)	63.61 (63.20)	5.34 (5.12)	8.24 (8.00)
$CO(L^3)SO_4$	$COC_{18}H_{25}N_5SO_4$	50	231	85.0	Pink	12.64 (12.24)	46.35 (46.22)	5.40 (5.36)	15.02 (14.85)

Table 2
Analytical data of ruthenium(III) complexes

Complexes	Empirical formula	Yield (%)	m.p. (°C)	Molar conductance (Ω^{-1} cm^2 mol^{-1})	Color	Elemental analysis calculated (found) (%)			
						Ru	C	H	N
$Ru(L^1)(NCS)_2$	$RuC_{32}H_{24}N_5S_5$	42	190	84.0	Light yellow	13.66 (13.52)	51.94 (51.63)	3.27 (3.10)	9.46 (9.12)
$Ru(L^2)(NCS)_2$	$RuC_{39}H_{36}N_7S_3$	41	198	96.0	Brownish yellow	12.63 (12.10)	58.55 (58.10)	4.54 (4.12)	12.26 (12.05)
$Ru(L^3)(NCS)_2$	$RuC_{21}H_{25}N_8S_3$	52	185	190	Light yellow	17.23 (17.10)	42.99 (42.63)	4.29 (4.00)	19.10 (18.9)
$Ru(L^1)(NO_3)_2$	$RuC_{29}H_{24}N_5S_2O_9$	57	210	90.0	Yellow	13.44 (13.13)	46.33 (46.21)	3.22 (3.10)	9.32 (9.00)
$Ru(L^2)(NO_3)_2$	$RuC_{36}H_{36}N_7O_9$	16	205	105	Light yellow	12.45 (12.32)	53.21 (5310)	4.42 (4.32)	12.08 (11.76)
$Ru(L^3)(NO_3)_2$	$RuC_{18}H_{25}N_8O_9$	39	200	110	Light yellow	16.89 (16.23)	36.12 (33.96)	4.21 (4.06)	18.72 (18.63)

atoms and the anions of coordinated metal. Molar conductance measurements provide important information regarding the position of anion in the coordination sphere (Tables 1 and 2).

2. Experimental

All the chemicals used in this investigation were of AR grade, and were purchased from Sigma Aldrich Chemical Co., USA. Ethanol used was of analytical grade procured from S.D. Fine Chemicals Pvt. Ltd. All the solvents were dried before use by passing over clean, dried sodium wire, refluxed for 30 min and distilled using a double-walled condenser at 78 °C.

3. Synthesis of macrocyclic ligands

3.1. *Preparation of diamines*

The diamines used are prepared as reported earlier [4].

3.2. *Preparation of macrocyclic ligands*

Ligand L^1—1,4-diphenyl-1,5-diaza-8,11-dithiacyclotrideca-1,4-diene [N_2S_2] and ligand L^2—2,4,9,11-tetraphelyl-6,13-dimethyl-1,5,8,12-tetraazacyclotetradeca-1,4,8,11-tetetraene [N_4] are prepared by the method given below.

To an EtOH solution (25 ml) of $C_6H_5COCH_2COC_6H_5$ (0.005 mol), an EtOH solution (25 ml) of $NH_2C_6H_4SCH_2CH_2SC_6H_4NH_2$ (0.005 mol) or $NH_2CH_2CH(CH_3)NH_2$ (0.005 mol) was added. The resulting solution was refluxed on water bath at 70–80 °C for 6–7 h. The solution was then concentrated to half of its volume under reduced pressure and kept overnight at ∼5 °C. The white crystals formed were filtered, washed with EtOH, and dried under vacuum over P_4O_{10}.

Ligand L^3: 1,4,7,10,13-pentaazacyclopentadecane [N_5].

To an EtOH solution (25 ml) of $NH_2C_6H_4NHCH_2CH_2NHC_6H_4NH_2$ (0.002 mol), an EtOH solution (25 ml) of $ClCH_2CH_2NHCH_2CH_2Cl$ (0.002 mol) was added. The resulting solution was refluxed on water bath at 75–80 °C for 4–5 h. The solution was then concentrated to half of its volume under reduced pressure and kept overnight at ∼5 °C. The white-off crystals formed were filtered, washed with EtOH, and dried under vacuum over P_4O_{10}.

3.3. *Characterization of macrocyclic ligands*

Ligand L^1 found C, 79.0, H, 5.0, N, 6.0% cald. for $C_{29}H_{24}N_2S_2$C, 74.9, H, 5.2, N, 6.0% and for ligand L^2 found C, 82.0, H, 6.5, N, 22.0% cald. for $C_{36}H_{36}N_4$C, 82.41, H, 6.92, N, 10.64%. The bands corresponding to $-NH_2$ and $>CO$ are not observed in the IR spectrum of these ligands, but shows sharp and new bands at 1596 and 1597 cm^{-1} respectively which may be assigned to the C=N group. It indicates that complete condensation takes place. The mass spectrum

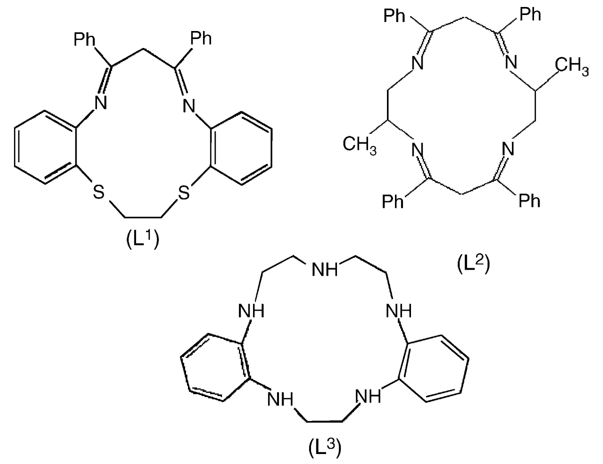

Fig. 1. Suggested structures of macrocyclic ligands.

of ligand L^1 shows a peak at 463 corresponding to the molecular ion ($M^+ + 1$). EIMS m/z (%) 463 (M^+, 75%) and the mass spectrum of the L^2 shows a peak at m/z 523 corresponding to the molecular ion ($M^+ + 1$). EIMS m/z (%) 523 (M^+, 70%).

Ligand L^3 found C, 69.5, H, 7.5, N, 22.0% cald. for $C_{18}H_{25}N_5$ C, 69.42, H, 8.09 N, 22.40%. The infrared spectrum of this ligand shows a band at 3250 cm^{-1} which may be assigned to the secondary amino group. The mass spectrum of the ligand shows a peak at 309 corresponding to the molecular ion ($M^+ + 1$). EIMS m/z (%) 310 (M^+, 65%) (Fig. 1).

3.4. Preparation of the complexes

EtOH solution of (25 ml) of the corresponding macrocyclic ligand (0.002 mol), was added to an EtOH solution of the (25 ml) hydrated cobalt(II) or ruthenium(III) salts (0.002 mol). The resulting solution was refluxed on a water bath at 70–80 °C for 7–8 h. The solution was then concentrated to half of its volume under reduced pressure and kept overnight at ~5 °C. The colored crystals formed were filtered, washed with EtOH and dried under vacuum over P_4O_{10}.

4. Physical measurements

The magnetic susceptibilities were measured on a Gouy balance using $Hg[Co(NCS)_4]$ as calibrating agent. These infrared spectra of the complexes were recorded on a Perkin-Elmer FTIR 1710 automatic-recording spectrophotometer in KBr pellets. Electronic Spectra (200–1100 nm) of the complexes were recorded on a Shimadzu DMR-21 automatic-recording spectrophotometer in DMSO. Mass spectra were carried out on a Jeol, JMX, DX-303 mass spectrophotometer. The EPR spectra of the complexes were recorded as polycrystalline samples at room temperature (25 °C) as well as in nitrogen atmosphere on a Varian E-4 EPR spectrometer operating at 9.4 GHz and 100 kHz field modulation and phase sensitive detection. Conductance measurements in nitromethane were carried out on a Leeds Northrup model 4995 conductivity bridge. Analyses of carbon and hydrogen were performed by the Microanalytical Laboratory of the Central Drug Research Institute, Lucknow. The nitrogen content of the complexes was determined using Kjeldahl's method. The cobalt content in the complexes was determined volumetrically. The voltammogram were recorded under nitrogen using freshly distilled, degassed DMF. A glass carbon electrode was used as the counter electrode. A non-aqueous reference electrode was employed. The electrode solution for non-aqueous reference electrode was prepared by dissolving 0.01 m $AgNO_3$ in 0.1 M tetramethylammonium perchlorate (TEAP) in DMF solution resulting an Ag/Ag^+ electrode. TEAP was applied as electrode on an x–y Houston-Ommigraphic 2000 recorder.

5. Result and discussion

5.1. Cobalt(II) complexes with ligands L^1 and L^2

On the basis of the elemental analyses, the cobalt(II) complexes have the general composition $Co(L^1 \text{ or } L^2)X_2$ (where X = NCS, NO_3, and $1/2SO_4$). All of the complexes show molar conductance 190, 95, and 10 $\Omega^{-1}\,cm^2\,mol^{-1}$ corresponding to 1:2, 1:1 and non-electrolytes (Table 1). On complexation the important ν(C=N) band in the infrared spectra are shifted to lower frequency as compared to the macrocyclic ligands [4].

This indicates that these ligands coordinated to the cobalt(II) through nitrogen of C=N. These complexes show magnetic moments corresponding to three unpaired electrons in the range 4.75–4.82 B.M. at room temperature (300 K) [5,6,13].

The infrared spectra of the $Co(L^1)(NCS)_2$ and $Co(L^2)(NCS)_2$ show sharp peaks at 2082 and 2081 cm^{-1}, indicating that the thiocyanate groups are coordinated through the nitrogen of the NCS group [7]. The electronic spectra of these complexes display three well-defined bands at 9510–9523 (ν_1), 16,395–16,445 (ν_2), and 23,225–23,809 (ν_3) cm^{-1} which may be assigned to the transitions, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2), and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3), respectively (Fig. 2) corresponding to a six-coordinated geometry [6] (Fig. 3).

In the infrared spectra of $Co(L^1 \text{ or } L_2)(NO_3)_2$ complexes show sharp bands at 1383 and 1382 cm^{-1} corresponding to an uncoordinated nitrate group [6,7] respectively. These complexes show magnetic moment corresponding to one unpaired electron in the range of 1.99–2.00 B.M. Electronic spectrum of these complexes display two bands at 10,250–10,300 and 20,730–20,840 cm^{-1} corresponding to a four coordinated geometry (Fig. 4).

$Co(L^1)SO_4$ and $Co(L^2)SO_4$ show magnetic moment in the range 4.85–4.90 B.M. indicating a high-spin configuration [9]. IR spectra $Co(L^1 \text{ or } L_2)SO_4$ show bands at 945-41 (ν_1), 1055-51 (ν_2) and 1160-58 (ν_3) cm^{-1} and

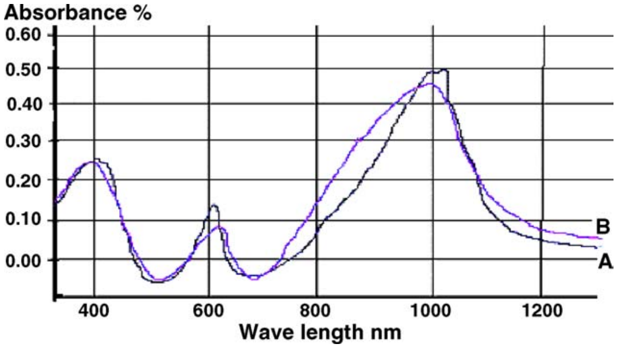

Fig. 2. Electronic spectrum of A and B are for $[Co(L^1)(NCS)_2]$ and $[Co(L^2)(NCS)_2]$.

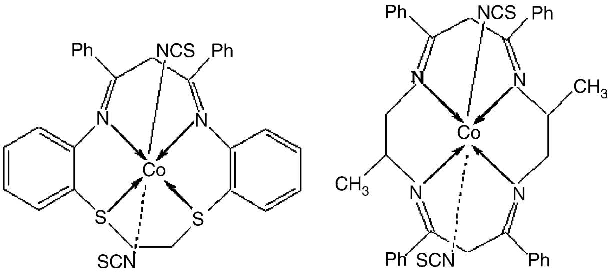

Fig. 3. Suggested structures of $[Co(L^1 \text{ or } L_2)(NCS)_2]$.

942-40 (ν_1), 1055-51 (ν_2) and 1165-62 (ν_3) cm^{-1} corresponding to unidentate nature of sulphato group [10]. The electronic spectra of these complexes display well-defined bands at 4765–4850, 5560–5665, 12,940–13,010 and 19,352–20,980 cm^{-1} these may assigned to $^4A_2(F) \rightarrow {}^4E$, $^4A_2(F) \rightarrow {}^4E(P)$ and $^4A_2(F) \rightarrow {}^4A_2(P)$ transition respectively according to five coordinated geometry. On the basis of above studies, a five-coordinate square pyramidal geometry (Fig. 5) may be suggested for these complexes.

5.2. *Cobalt(II) complexes with the ligand L^3*

On the basis of elemental analyses, these complexes have the general composition $CoL^3(X)_2$ (where L = NCS, and NO_3). These complexes show magnetic moment in the range 4.75–4.82 B.M. at room temperature (300 K) [10–13] corresponding to three unpaired electrons. These complexes show molar conductance 195–180 $\Omega^{-1}\,cm^2\,mol^{-1}$ corresponding to 1:2 electrolytes but sulphate complex is non-electrolyte [12]. So that these complexes may be formulated as $[Co(L^3)](SCN)_2$, $[Co(L^3)](NO_3)_2$ and $[Co(L^3)(SO_4)]$. On complexation, the position of the important infrared spectral bands (amide II [(N–H)], and –CH_2–NH–CH_2–) are shifted to lower frequency as comparative the free macrocyclic ligand [7].

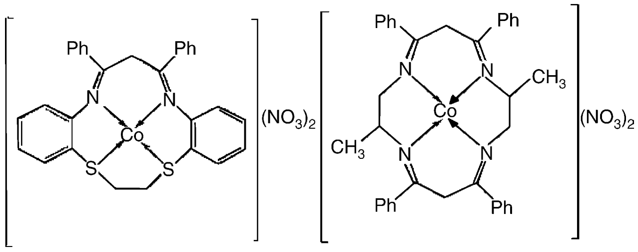

Fig. 4. Suggested structures of $[Co(L^1 \text{ or } L_2)](NO_3)_2$.

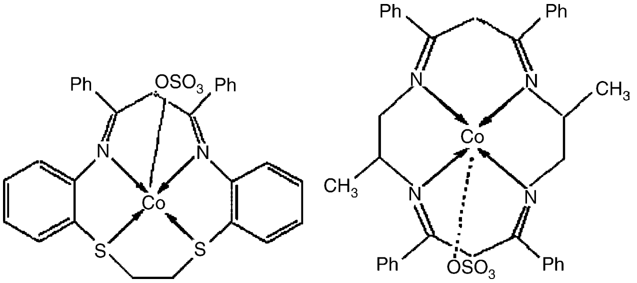

Fig. 5. Suggested structures of $[Co(L^1 \text{ or } L_2)SO_4]$.

The infrared spectra of $[Co(L^3)](NO_3)_2$ and $[Co(L^2)](NCS)_2$ complexes show bands at 1383 and 2050 cm^{-1} corresponding to an uncoordinated nitrate and thiocyanate groups [2,6]. The electronic spectra of these complexes display well-defined bands at 4700–4866, 9990–9741, 12,345–12,500 and 16,650–16,949 cm^{-1} these may assigned to $^4A_2(F) \rightarrow {}^4E$, $^4A_2(F) \rightarrow {}^4E(P)$ and $^4A_2(F) \rightarrow {}^4A_2(P)$ (Fig. 6) transition respectively. Thus, a five-coordinate geometry may be suggested for these complexes (Fig. 7).

In the infrared spectrum of $[Co(L^3)]SO_4$ shows absorption at 1103 and 930 cm^{-1} indicating coordinated nature of sulphate group. The electronic spectrum of the $[Co(L^3)]SO_4$ display three well-defined bands at 9017 (ν_1), 16,640 (ν_2), and 21,210 (ν_3) cm^{-1} which may be assigned to the transitions, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ (ν_2), and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3), respectively, corresponding to a six-coordinate geometry [5,6] (Figs. 8 and 9).

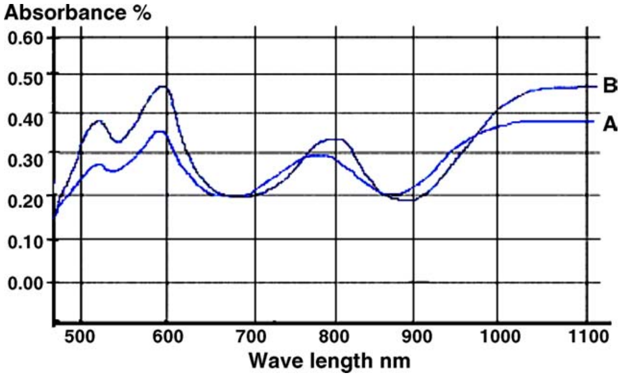

Fig. 6. Electronic spectra of A and B of $[Co(L^3)](X)_2$ where (X = SCN and NO_3).

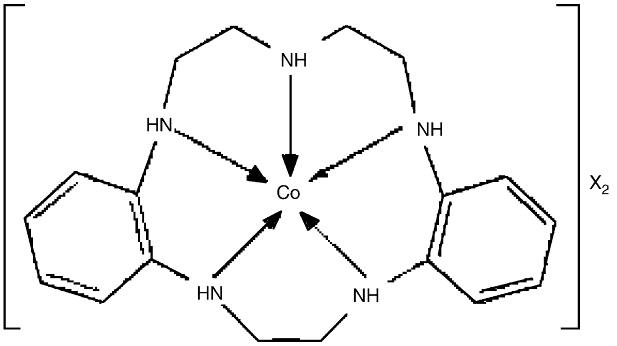

Fig. 7. Suggested structure of $[Co(L^3)](X)_2$ where (X = SCN and NO_3).

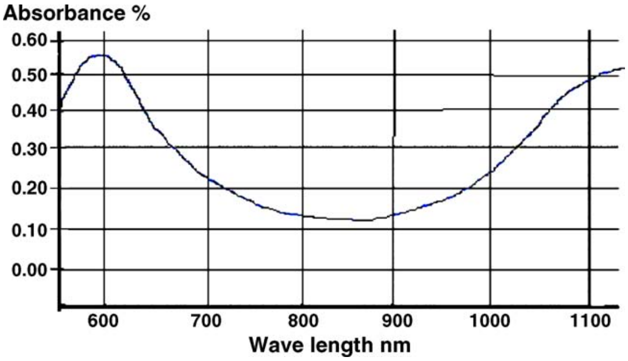

Fig. 8. Electronic spectrum of $[Co(L^3)SO_4]$.

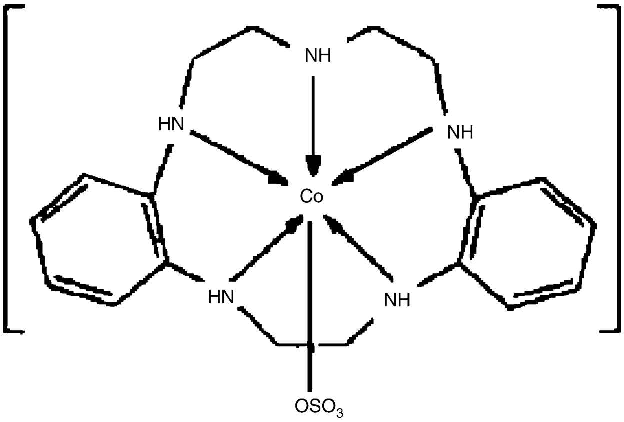

Fig. 9. Suggested structure of $[Co(L^3)(SO_4)]$.

6. EPR spectra

The EPR spectra of the complexes under study were recorded at liquid nitrogen temperature because the rapid spin lattice relaxation of cobalt(II) broadens the lines at higher temperature. The higher deviation of the g values from the free electron value ($g = 2.0023$) is due to orbital contributions [8,9]. $g_{||}$ and $g_{\perp}$ values were calculated and found in the range of 3.40–4.55.

7. Cyclic voltammetry

Cyclic voltammetry was used to confirm the oxidation levels of the metal centers in the cobalt(II) complexes. The electrochemical properties of metal complexes, particularly with sulphur donor atoms have been studied in order to consider spectral and structural changes accompanying with electron transfer. The redox behaviour of the cobalt(II) complexes has been examined in DMSO at a glassy carbon as working electrode using electrochemical analyzer. All these complexes are electroactive only with respect to metal center. The observation of a single, strong peak which is not exhibited by the corresponding ligand indicates oxidation of cobalt(II) to cobalt(III) on the cyclic voltammetric time scale and suggests that in one complex, the metal center are symmetrically located. Comparison of the oxidation potential of the nitrogen or sulphur donor complexes reveals that both have different oxidation potentials. It is due to the greater difference in the electron withdrawing ability of donor atoms. The complexes of cobalt(II) exhibit both metal and ligand-centered electrochemistry in the potential range ±1.7 V versus the Ag/AgCl, CI^- electrode. All the complexes exhibit one quasi-reversible oxidation process as evident by the peak to peak separation, $\Delta E_p > 100$ mV, and show redox potentials in the range of 1.0–1.25 V. In all cobalt(II) complexes the cathodic and anodic peak heights (I_{pc} and I_{pa}) are the same. The one-electron nature of the couple is confirmed on comparing with the current height of the $Fe(CN)_6{}^{3-}/Fe(CN)_6{}^{4-}$ system. The electrochemical behaviour of the cobalt(II) complexes is due to the Co(III)/Co(II) couple. The positive potential indicates that metal in lower oxidation state is strongly bound to the ligand.

7.1. Reduction process

Cobalt(II) complexes show a quasi-reversible two step single electron transfer process. $E_{1/2}$ values are independent of scan rate. The ΔE_p increases with increasing scan rate and is always greater than 60 mV.

Voltammetric parameters are studied in the scan range of 60–800 mV s^{-1}. The ratio between the cathodic peak current and square root of the scan rate ($I_{pc}/v^{1/2}$) is approximately constant [10,14]. The peak potential shows a small dependence with the scan rate. The ratio (I_{pa}/I_{pc}) is close to unity. Form these data, it can be deduced that this redox couple is related to a reversible one-electron transfer process controlled by diffusion (Figs. 10 and 11).

7.2. Oxidation process

The cyclic voltammogram of cobalt(II) complexes shows two peaks corresponding to two single electron transfer process.

The difference between the potential of the anodic peak and cathodic peak remains constant. Also, the ratio between the cathodic peak current and square root of the scan rate is practically constant in the range studied. All the data are

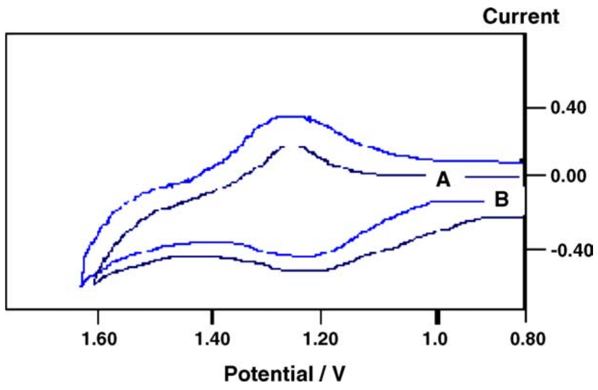

Fig. 10. Cyclic voltammogram of A and B are for [Co(L^1 or L^2)(NCS)$_2$] in anodic region.

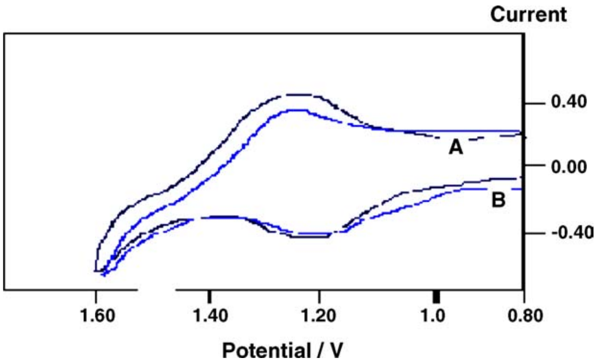

Fig. 11. Cyclic voltammogram of A and B are for [Co(L^1 or L^2)(NO$_3$)$_2$] in anodic region.

diagnostic for a simple quasi-reversible one-electron charge transfer controlled by diffusion method.

The redox responses are negative which are relative to reference electrode due to ligand reductions. The >C=N, −NH−, and Ph−S−CH$_2$− groups in the ligands are known as potential electron transfer centers [14]. We observed two one-electron quasi-reversible reductions ($\Delta E_p > 100$ mV) in the potential range 0.2 to −0.3 and −0.4 to −0.6 V along with a two-electron reduction at −1.0 to −1.3 V (Figs. 12 and 13).

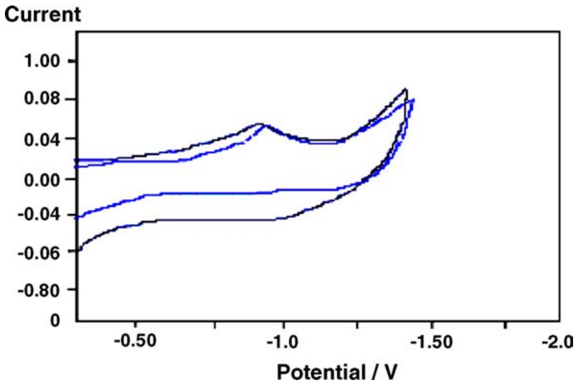

Fig. 12. Cyclic voltammogram of A and B are for [Co(L^1 or L^2)(NCS)$_2$] in cathodic region.

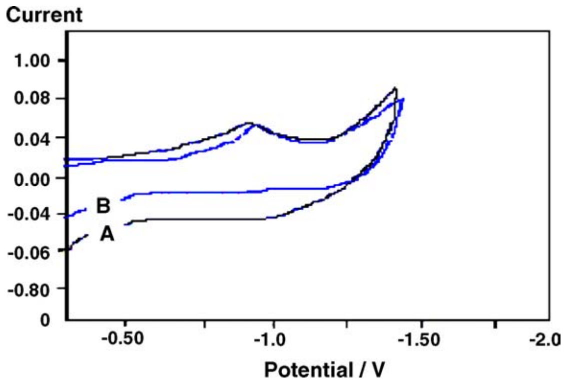

Fig. 13. Cyclic voltammogram of A and B are for [Co(L^1 or L^2)](NO$_3$)$_2$ in cathodic region.

8. Ruthenium(III) complexes with ligands L^1, L^2 and L^3

On the basis of elemental analyses, all the complexes were found to have general composition RuL(X)$_3$. The molar conductance measurement indicates that the complexes are 1:1 and 1:2 electrolyte in nature. Thus, these complexes may be formulated as [RuL^1 or L^2(X)$_2$](X) and [RuL^3(X)](X)$_2$ (where X = NO$_3$ and SCN) respectively (Table 2). The Ru(III) complexes show magnetic moments at room temperature in the range of 1.76–1.80 B.M., which is lower than the predicted value of 2.10–2.15 B.M. [13,15] The lowering in μ_{eff} values may be due to either lower symmetry ligand fields, metal–metal interaction or extensive electron delocalization [13].

The infrared spectra of the thiocyanate and nitrate complexes of ruthenium show bands corresponding to coordinated as well as uncoordinated nature of both groups and also indicates that the thiocyanate groups is coordinated through the nitrogen of the NCS group [7,16].

The electronic spectra of ruthenium(III) complexes display three bands at 15,625–15,873 (ν_1), 17,241–16,522 (ν_2) and 25,000–26,315 cm^{-1} (ν_3). These bands may be assigned to $^2T_{2g} \rightarrow {}^4T_{1g}$, $^2T_{2g} \rightarrow {}^4T_{2g}$ and $^2T_{2g} \rightarrow {}^4A_{1g}$ transitions in order of increasing energy [13] (Figs. 14 and 15).

The position of bands is in tune with the prediction of octahedral arrangement around of the metal ion. The ligand field parameters Δ, B and β have been calculated by using the relation $\nu_1 = \Delta - 4B + 86(B)^2/\Delta$ and $\nu_2 = \Delta + 12B + 2(B)^2/\Delta$ [5,6]. The value of B in free ion is ruthenium(III) 630 cm^{-1}.

The value of β indicates that there is low covalency in the metal ligand σ-band (Figs. 16 and 17). Suggested structures of these complexes are given in figures.

9. Electrochemical studies

The electrochemical properties of complexes show a variety of chemically reversible processes i.e. cathodic and

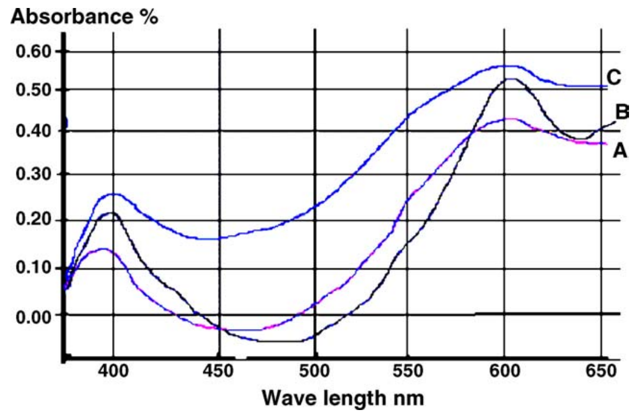

Fig. 14. Electronic spectra of A and B are [Ru(L^1or L^2)$(NCS)_2$](NCS) and [Ru(L^3)$(NCS)_2$](NCS).

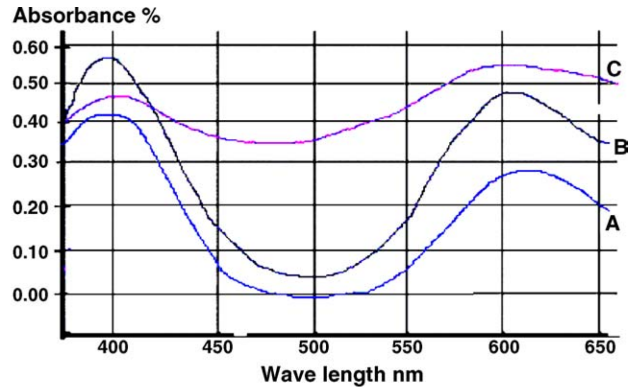

Fig. 15. Electronic spectra of A, B and C [Ru(L^1or L^2)$(NO_3)_2$](NO_3) and [Ru(L^3)$(NO_3)_2$](NO_3).

anodic peak currents whereas equal intensity over a wide range of scan rates.

9.1. Metal-based couples

The metal-based couples are most significant for assessing the electronic properties of the ligands and metal complexes. For the N_4 coordinated, ruthenium(III) couple occurs at 20.07 V versus the ferrocene–ferrocenium couple, a substantial shift from the value of +0.89 V for (L^2). The first change is in the overall charge on the complex; the +1 charge

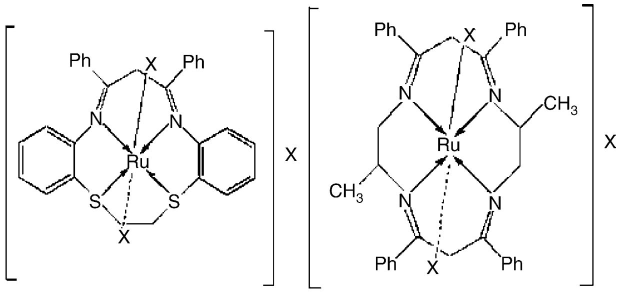

Fig. 16. Suggested structures of [Ru(L^1 or L^2)$(X)_2$](X).

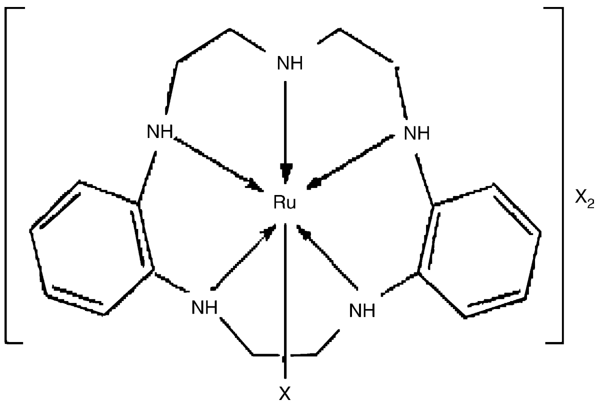

Fig. 17. Suggested structure of [Ru(L^3)(X)]$(X)_2$.

of L^1 as compared to the +2 charge L^2. It means that removal of an electron will be electro statically much easier in the former case, irrespective of the nature of the donor atoms of the ligands.

The second contribution arises from the inherently different electron donor/acceptor properties of a ligand as compared to an L^2 and L^3 ligands. Although it is not possible to separate the two effects, but it has been known that the electrostatic effect is the more significant, with changes in the nature of the ligands. It suggests that the electrostatic contribution to stabilization of the ruthenium(III) state will be similar in both cases. The additional +0.1 V stabilization of the ruthenium(III) state in L^1 as compared to L^2, may be due to the different electronic properties of the sulphur ligands, and apparently suggests that the electron donor ability is dependent upon the nature of donor atoms. This is inconsistent with the known sulphur donor abilities of these ligands that indicates the stronger electron donor property of ligand. However, such a simplistic electrostatic picture ignores the effects of covalency, in particular the greater polarisability of the lone-pair electrons on sulphur compared to those on nitrogen, which is clearly a dominant effect here.

For complex L^1 (N_2S_2 donor set) there are, surprisingly, two one-electron redox processes at moderate potentials which shows two waves corresponding to Ru(II)/Ru(III) and Ru(III)/Ru(IV) couples. The Ru(II)/Ru(III) couple of L^2 may be ascribed to the process at 21.43 V. The difference between the electronic effects of sulphur and nitrogen donors is less obvious here, with the two complexes having their Ru(II)/Ru(III) couples at very similar potentials. The negative shift of 2.32 V with respect to parent complex corresponds to 0.76 V, which is somewhat smaller than the shift of 0.96 V observed for L^2.

When significant covalency is involved we would not necessarily expect the effects to be exactly additive. For example, in complex L^1, where there are two sulphur donors, it is quite reasonable that each one should donate rather less electron density to the metal than does the single as in donor of L^2 (the electro neutrality principle), and this is reflected in the electrochemical results.

The electrochemical properties of ruthenium(III) complexes in which two sulphur atoms present in ligand were attached to a ruthenium(L^3) fragment, and these provide a convenient basis for comparison with L^2 and L^1. The couple at 20.21 V versus ferrocene/ferrocenium for complex L^1 we assign to the expected Ru(III)/Ru(IV) couple, by comparison with ruthenium(L^2) for which this couple occurs at +0.14 V. The ruthenium(IV) state is therefore stabilized in L^1 by 0.35 V more than it is in L^2. This difference in potential between the Ru(III)/Ru(IV) couples is much larger than the difference between the Ru(II)/Ru(III) couples for the same pair of complexes. The electron-donating properties to ruthenium become more pronounced as the oxidation state of the metal center increases, which is consistent with the fact that the electrons on sulphur are more polarisable than those on other atoms: the ligands can adjust to the higher oxidation state by transferring more electron density to the metal, which the more electronegative and less polarisable sulphur atoms are unable to do so well.

9.2. Ligand-based couples

The third redox process of complex L^1, at +0.56 V, was entirely unexpected as it has no counterpart as in RuL^2. It is highly unlikely to be a Ru(IV)/Ru(V) couple as ruthenium(V) complexes are very rare and are unknown with this type of ligands. If two atomic orbitals, each containing a lone pair, overlap slightly then bonding and antibonding sum-and-difference combinations will form. Normally both of these contain two electrons so there is no net bonding interaction, but one-electron oxidation of the pair will give a this interaction which will be particularly strong for a pair of sulphur atoms.

10. Conclusion

In this paper we reported the synthesis and characterization of 13-, 14- and 15-membered macrocyclic ligands. The size is effected the complexation behaviour of these ligands. Recently we published the complexation behaviour of 12-membered ligands with first row transition metals. But in this paper, the nature of the ligands and its effect on the stability of the complexes are observed constantly by using 12–15-membered macrocyclic ligands.

The second important behaviour of macrocyclic ligands with different oxidation state metals i.e. first row transition metals cobalt(II) and second-row transition metal ruthenium(III) are observed. Both metals oxidation states are also examined by cyclic voltammetry. The oxidation and reduction behaviour of our complexes explains the stability of metal ions in complexes in present study.

The coordination behaviour of the nitrato and thiocyanato groups in L^3 confirms the stability of metal ion in the ring. The stability of the complexes is also depending on the number of donating atoms in the macrocyclic ring and upon the nature transition metal. In the cobalt(II) and ruthenium(III) complexes of L^3, which is a pentadentate ligand, the anions are coordinated as well as uncoordinated. Cyclic voltammetry explain the relation between the stability of complexes and the donor atoms which is highly dependable on electro negativity of donor atoms and the nature of metal ion.

Acknowledgements

One of the authors (Rajiv Kumar) is greatly indebted to his younger brother Bitto for motivation. The University Grants Commission, Delhi for financial assistance and the University Science Instrumentation Centre, New Delhi University, for recording IR spectra. Thanks to Nitin Kampani, Central Science Library, Delhi University for providing guidance in computer software programming and the Solid State Physics Laboratory, Delhi for recording magnetic moments and thanks to I.I.T. Bombay for recording EPR spectra.

References

[1] S. Chandra, R. Kumar, Trans. Synth. React. Inorg. Met.-Org. Nano-Met. Chem. 35 (2005) 161.
[2] S. Chandra, R. Kumar, Spectrochim. Acta Part A 61 (61) (2005) 437.
[3] S. Chandra, R. Kumar, Trans. Synth. React. Inorg. Met.-Org. Nano-Met. Chem. 35 (2005) 103.
[4] S. Chandra, R. Kumar, Trans. Met. Chem. 29 (2004) 269.
[5] F.A. Cotton, G.S. Wilkinson, Advances in Inorganic Chemistry, 5th ed., Wiley, New York, 1988.
[6] A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.
[7] K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 3rd ed., Wiley Interscience, New York, 1978, p. 171.
[8] L. Sacconi, G.P. Speroni, Inorg. Chem. 7 (1976) 295.
[9] A. Bencini, D. Gatteschi, EPR of Exchange Coupled Systems, Springer Verlag, Berlin/Heidelberg, 1990.
[10] W. Rossister, J.F. Hamilton, Physical Method of Chemistry, 2nd ed., Wiley, New York, 1985.
[11] A. Escuer, R. Vicente, M.A.S. Goher, F.A. Mautner, Inorg. Chem. 35 (1996) 6386.
[12] J.A. Jensen, J.E. Gozum, D.M. Pollina, G.S. Girolami, J. Am. Chem. Soc. 110 (1988) 1643.
[13] O. Kahn, Molecular Magnetism, VCH, New York, 1993.
[14] E.L. Solomon, T.C. Brunold, M.Z. Davis, J.N. Kemsley, S.-K. Lee, N. Lehnert, A.J. Skulan, Y.S. Yang, J. Zhou, Chem. Rev. 100 (2000) 235.
[15] H. Hu, Y. Liu, D. Zhang, C. Liu, J. Mol. Struct. 73 (2001) 546.
[16] C.N.R. Roa, Chemical Applications of Infrared Spectroscopy, Academic Press, New York, 1963.