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Synthesis, Electrochemistry and Spectral Studies on Cobalt(II) and Manganese (II) Complexes with 12-,14-,15-, and 18-membered N_4, N_2O_2, N_2O_2S, N_6 Donor Macrocyclic Ligands

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13-, 14-, 15-, and 18-membered N_2O_2, N_4, N_2O_2S, and N_6 donor macrocyclic ligands and their complexes with cobalt(II) and manganese(II) of the general composition ML,$(NCS)_2$ (where M = cobalt(II) and manganese(II) and ligands L = L^1, L^2, L^3, and L^4 have been synthesized. All of the macrocyclic ligands and their complexes have been characterized by elemental analyses, IR, mass, ^{1}H NMR, magnetic moments, electronic and EPR spectral studies. The structures of the complexes and the various coordinating groups such as >C=N, >CONH, Ph—O—CH_2— and >NH are discussed. The redox properties of the complexes were examined by cyclic voltammetery. They exhibit a high potential Co(III)/Co(II) couple along with ligand reduction.

Keywords Magnetic moments, IR, ^{1}H NMR, Cobalt(II), Manganese(II), Macrocyclic ligands, Cyclic voltammetry

INTRODUCTION

Interest in the transition metal coordination chemistry of >C=N, —CONH, and >NH groups is rapidly expanding in several areas ranging from organometallic chemistry, metal-assisted organic transformation, radical chemistry, stabilization of low-valent metal oxidation state to DNA labeling (Fang et al., 1993) and anticancer drugs (Mishra et al., 2003). Interest in such macrocycles is growing on account of their utility in enzyme mimicking studies and catalysis, and their rapidly growing applications as radiopharmaceuticals, magnetic resonance imaging reagents, and fluorescent probes (Herrera et al., 2003).

The activities of such groups depends on the nature of the substituents, the number of heteroatoms and ring size of the macrocycle (Chandra and Kumar 2004; Salavati-Niasari and Najafian 2003). The most significant change has been observed on changing the ring size of the ligand (Autzen et al., 2003; Cruz et al., 2003). Macrocycles with a large cavity, which can accommodate two metal ions, can be used to bind the metal center at fixed distances. In these systems, there is often an additional internal or external bridging group, which completes the structure of the binuclear species which has the advantage of being relatively rigid and thus give structurally well-defined moieties (Lodeiro et al., 2003). Due to our continuous research in this field we expanded the synthesis of new series of macrocyclic ligands and their metal complexes which may be widely used in chemistry, molecular electronics, and biology due to their appearance in biosystems (Gao and Martell 2003; Sengupta et al., 2003). The macrocycles as well as their manganese(II) and cobalt(II) complexes play important roles as catalysts in the activation of small molecules. In view of the above applications, in this article we report the synthesis of cobalt(II) and manganese(II) complexes with the macrocyclic ligands L^1, L^2, L^3, and L^4 (Figure 1).

EXPERIMENTAL

All the chemicals used in this investigation 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. All the solvents were dried before use by passing over clean, dried sodium wire, refluxed for 30 minutes and distilled at 78 °C using a double-walled condenser.

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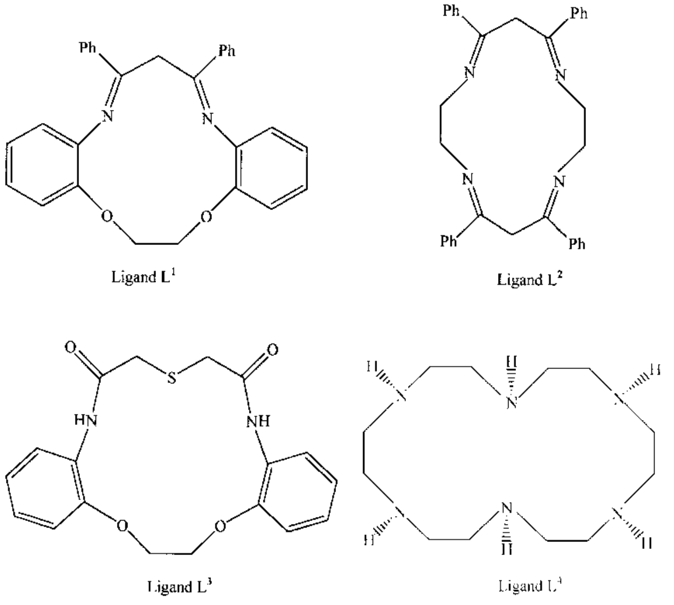

FIG. 1. Structures of macrocyclic ligands.

Preparation of Macrocyclic Ligands

Ligand L^1 (2,4-Diphenyl-1,5-diaza-8,11-dioxo-6,7:12,13-dibenzocyclotrideca-1,4-diene[N_2O_2]ane) and Ligand L^2 (2,4,9,11-Tetraphenyl-1,5,8,12-traazacyclotertr-adeca-1,4,8,11-tetraene[N_4]ane

To an EtOH solution of (25 mL) dibenzoylmethane (0.05 mole, 11.2 g), an EtOH solution (25 mL) of the diamine, i.e., 1,2-di(*o*-aminophenoxy)ethane (0.05 mole, 12.2 g) or diaminoethane (0.05 mole, 3.0 g) was added in the presence of a few drops (~1 mL) of conc. HCI. The solution was refluxed on a water bath at 75–80 °C for 2–3 h. The solution was then concentrated to half its volume under reduced pressure and kept over night at ~5 °C. The off-white crystals formed were filtered, washed with EtOH, and dried under vacuum over P_4O_{10}.

Ligand L^3 (1,7-Diaza-4-monothia-10,13-dioxo-8,9:14,15-cyclopetdeca-2,6-di-one [N_2O_2S]ane

To an EtOH solution (25 mL) of thiodiglycolic acid (0.05 mole, 7.49 g), an EtOH solution (25 mL) of 1,2-di(o-aminophenoxy)ethane (0.05 mole, 12.21 g) was added. The resulting solution was refluxed on a water bath at 75 °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 off-white crystals formed were filtered, washed with EtOH, and dried under vacuum over P_4O_{10}.

Ligand L^4 (1,4,7,10,13,16-Hexaazacyclooctadecane[N_6]ane

To an EtOH solution (20 mL) of Bis(2-chloroethyle)amine (0.05 mole, 7.12 g), an EtOH solution (20 mL) of diaminoethane (0.05 mole, 3.0 g) was added. The resulting solution was refluxed on a water bath at 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 crystals formed were filtered, washed with EtOH, and dried under vacuum over P_4O_{10}.

Characterization of Macrocylic Ligands

Ligand L^1

The infrared spectrum of this ligand (Figure 2) shows bands at 1610 and 1510 cm^{-1}, which may be assigned to C=N and Ph—O—CH_2— groups, respectively. The mass spectrum of the ligand shows a peak at m/z 431 corresponding to the molecular ion ($M^+ + 1$). EIMS m/z: 30 (M^+, 60%), 239 (40%), 149 (65%) and 105 (45%).

Ligand L^2

The infrared spectrum of the ligand shows a band at 1595 cm^{-1}, which may be assigned to the C=N group (Figure 3). The mass spectrum of the ligand shows a peak at m/z 495 corresponding to the molecular ion ($M^+ + 1$). EIMS m/z: 495 (M^+, 75%), 419 (60%), 342 (65%), 266 (70%), and 182 (45%).

Ligand L^3

The infrared spectrum of the ligand shows various bands at 1637–1645, 1551–1575, 1371–1382, and 690–771 cm^{-1}. These bands may be assigned to amide I [ν(C=O)], amide II [ν(C—N)], amide III [δ(N—H) and amide IV [δ(C=O)], respectively. The mass spectrum of the ligand shows a peak at m/z 357 corresponding to molecular ion ($M^+ + 1$). EIMS m/z: 365 (M^+, 70%), 259 (45%), 183 (70%), and 139 (65%).

Ligand L^4

The infrared spectrum of the ligand shows bands at 3330 and 3310 cm^{-1}, which may be assigned to amide II (NH). The mass spectrum of ligand shows a peak at m/z 257 corresponding to molecular ion ($M^+ + 1$). EIMS m/z: 257(M^+, 60%). 195 (40%), 165 (20%), 109 (80%), and 70 (50%). All the ligands

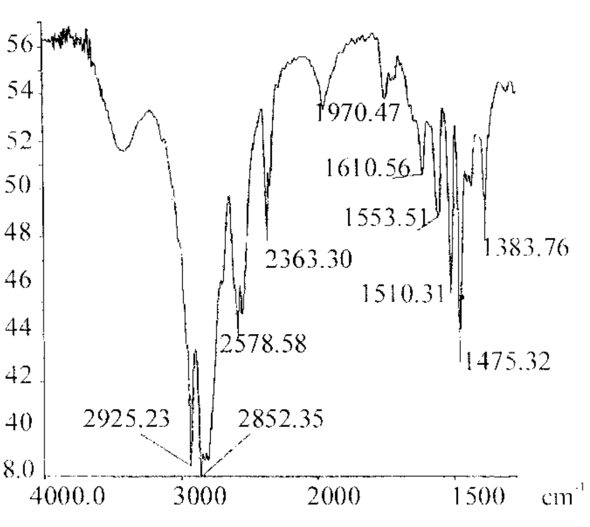

FIG. 2. IR spectrum of the macrocyclic ligand L^{-1}.

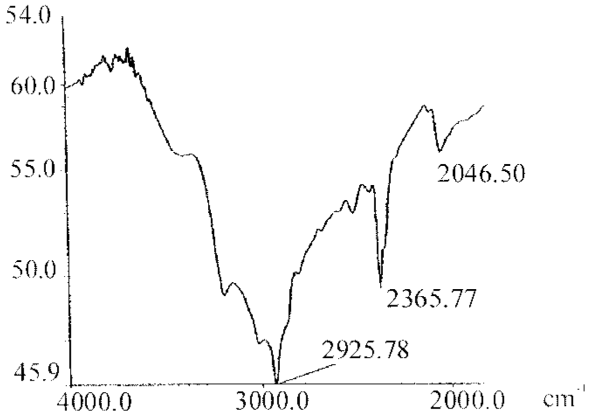

FIG. 3. IR spectrum of the macrocyclic ligand L^{-2}.

were also characterized by ^1H NMR and ^1H NMR spectral data are given in Table 1.

Preparation of the Complexes

To an EtOH solution of (20 mL) containing the macrocyclic ligand (0.05 mole), was added an EtOH solution 20 mL of the metal salt (0.05 mole), and the resulting solution was refluxed on a water bath at 75–85 °C for 3–5 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}

Physical Measurements

The magnetic susceptibilities were measured on a Gouy balance using $Hg[Co(NCS)_4]$ as a calibrating agent. KBr pellets of the complexes were prepared and their IR spectra of the complexes were recorded on a Perkin-Elmer FTIR 1710 automatic-recording spectrophotometer. Electronic Spectra (200–1100 nm) of the complexes were recorded on a Shimadzu DMR-21 automatic-recording spectrophotometer in Nujol mulls. Mass spectra were carried out on a Jeol, JMX, DX-303 mass spectrophotometer. ^1H NMR spectra were recorded on a Bruker Advance 300 spectrometer at 100 kHz modulation at room temperature. The EPR spectra of the complexes were recorded as polycrystalline samples at room temperature (25 °C) 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, and the manganese content gravimetrically as $Mn_2P_2O_7$. The voltammograms were recorded on an x-y Houston-Ommigraphic 2000 recorder.

RESULTS AND DISCUSSION

Cobalt(II) Complexes with Ligands L^1 and L^2

The formation of the complexes may be represented by the following equation:

$$Co(NCS)_2 \cdot nH_2O + L \longrightarrow CoL(NCS)_2 + nH_2O$$

On the basis of the elemental analyses, the cobalt(II) complexes have the general composition $CoL(NCS)_2$ (where L = ligand L^1 or L^2). All of the complexes show molar conductances in the range 5–16 $\Omega^{-1}cm^2mol^{-1}$ corresponding to non-electrolytes (Table 2). On complexation the positions of the important bands in the infrared spectrum due to the groups Ph—O—CH_2— and C=N were shifted to lower frequency compared to the macrocyclic ligands (Mandal and Nag, 1983; Ray et al., 2003). The infrared spectra of the $Co(L^1)(NCS)_2$ and $Co(L^2)(NCS)_2$ complexes show sharp peaks at 2080 and 2085 cm^{-1} respectively, indicating that the thiocyanate groups coordinate through the nitrogen of the NCS groups (Bentini and Sabatini, 1966). Thus, these complexes may be formulated as $[Co(L^1)(NCS)_2]$ and $[Co(L^2)(NCS)_2]$, respectively.

The magnetic moments of the complexes at room temperature (300 K) are 4 85–5.0 B.M. (Cotton and Willcinson, 1988; Ray et al., 2003) corresponding to three unpaired electrons. The electronic spectra of the cobalt(II) complexes display three well-defined bands at 8,870–8,890 (ν_1,), 16,345–16,395 (ν_2), and 20,110–20,225 (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 (Figure 4) octahedral geometry (Lever, 1984; Malik and Phillips, 1975).

Cobalt(II) Complexes with Ligand L^3.

The formation of the complex may be represented following equation:

$$Co(NCS)_2 \cdot nH_2O + L^3 \longrightarrow CoL(NCS)_2 + nH_2O$$

On the basis of elemental analyses, the cobalt(II) complex of the ligand L^3 has the general composition $CoL^3(NCS)_2$. This complex shows a molar conductance at 150 $\Omega^{-1}cm^2mol^{-1}$ corresponding to a 1:2 electrolytes (Chandra, 1982) (Table 2). This complex thus may be formulated as $[Co(L^3)](NCS)_2$. On complexation, the position of the important bands in the infrared spectrum due to the following groups: amide II [ν(C—N)], amide III [δN—H)], Ph—O—CH_2 and CH_2—S—CH_2— groups, are shifted to lower frequency compared to the free macrocyclic ligand (Abu Ismaiel et al., 2001) (Table 3). The infrared spectrum of $[Co(L^3)](NCS)_2$ displays a sharp band at 2050 cm^{-1} corresponding to uncoordinated thiocyanate groups (Abu Ismaiel et al., 2001; Nakamoto, 1978). The magnetic moment of this complex is 4.85 B.M. indicating a high-spin configuration (Ray et al., 2003). The electronic spectrum of this complex displays well-defined bands at

TABLE 1

^{1}H NMR spectral data of the macrocyclic ligands L^1, L^2, L^3, and L^4

S. no.	Compound	Phenyl	Benzene (subst.)	—NH	Ph—CH$_2$—Ph	Ph—O—CH$_2$	—CH$_2$— (C=N)	—S—CH$_2$	—NH—CH$_2$
(1)	L^1 $C_{29}H_{24}N_2O_2$	7.2–7.3 (10H, m)	7.1, 7.0, 6.9, 6.6 (2H, m) (2H, d, J = 7.3) (2H, d, J = 7.1) (2H, m)	—	4.1 (2H, s)	4.0 (4H, m)	2.8 (8H, m)	—	—
(2)	L^2 $C_{34}H_{32}N_4$	6.8, 6.4, 6.1 (4H, m) (8H, m) (8H, d, J = 6.5)	—	—	4.4 (4H, m)	—	—	—	—
(3)	L^3 $C_{18}H_{18}N_2O_4S$	—	7.2, 6.8, 6.5 (4H, m) (2H, d, J = 7.1) (2H, d, J = 6.8)	5.1 (2H, s)	—	3.0 (4H, m)	—	2.8 (4H, s)	—
(4)	L^4 $C_{12}H_{30}N_6$	—	—	9.1 (6H, s)	—	—	—	—	3.2 (24H, m)

4,765, 5,560, 12,940 and 16,590 cm^{-1}, which are assigned to ${}^4A_2(F) \rightarrow {}^4E'$, ${}^4A_2'(F) \rightarrow {}^4E'(P)$, and ${}^4A_2'(F) \rightarrow {}^4A_2'(P)$. A similar spectrum has been reported for other high-spin five-coordinated (Figure 5) cobalt(II) complexes (Sacconi and Speroni, 1976).

Cobalt(II) Complexes with Ligand L^4

The formation of the complex may be represented by the following equation:

$$Co(NCS)_2 \cdot nH_2O + L^4 \longrightarrow CoL^4(NCS)_2 + nH_2O$$

On the basis of elemental analyses, the cobalt(II) complex of the ligand L^4 has the general composition [CoL^4](NCS)$_2$. Molar conductance of this complex is 146 Ω^{-1} cm^2 mol^{-1} (Table 2) corresponding to a 1:2 electrolyte (Chandra, 1982). On complexation, the position of the important bands in the infrared spectrum due to >NH groups are shifted to lower frequency compared to the macrocyclic ligands (Chandra and Kumar, 2004; Raman et al., 2003). The infrared spectrum of this complex displays a sharp peak at 2055 cm^{-1} corresponding to uncoordinated thiocyanate groups (Table 3). This complex shows a magnetic moment of 4.53 B.M. (Ray et al., 2003). The electronic spectrum of the [CoL^4](NCS)$_2$ complex displays three well-defined bands at 8,870, 15,995 and 20,190 cm^{-1}, which may be assigned to the following transitions, ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_2) and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P)$ (ν_3), corresponding to six-coordinated (Figure 6) octahedral geometry (Chandra and Singh, 1985; Lever, 1984.; Malik and Phillips, 1975).

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 g-values are given in Table 4. The higher deviation of the g values from the free electron value ($g = 2.0023$) is due to orbital contribution (Bencini and Gatteschi, 1990; Brown and West, 2003; Chandra et al., 1991) and $g_{\|}$ and $g_{\perp}$ values were found in the range of 3.45–4.50.

TABLE 2
Elemental analyses and magnetic moments of cobalt(II) and manganese(II) complexes

S. no.	Compound	Formula weight	Color	Decomp. Temp. (°C)	Yield (%)	Elemental analyses (%) found/(calcd.)				μ_{eff} (B.M.)
						M	C	N	H	
(1)	L^1	435.51	White	180	40		80.00	6.41	5.65	
	$C^{29}H^{24}N^2O^2$						(80.05)	(6.50)	(5.65)	
(2)	[Co(L^1)(SCN)$_2$]	607.56	Pink	210	50	9.60	61.01	9.11	3.90	4.85
	$C_{31}H_{24}CON_4O_2S_2$					(9.70)	(61.28)	(9.22)	(4.00)	
(3)	[Mn(L^1)(SCN)$_2$]	603.57	Light	215	55	9.06	61.30	9.22	3.83	5.90
	$C_{31}H_{24}MnN_4O_2S_2$		yellow			(9.10)	(61.68)	(9.30)	(4.43)	
(4)	L^2	496.66	White	190	65		81.15	11.11	6.40	
	$C_{34}H_{32}N_4$						(82.26)	(11.26)	(6.55)	
(5)	[Co(L^2)(SCN)$_2$]	671.71	Pink	225	60	8.72	64.15	12.42	4.65	5.01
	$C_{36}H_{32}CoN_6S_2$					(8.79)	(64.38)	(12.50)	(4.48)	
(6)	[Mn(L^2)(SCN)$_2$]	667.72	White	215	55	8.12	64.30	12.14	4.65	5.92
	$C_{36}H_{32}MnN_6S_2$					(8.23)	(64.77)	(12.58)	(4.84)	
(7)	L^3	358.06	White	211	60		60.20	7.50	6.10	
	$C_{18}H_{18}N_2O_4S$						(60.35)	(7.80)	(5.07)	
(8)	[Co(L^3)](SNC)$_2$	533.11	Light	226	55	11.00	45.00	10.4	3.30	5.00
	$C_{20}H_{18}CoN_4O_4S_3$		pink			(11.07)	(45.06)	(10.5)	(3.4)	
(9)	[Mn(L^3)(SCN)](SNC)	529.12	Yellow	231	50	10.30	45.3	10.5	3.40	5.95
	$C_{20}H_{18}MnN_4O_4S_3$					(10.40)	(45.4)	(10.6)	(3.44)	
(10)	L^4	258.42	White	201	40		55.00	32.10	11.70	
	$C_{12}H_{30}N_6$						(55.77)	(32.55)	(11.73)	
(11)	[Co(L^4)](SCN)$_2$	433.47	Pink	206	45	13.50	38.5	25.5	6.75	4.90
	$C_{14}H_{30}CoN_8S_2$					(13.59)	(38.8)	(25.8)	(7.0)	
(12)	[Mn(L^4)](SCN)^2	429.48	Yellow	217	35	12.60	38.99	26.0	6.7	5.92
	$C_{14}H_{30}MnN_8S_2$					(12.79)	(39.2)	(26.1)	(7.0)	

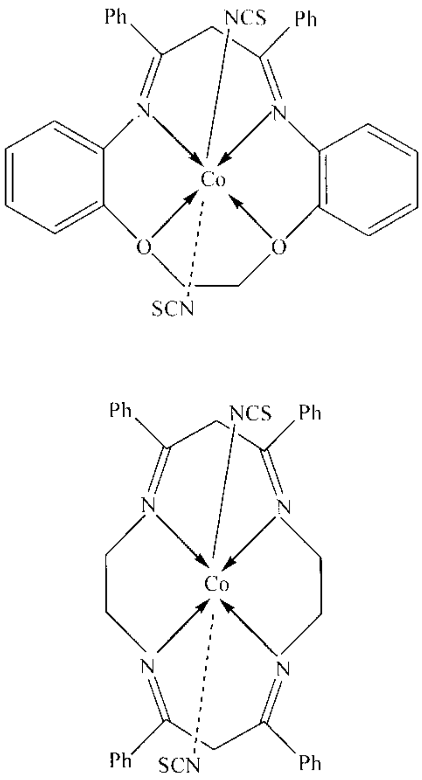

FIG. 4. Suggested structure of $[Co(L^1)(NCS)_2]$ and $[Co(L^2)(NCS)2]$.

Manganese(II) Complexes with Ligands L^1, L^2, L^3, and L^4

The formation of the complexes may be represented by the following equation:

$$Mn(NCS)_2 \cdot nH_2O + L \longrightarrow Mn(L)(NCS)_2 + nH_2O$$

Elemental analyses suggest that all the manganese(II) complexes have the general composition $MnL(NCS)_2$ ($L = L^1, L^2, L^3$ and L^4). In the complex of L^1, coordination occurs through the oxygen of Ph—O—CH_2— and the nitrogen of >C=N, for L^2, the nitrogen of >C=N and for L^3 through the nitrogen of —CONH and for L^4 through the nitrogen of >NH (Brown and West, 2003; Ray et al., 2003). The molar conductance data (Table 2) are 06, 10, 107, and 150 $\Omega^{-1}\,cm^{-2}mol^{-1}$ for the complexes of the ligands L^1, L^2, L^3, and L^4, respectively.

The infrared spectra (Figure 7) of the thiocyanato complexes of the ligands L^1 and L^2 show sharp peaks at 2085 and 2087 cm^{-1} due to the N-bonded thiocyanato group (Bentini and Sabatini, 1966). But the thiocyanato complex of L^3 shows two sharp peaks at 2080 and 2050 cm^{-1}, one corresponding to coordinated N-bonded thiocyanate and the other corresponding to an uncoordinated thiocyanato group (Ferguson et al., 1963). The thiocyanoto complex of L^4 shows a peak at 2045 cm^{-1} suggesting the uncoordinated nature of the thiocyanato groups. On the basis of the above studies these complexes may be formulated as $[Mn(L^1 \text{ or } L^2)(NCS)_2]$, $[Mn(L^3)(NCS)](NCS)$, and $[Mn(L^4)](NCS)_2$, respectively.

The present complexes show magnetic moments in the range 5.86–6.00 B.M. The electronic spectra of the manganese(II) complexes show bands at 17,565–17,615 (ν_1), 24,550–24,610 (ν_2), 28,640–28,715 (ν_3), and 31,250–31,315 cm^{-1} (ν_4), which may be assigned as ${}^6A_{1g} \rightarrow {}^4T_{1g}(4G)$ (ν_1), ${}^6A_{1g} \rightarrow {}^4E_g(4G)$ (ν_2), ${}^6A_{1g} \rightarrow {}^4E_g(4D)$ (ν_3), and ${}^6A_{1g} \rightarrow {}^4T_{1g}(4P)$ (ν_4) transitions, respectively. The ligand field parameter values Dq, B, C, β, F_4, and F_2 were calculated and are given in Table 5.

The electron-electron repulsion in the complexes is less than that in the free ion, resulting in an increased distance between electrons and thus an effective increase in the size of the orbital. On increasing delocalization the value of β decreases and is less than one in the complexes. The numerical value 786 cm^{-1} for B of the free manganese(II) ion has been used to calculate the value of β. The calculated values of β

TABLE 3
IR spectral data of the macrocylic ligands L^1, L^2, L^3, and L^4 and their manganese(II) and cobalt(II) complexes (cm^{-1})

S. no.	Compound	ν(NH)	Amide(I) ν(C=O)	Amide(II) ν(C—N)	ν(C=N)	Ph—CO—CH_2—	ν(SCN)
(1)	L^1	—	—	—	1,610 m	1,510 s	—
(2)	$[Co(L^1)(SCN)_2]$	—	—	—	1,608 m	1,507 s	2,080 s
(3)	$[Mn(L^1)(SCN)_2]$	—	—	—	1,607 m	1,508 s	2,085 s
(4)	L^2	—	—	—	1,595 s	—	—
(5)	$[Co(L^2)(SCN)_2]$	—	—	—	1,590 s	—	2,085 s
(6)	$[Mn(L^2)(SCN)_2]$	—	—	—	1,593 s	—	2,087 s
(7)	L^3	—	1,645 m	1,575 m	—	1,515 m	—
(8)	$[Co(L^3)](SNC)_2$	—	1,640 m	1,570 m	—	1,520 m	2,050 m
(9)	$[Mn(L^4)(SCN)](SNC)$	—	1,637 m	1,500 m	—	1,512 m	2,080 s, 2,050 m
(10)	L^4	3,330 s, 3,310 m	—	—	—	—	—
(11)	$[Co(L^4)](SCN)_2$	3,326 s, 3,300 m	—	—	—	—	2,055 s
(12)	$[Mn(L_4)](SCN)_2$	3,329 s, 3,309 m	—	—	—	—	2,045 s

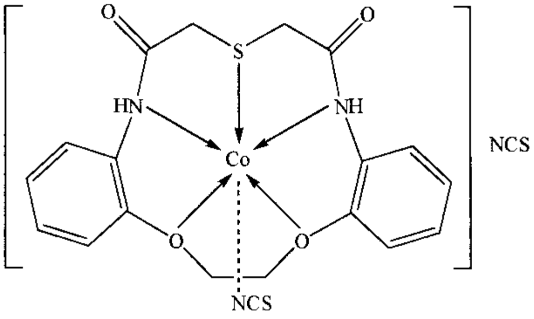

FIG. 5. Suggested structure of $[Co(L^3)](NCS)_2$.

(0.71–0.80) indicate that the complexes under study have appreciable covalent character.

EPR Spectra

The EPR spectra of the complexes have been recorded as polycrystalline samples at room temperature and g values are given in Table 5. Tile polycrystalline samples give one broad isotropic signal centered at ca. 3200. The free electron g-value is $g_0 = 2.0023$. In DMF, the EPR spectra of the complexes clearly show that they exist as monomeric units (Ferguson et al., 1963). The nuclear magnetic quantum number, MI, corresponding to these lines are $-5/2$, $-3/2$, $-1/2$, $+1/2$, $+3/2$, $+5/2$ from low to high field (Hankare and Chavan, 2003). Thus, on the basis of above studies the structures in Figure 8 may be suggested for the manganese(II) complexes.

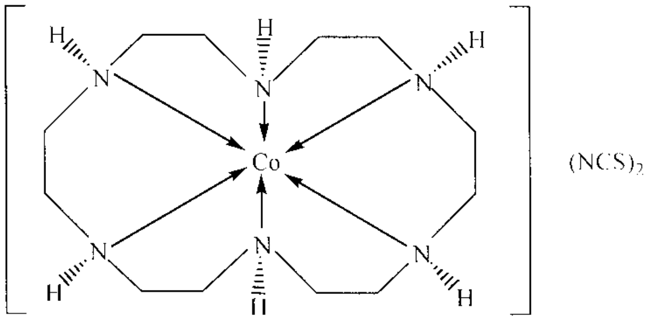

FIG. 6. Suggested structure of $[Co(L)](NCS)_2$.

TABLE 4
Ligand field parameters and EPR data of cobalt(II) complexes with the ligands L^1, L^2, L^3, and L^4

S. no	Complex	Dq	B (cm^{-1})	β	C.F.S.E	$g_{\parallel}$	$g_{\perp}$
(2)	$[Co(L^1)(SCN)_2]$	1120	641	0.57	108	2.61	4.50
(5)	$[Co(L^2)(SCN)_2]$	1060	685	0.61	102	2.00	4.23
(8)	$[Co(L^3)](SCN)_2$	1105	648	0.57	106	2.71	4.40
(11)	$[Co(L^4)](SCN)_2$	1090	656	0.50	105	2.53	3.45

Cyclic Voltammetry

The complexes of cobalt(II) exhibit both metal and ligand-centered electrochemistry in the potential range ± 1.7 V versus the Ag/AgCl, Cl^- electrode. All the complexes exhibit one quasi-reverisible oxidation process as evident by the peak-to-peak separation, $\Delta Ep \geq 100$ 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 when compared with the current height of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system. The electrochemical behavior (Figures 9 and 10) of

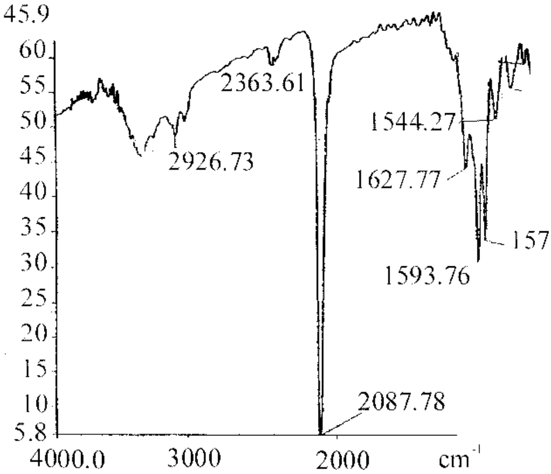

FIG. 7. IR spectrum of $[Mn(L^2)(NCS)_2]$.

TABLE 5
Ligand field parameters and EPR data of manganese(II) complexes with the ligands L^1, L^2, L^3, and L^4

S. No	Complex	Dq	B (cm^{-1})	C (cm^{-1})	β	F_4	F_2	h_x	g_{av}
(3)	$[Mn(L^1)(SCN)_2]$	1760	584	3742	0.74	107	1119	3.7	1.92
(6)	$[Mn(L^2)(SCN)_2]$	1756	585	2674	0.74	76	965	3.7	1.99
(9)	$[Mn(L^3)(SCN)](SNC)$	1761	585	2678	0.74	76	965	3.7	1.95
(12)	$[Mn(L^4)](SCN)_2$	1759	586	2678	0.74	76	966	3.7	1.93

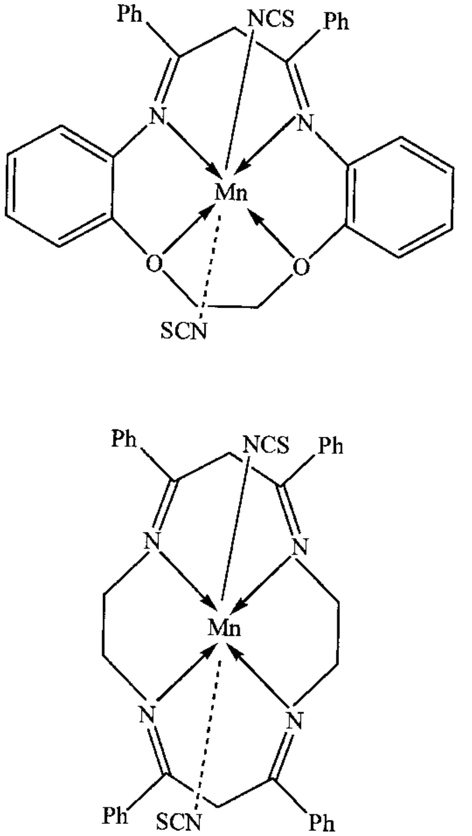

FIG. 8. Suggested structures of [Mn(L^1)(NCS)$_2$], [Mn(L^2)(NCS)$_2$], [Mn(L^3)(NCS)]NCS, and [Mn(L^4)] (NCS)$_2$.

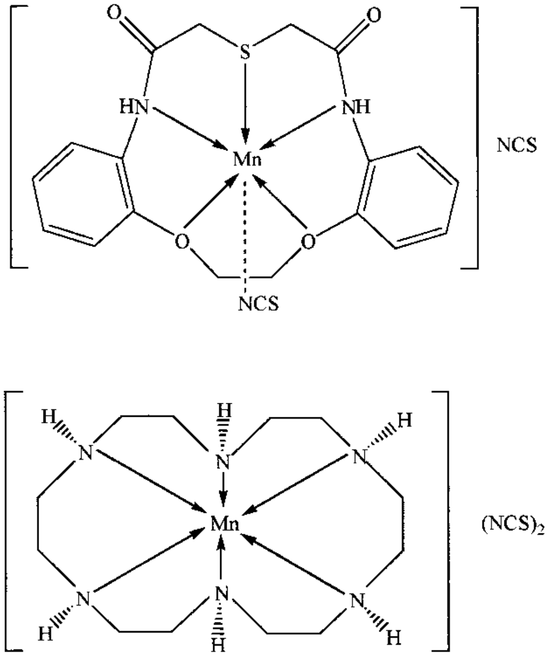

FIG. 8. Continued.

the cobalt(II) complexes is due to the Co(III)/Co(II) couple. The more positive the potential, the stronger is the binding to the lower oxidation state. The redox responses, which are negative relative to the reference electrode, are due to ligand reductions. The >C=N, —CONH, Ph—CO—CH$_2$— and >NH groups in the ligands are known as potential electron transfer centers (Basosi et al., 1975; Mayer et al., 2003). We observed two one-electron quasi-reversible reductions (ΔEp $\geq$ 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.

The redox property of the manganese(II) complexes was studied in the potential range of $+1.0$ to -1.6 V. Cyclic voltammograms of Mn(II) complexes are shown in Figure 11 for the cathodic region and Figure 12 for the anodic region. All the complexes show two reduction waves in the cathodic region at different potentials. During the reverse sweep, the complexes exhibit two oxidation waves at different potentials (Donzello et al., 2003). It indicates that each reduction is associated with a single-electron transfer process (Rossister and Hamilton, 1985). ΔE_p ($\Delta E_p = E_{pc} - E_{pa}$) values for the

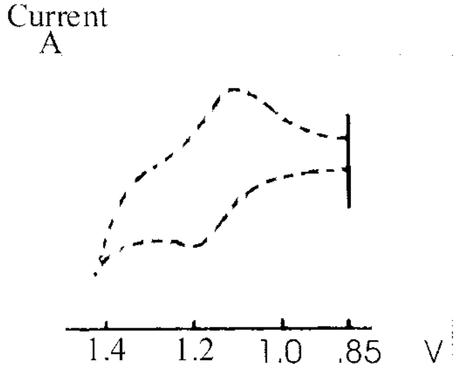

FIG. 9. Cyclic voltammogram for [Co(L^1)(NCS)$_2$] in the anodic region. Scan rate 50 m Vs^{-1}.

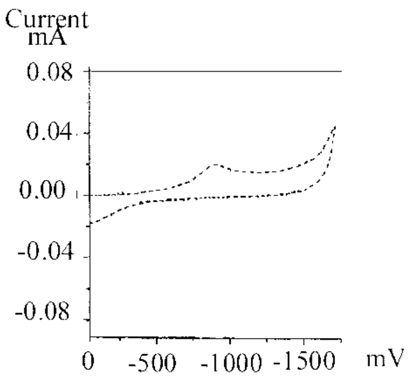

FIG. 10. Cyclic voltammogram of [Co(L^1)(NCS)$_2$] in the cathodic region. Scan rate 50 m V s^{-1}.

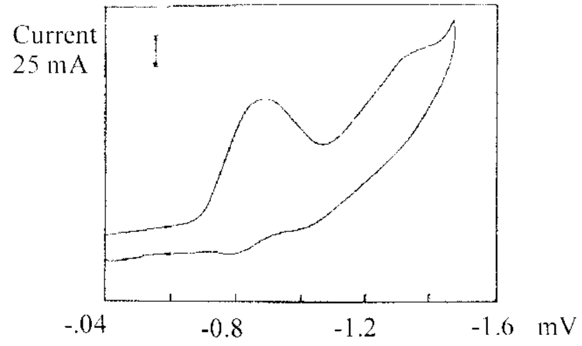

FIG. 11. Cyclic voltammogram for [Mn(L^1)$(NCS)_2$] in the cathodic region. Scan rate 50 m V s^{-1}.

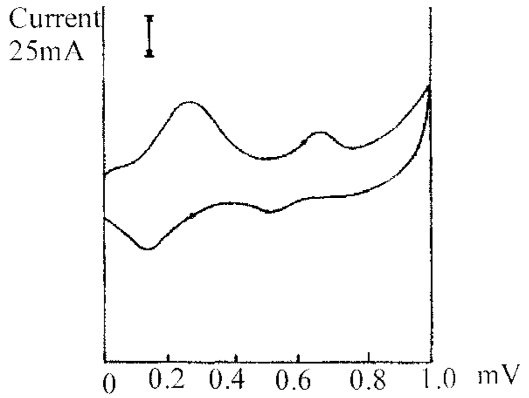

FIG. 12. Cyclic voltammogram for [Mn(L^1)$(NCS)_2$] in the anodic region. Scan rate 50 m V s^{-1}.

first redox couple are higher than for the second redox couple for all of the complexes. The first redox couple for all of the complexes is more than 300 mV and the second redox couple is more than 200 mV. E_p values are higher for all of the complexes due to the difference between the original complexes and the reduced species.

It has been observed that the first reduction of the metal center is influenced by the macrocyclic ring seize. It is shifted to more anodic values as the size increases.

CONCLUSION

The coordination behavior of the thiocyanato group is related to the number of donating atoms in the macrocyclic ring and it also depends upon the transition metal. In the Co(II) complex of L^3, which is a pentadentate ligand, the thiocyantao group shows uncoordinated nature, but with manganese(II), it shows coordinated behavior.

The M(II)/M(I) peak to peak separation in the manganese(II) complexes is considerably smaller as compared to that of Co(II) complexes.

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