Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

Synthesis, Physicochemical and Electrochemical Studies on Mn(II), Co(II), Ni(II), and Cu(II) Complexes with an N-Donor Tetradentate (N_4) Macrocycle Ligand Derived from Ethyl Cinnamate

Sulekh Chandra [a], Lokesh Kumar Gupta [a] & Sangeetika [a]
[a] Department of Chemistry, Zakir Husain College, University of Delhi, JLN-Marg, New Delhi, 110 002, India

To cite this article: Sulekh Chandra , Lokesh Kumar Gupta & Sangeetika (2004) Synthesis, Physicochemical and Electrochemical Studies on Mn(II), Co(II), Ni(II), and Cu(II) Complexes with an N-Donor Tetradentate (N_4) Macrocycle Ligand Derived from Ethyl Cinnamate, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 34:9, 1591-1604, DOI: 10.1081/SIM-200026596

To link to this article: http://dx.doi.org/10.1081/SIM-200026596

SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY
Vol. 34, No. 9, pp. 1591–1604, 2004

Synthesis, Physicochemical and Electrochemical Studies on Mn(II), Co(II), Ni(II), and Cu(II) Complexes with an N-Donor Tetradentate (N_4) Macrocycle Ligand Derived from Ethyl Cinnamate

Sulekh Chandra,* Lokesh Kumar Gupta, and Sangeetika

Department of Chemistry, Zakir Husain College, University of Delhi,
New Delhi, India

ABSTRACT

Manganese(II), cobalt(II), nickel(II), and copper(II) complexes with a new tetradentate ligand, 1,3,7,9-tetraaza-4,10-diketo-6,12-diphenyl-2,8-dithiocyclododecane (L), were synthesized and characterized by elemental analyses, molar conductance measurements, magnetic susceptibility measurements, mass, ^{1}H NMR, IR, electronic, EPR spectral and cyclic voltammetric studies. On the basis of the IR, electronic, and EPR spectral studies, an octahedral geometry has been assigned for the Mn(II) and

---

*Correspondence: Sulekh Chandra, Department of Chemistry, Zakir Husain College, University of Delhi, JLN-Marg, New Delhi 110 002, India; Fax: 91-11-23215-906; E-mail: schandra_00@yahoo.com.

DOI: 10.1081/SIM-200026596 0094-5714 (Print); 1532-2440 (Online)
www.dekker.com

Co(II) complexes, a square-planar one for the Ni(II) and a tetragonal one for the Cu(II) complexes.

Key Words: Tetradentate ligand; Complexes; Ligand field parameters; Electrochemical behavior.

INTRODUCTION

Coordination compounds containing macrocyclic ligands have been studied during the past decades owing to their wide applications in biological and sensor fields.[1,2] Different neutral donors have been incorporated into the ligand backbone.[3–6] Nature prefers macrocyclic derivatives for many fundamental biological functional systems such as photosynthesis and transportation of oxygen in mammalian and other respiratory systems.[7,8] In the present paper, we report the synthesis and characterization of Mn(II), Co(II), Ni(II), and Cu(II) complexes with a 12-membered tetradentate (N_4) macrocyclic ligand, 1,3,7,9-tetraaza-4, 10-diketo-6,12-diphenyl-2,8-dithiocyclododecane (L), shown in Fig. 1.

EXPERIMENTAL

Ethyl cinnamate and thiourea used were of AnalaR grade and procured from Fluka. Metal salts were purchased from E. Merck and were used as

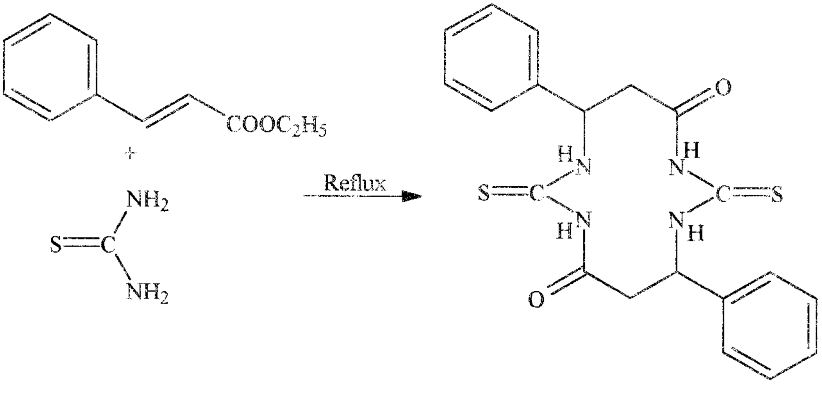


Figure 1. Synthesis and structure of the ligand.

received. All solvents used were purified before use according to standard procedures.[9]

Synthesis of Ligand

A hot ethanolic solution (20 mL) of ethyl cinnamate (3.52 g, 0.02 mol) and a hot ethanolic solution (20 mL) of thiourea (1.52 g, 0.02 mol) were mixed slowly with constant stirring. This mixture was refluxed at 82 °C for 12 hr in the presence of a few drops of concentrated hydrochloric acid. Cooling at 5 °C gave a white precipitate, which was filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10}.

Synthesis of Complexes

A hot ethanolic solution (20 mL) of the ligand (0.82 g, 0.002 mol) and a hot ethanolic solution (20 mL) of the metal salt (0.002 mol) were mixed together with constant stirring. The mixture was refluxed for 8–16 hr at 65–90 °C. On cooling to 5 °C, the colored complexes precipitated out. They were filtered, washed with cold EtOH, and dried under vacuum over P_4O_{10}.

Physical Measurements

C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. Molar conductances were measured on an Elico (CM82T) conductivity bridge. Magnetic susceptibilities were measured at room temperature on a Gouy balance using $CuSO_4 \cdot 5H_2O$ as a calibrant. Electron impact mass spectra were recorded on a Jeol, JMS, DX-303 mass spectrometers. ^1H NMR spectra were recorded on a model R-600 Hitachi FT-NMR, model R-600 spectrometer using deuterated DMF as solvent, chemical shifts are given in ppm relative to tetramethylsilane. IR spectra (KBr) were recorded on a FTIR Spectrum BX-II spectrophotometer. The electronic spectra were recorded in DMSO on a Shimadzu UV mini-1240 spectrophotometer. EPR spectra of the complexes were recorded as polycrystalline samples and in solution in DMSO at liquid nitrogen temperature for the Co(II) and at room temperature for the Mn(II) and Cu(II) complexes on an E_4 EPR spectrometer using DPPH as the g-marker. Cyclic voltammetry of the complexes was recorded in DMF at a scan rate of $100\,mV\,sec^{-1}$. The redox potential was recorded with Ag/AgCl as reference electrode and platinum as working electrode, tetrabutylammonium phosphate was the supporting electrolyte and the concentration of the complex was 1×10^{-3} M.

RESULTS AND DISCUSSION

The formation of the ligand and the complexes may be represented by the following reactions:

$$2\mathrm{PhCH{=}CH{-}COOEt} + 2\mathrm{SC(NH_2)_2} \xrightarrow[\text{Conc. HCl}]{\text{Reflux 12 hr}} \underset{\text{Ligand (L)}}{\mathrm{C_{20}H_{20}N_4O_2S_2}} + 2\mathrm{C_2H_5OH}$$

$$\mathrm{L} + \mathrm{MX_2} \xrightarrow{\text{Reflux}} \mathrm{MLX_2}$$

Ligand

The electron impact mass spectrum of the ligand (L) confirmed the proposed formula by showing a peak at 412 amu corresponding to the macrocyclic moiety ($C_{20}H_{20}N_4O_2S_2$). It also showed a series of peaks at 74, 78, 132, 162, 206, 212, 250, 280, and 363 amu corresponding to various fragments. Their intensity revealed the stability of these fragments (Fig. 2). The ^{1}H NMR spectrum of the ligand (L) does not give any signal corresponding to primary amine and ethyl protons. It gives a doublet at 8.57 ppm, which is due to the thio-amide group (–NH–CS–, 2H) protons.[10] Other signals appear at 1.53, 2.39, and 7.22 ppm. These signals correspond to methyne (–CH–CH$_2$–), methlene (–CH$_2$–CO–), and benzenoid protons, respectively. The presence of a broad signal at δ 5.18 ppm is due to the protons of the –NH groups.[11] The IR spectrum of the ligand does not exhibit any band corresponding to the free primary amino and ketonic groups. The absorptions in the IR spectrum of L in the range of 720–780 and 1430–1630 cm^{-1} are due to the presence of a phenyl group. The bands in the region ~809–1478 cm^{-1} are due to the thioamide-I and thioamide-II bands. Four new bands in the spectrum of the free ligand at 1620, 1590, 1248, and 780 cm^{-1} are assignable to amide-I ν(C=O), amide-II [ν(C–N) + δ(N–H)], amide-III [δ(N–H)], and amide-IV [δ(C=O)] bands, respectively.[8,12] A sharp band observed at 3278 cm^{-1} may be assigned to ν(N–H) of the secondary amido group.[10] The ligand may be racemic or meso, however, this will not affect the geometry of the complexes. Thin-layer chromatography has been performed, which indicates that the ligand is not a mixture.

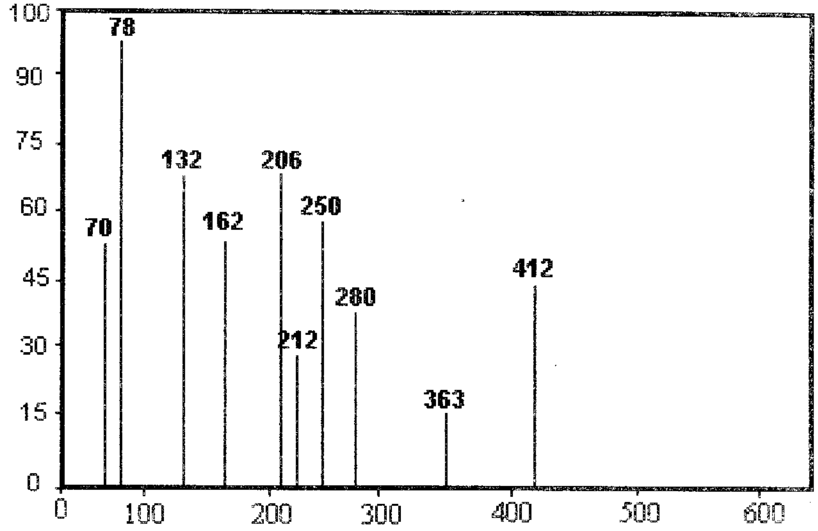


Figure 2. Electron impact mass spectrum of the ligand (L).

Complexes

On the basis of the elemental analyses, the complexes were assigned the compositions shown in Table 1. The molar conductance measurements of the complexes in DMSO correspond to the non-electrolytic nature for the Mn(II), Co(II), and Cu(II) complexes and a 1 : 2 electrolyte for the Ni(II) complex. Thus, these complexes may be formulated as $[M(L)X_2]$ and $[Ni(L)]X_2$ [where M = Mn(II), Co(II), and Cu(II) and $X = Cl^-$ and NO_3^-]. On complexation, the IR bands corresponding to ν(NH), amide-I, and amide-II are shifted to lower frequency when compared with the macrocyclic ligand. This indicates that the coordination of the ligand has taken place through the nitrogen of –NH group $[N_4]$.

IR Bands Due to Anions

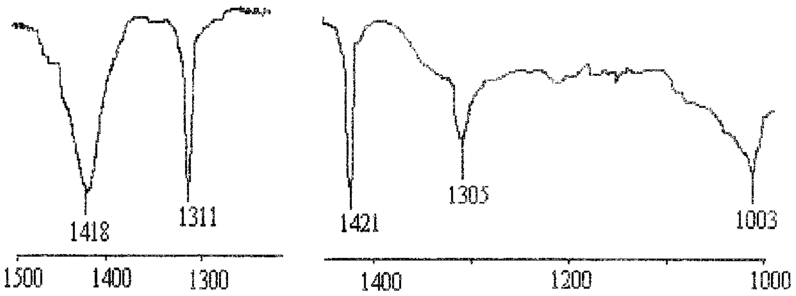
The IR spectra (Fig. 3) of nitrato complexes display three (N–O) stretching bands [Fig. 3(a), (b), and (d)] at ~1418–1427 cm^{-1} (ν_5), 1303–1311 cm^{-1} (ν_1), and 1003–1012 cm^{-1} (ν_2). The position of bands in the IR spectra of the complexes indicates that both nitrate groups are coordinated to the central metal ion in an unidentate manner.[13]

Table 1. Molar conductance and elemental analysis data of the complexes.

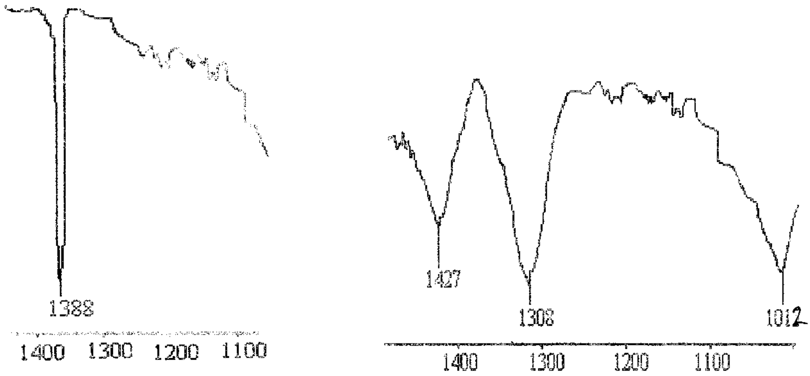
Complex	Atomic mass (amu)	Molar conductance[a] (Ω^{-1} cm^2 mol^{-1})	Color	M.p.[b] (°C)	Yield (%)	Elemental analysis data (%) found (calcd)			
						Metal	C	H	N
Ligand (L)	412	—	White	281	87	—	58.38	4.87	13.64
$C_{20}H_{20}N_4O_2S_2$							(58.25)	(4.86)	(13.59)
[Mn(L)Cl_2]	538	13.23	Gray	293	73	10.17	44.59	3.71	10.39
$C_{20}H_{20}MnN_4O_2S_2Cl_2$						(10.22)	(44.61)	(3.72)	(10.41)
[Mn(L)$(NO_3)_2$]	591	11.78	Pinkish white	289	76	9.37	40.63	3.39	14.25
$C_{20}H_{20}MnN_6O_8S_2$						(9.31)	(40.61)	(3.38)	(14.21)
[Co(L)Cl_2]	542	12.56	Black	<300	87	10.83	44.26	3.75	10.31
$C_{20}H_{20}CoN_4O_2S_2Cl_2$						(10.89)	(44.28)	(3.69)	(10.33)
[Co(L)$(NO_3)_2$]	595	14.19	Dark green	<300	84	9.88	40.31	3.33	14.07
$C_{20}H_{20}CoN_6O_8S_2$						(9.92)	(40.34)	(3.36)	(14.11)
[Ni(L)]Cl_2	542	233	Purple red	293	81	10.80	44.35	3.77	10.29
$C_{20}H_{20}N_4NiO_2S_2Cl_2$						(10.89)	(44.28)	(3.69)	(10.33)
[Ni(L)]$(NO_3)_2$	595	236	Shiny orange	297	80	9.85	40.33	3.35	14.15
$C_{20}H_{20}N_6NiO_8S_2$						(9.92)	(40.34)	(3.36)	(14.12)
[Cu(L)Cl_2]	547	10.36	Light yellow	298	79	11.67	43.89	3.67	10.21
$C_{20}H_{20}CuN_4O_2S_2Cl_2$						(11.70)	(43.88)	(3.66)	(10.24)
[Cu(L)$(NO_3)_2$]	600	11.83	Black	>300	82	10.56	40.06	3.38	14.02
$C_{20}H_{20}CuN_6O_8S_2$						(10.67)	(40.00)	(3.33)	(14.00)

[a] Error limit ±2%.

[b] Decomposition temperature.



(a) $[Mn(L)(NO_3)_2]$ (b) $[Co(L)(NO_3)_2]$



(c) $[Ni(L)](NO_3)_2$ (d) $[Cu(L)(NO_3)_2]$

Figure 3. IR Spectral bands of the anions.

However, the IR spectrum of the Ni(II) nitrate complex displays a sharp and strong band [Fig. 3(c)] at 1388 cm^{-1}, which suggests that the nitrate groups are uncoordinated.[13]

Manganese(II) Complexes

The manganese(II) complexes show a magnetic moment at room temperature in the range of 5.83–5.97 BM corresponding to five unpaired electrons. The electronic spectra of the Mn(II) complexes exhibit four weak-intensity absorption bands in the ranges 18,519–18,911 ($\varepsilon = 41–55$ L mol^{-1} cm^{-1}), 22,553–23,105 ($\varepsilon = 41–43$ L mol^{-1} cm^{-1}), 29,349–29,733 ($\varepsilon = 69–74$ L mol^{1-} cm^{-1}), and 37,583–38,129 cm^{-1}

($\varepsilon = 127-131\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), Table 2. These bands may be assigned to the transitions: ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$, ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^4A_{1g}({}^4G)$ $(10B + 5C)$, ${}^6A_{1g} \rightarrow {}^4E_g({}^4D)$ $(17B + 5C)$, and ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4P)$ $(7B + 7C)$, respectively.[14,15]

The values of the Racah parameters B and C were calculated from the second and third transitions because these transitions are free of crystal-field splitting and depend only on the B and C parameters.[8] The calculated values of the ligand field parameters are given in Table 5.

EPR spectra were recorded at room temperature for a polycrystalline sample and in a solution of DMSO. The polycrystalline spectra were isotropic and exhibit the 'g' value in the range 2.0054–2.0099 (Table 3). In DMSO solution, the Mn(II) complexes give EPR spectra (Table 4) containing the six lines arising due to the hyperfine interaction between the unpaired electron with the ^{55}Mn nucleus ($1 = 5/2$). The nuclear magnetic quantum number M_1, corresponding to these lines, are $-5/2$, $-3/2$, $-1/2$, $+1/2$, $+3/2$, and $+5/2$ from low to high field.

Cobalt(II) Complexes

At room temperature, the magnetic moment measurements of cobalt(II) complexes lie in the range 4.89–4.97 BM[16] corresponding to three unpaired electrons, Table 2.

The electronic spectra of all the cobalt(II) complexes exhibit absorptions in the regions 10,173–11,198 ($\varepsilon = 72-79\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), 14,620–14,793 ($\varepsilon = 81-84\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), 18,657–18,692 ($\varepsilon = 90-92\,\mathrm{L\,mol^{-1}\,cm^{-1}}$),

Table 2. Magnetic moment and electronic spectral data of the complexes.

Complex	μ_{eff} (BM)	$\lambda_{\max}$ (cm^{-1}) ε (L mol^{-1} cm^{-1})[a]
$[\mathrm{Mn(L)Cl_2}]$	5.83	18,519 (49), 22,553 (55), 29,349 (74), 37,593 (131)
$[\mathrm{Mn(L)(NO_3)_2}]$	5.97	18,911 (47), 23,105 (51), 29,733 (69), 38,129 (127)
$[\mathrm{Co(L)Cl_2}]$	4.89	10,173 (79), 14,620 (81), 18,692 (90), 26,596 (147)
$[\mathrm{Co(L)(NO_3)_2}]$	4.97	11,198 (72), 14,793 (84), 18,657 (92), 32,680 (139)
$[\mathrm{Ni(L)]Cl_2}$	Diamagnetic	16,178 (61), 22,090 (93), 29,543 (137)
$[\mathrm{Ni(L)](NO_3)_2}$	Diamagnetic	16,548 (57), 21,307 (95), 29,825 (132)
$[\mathrm{Cu(L)Cl_2}]$	1.93	10,905 (61), 11,249 (63), 16,447 (159)
$[\mathrm{Cu(L)(NO_3)_2}]$	2.04	10,183 (57), 11,223 (61), 16,260 (153)

[a] ε Values in parentheses.

Table 3. EPR spectral data of the complexes (as polycrystalline sample).

Complexes	Temperature	$g_{\parallel}$	$g_{\perp}$	g_{iso}	G
$[Mn(L)Cl_2]$	RT	—	—	2.0054	—
$[Mn(L)(NO_3)_2]$	RT	—	—	2.0099	—
$[Co(L)Cl_2]$	LNT	2.3268	2.0098	2.1155	—
$[Co(L)(NO_3)_2]$	LNT	2.3387	2.0174	2.1245	—
$[Cu(L)Cl_2]$	RT	2.0853	2.0597	2.0682	1.4288
$[Cu(L)(NO_3)_2]$	RT	2.1182	2.0669	2.0840	1.7668

Note: RT, room temperature and LNT, liquid nitrogen temperature.

and 26,596–32,680 cm^{-1}($\varepsilon = 139-147\,\mathrm{L\,mol^{-1}\,cm^{-1}}$). These bands may be assigned to the transitions: $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ (ν_1), $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2), and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ (ν_3), respectively. The fourth band may be due to charge transfer. The position of these bands indicates that these complexes have a distorted octahedral geometry,[17,18] Fig. 4, and might possess D_{4h} symmetry. The d^7 system has the ground state term ^4F in an octahedral crystal-field and is split into three states. Since these states are connected by spin–orbit coupling, the spin–lattice relaxation times are short, making EPR measurements possible only at very low temperature. That is why EPR spectra of the cobalt(II) complexes were recorded as polycrystalline samples and in DMSO solutions at liquid nitrogen temperature. The 'g' values were found to be almost the same in the polycrystalline form as well as in solution (Table 3).

Nickel(II) Complexes

At room temperature, these complexes show diamagnetic behavior, indicating a square-planar environment around the Ni(II) ion, Fig. 4.

Table 4. EPR spectral data of the complexes (in DMSO solution).

Complexes	Temperature	$g_{\parallel}$	$g_{\perp}$	g_{iso}	G
$[Mn(L)Cl_2]$	RT	—	—	2.0017	—
$[Mn(L)(NO_3)_2]$	RT	—	—	2.0020	—
$[Co(L)Cl_2]$	LNT	2.3256	2.0179	2.1205	—
$[Co(L)(NO_3)_2]$	LNT	2.3298	2.0053	2.1135	—
$[Cu(L)Cl_2]$	RT	2.1329	2.0701	2.0910	1.8959
$[Cu(L)(NO_3)_2]$	LNT	2.0831	2.0690	2.0737	1.2043

Note: RT, room temperature and LNT, liquid nitrogen temperature.

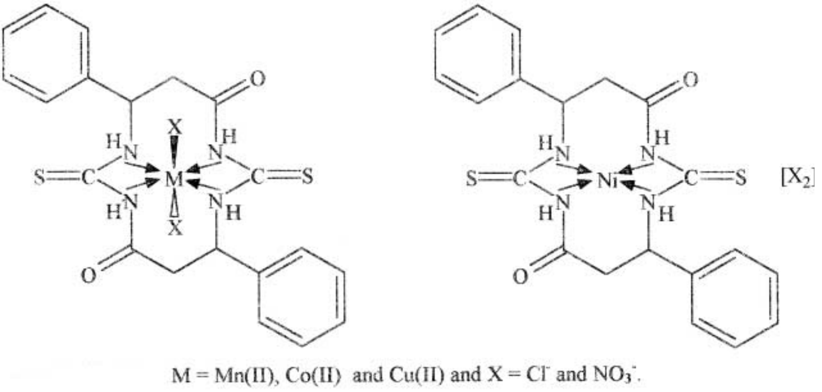


Figure 4. Suggested structures of the complexes.

The electronic spectra of the Ni(II) complexes exhibit three absorption bands in the ranges 16,178–16,548 ($\varepsilon = 57–61\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), 21,307–22,090 ($\varepsilon = 93–95\,\mathrm{L\,mol^{-1}\,cm^{-1}}$), and 29,543–29,825 $\mathrm{cm^{-1}}$ ($\varepsilon = 132–137\,\mathrm{L\,mol^{-1}\,cm^{-1}}$). An examination of these bands indicates that the complexes have square-planar geometry. For diamagnetic square-planar Ni(II) complexes; the five degenerate d-orbitals are split as follows- $d_{x^2-y^2}(b_{1g})$, $d_{xy}(b_{2g})$, $d_{z^2}(A_{1g})$, d_{xz}, d_{yz} (e_g). The electronic ground state in a spin triplet state is $^3A_{2g}$ and in an excited state $^1A_{1g}$. The relative stabilities of the $^1A_{1g}$ and $^3A_{2g}$ states are determined by the energy separation Δ_1, of the d_{xy} and $d_{x^2-y^2}$ orbitals. Thus, these bands may be assigned to the three spin-allowed transitions: $^1A_{1g}(D) \rightarrow {}^1A_{2g}(G)$ (ν_1), $^1A_{1g}(D) \rightarrow {}^1B_{2g}(G)$ (ν_2), and $^1A_{1g}(D) \rightarrow {}^1E_g(G)$ (ν_3), respectively.

Copper(II) Complexes

The magnetic moment measurements of the Cu(II) complexes at room temperature lie in the range 1.97–2.09 BM corresponding to one unpaired electron.[19,20]

Electronic spectra of copper(II) complexes display bands in the ranges 10,183–10,905 ($\varepsilon = 57–61\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) ($\nu_1$), 11,223–11,249 ($\varepsilon = 61–63\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) ($\nu_2$) and 16,260–16,447 $\mathrm{cm^{-1}}$ ($\varepsilon = 153–159\,\mathrm{L\,mol^{-1}\,cm^{-1}}$) ($\nu_3$), corresponding to the following transitions[18]: $^2B_{1g} \rightarrow {}^2A_{1g}$ ($d_{x^2-y^2} \rightarrow d_{z^2}$) ν_1, $^2B_{1g} \rightarrow {}^2B_{2g}$ ($d_{x^2-y^2} \rightarrow d_{zy}$) ν_2, and $^2B_{1g} \rightarrow {}^2E_g$ ($d_{x^2-y^2} \rightarrow d_{zy}$, d_{yz}) ν_3, respectively.

Room temperature EPR spectra of Cu(II) complexes were recorded as a polycrystalline sample and in DMSO solution, on X-band at a frequency of 9.5 GHz and magnetic field strength of 3400 ± 2000 G. Polycrystalline spectra exhibit a single broad signal resulting from the interaction of the unpaired electron. No band corresponding to $\Delta M_s = \pm 2$ transitions was observed in the spectrum to suggest Cu–Cu interaction.[21,22] The absence of this transition can be explained by proposing that interaction between two paramagnetic centers is negligible. The analysis of the spectra gives $g_{\parallel} = 2.0831–2.1329$ and $g_{\perp} = 2.0597–2.0701$. The observed $g_{\parallel}$ values for the complexes are less than 2.3 in agreement with the covalent character of the metal–ligand bond. The trend $g_{\parallel} > g_{\perp} > 2.0023$ observed for the complexes indicates that the unpaired electron is localized in a $d_{x^2-y^2}$ orbital of the Cu(II) ion and the spectra are characteristic of axial symmetry. Tetragonally elongated structures are thus confirmed for the Cu(II) complexes.

Electrochemical Behavior

The cyclic voltammogram of the copper(II) complexes in DMSO were recorded at room temperature using a glassy carbon as working electrode and TBAP as supporting electrolyte. Both complexes of Cu(II) show a quasi-reversible peak.

The chloro complex of copper gives a peak at 0.72 V, which corresponds to copper(II) → copper(III), and a cathodic peak at $E_{pc} = 0.39$ V, which corresponds to Cu(III) → Cu(II). While the nitrato complex gives peaks at $E_{pc} = 0.69$ and 0.42 V.

The complexes exhibit two irreversible peaks characteristic for copper(II) → copper(I), [$CuLCl_2$] ($E_{pc} = -0.69$ V) and [$CuL(NO_3)_2$] ($E_{pc} = -0.56$ V) and copper(I) → copper(0) for [$CuLCl_2$] ($E_{pc} = -0.95$ V) and for [$CuL(NO_3)_2$] ($E_{pc} = -0.91$ V). These peaks suggest single-electron reduction processes. On the anodic side, two peaks are also observed, which correspond to oxidation of Cu(0) → Cu(II). This quasi-reversible behavior of the Cu(II)/Cu(III) couple was observed by varying the scan rates with peak potentials.

The $E_{1/2}$ values are independent of the scan rate. It has been observed that ΔE_p increases with the increasing scan rate. I_{pc}/I_{pa} being equal to unity indicates the chemical reversibility of the redox process. The reversibility of the reduction behavior on the ΔE_p value may arise due to the stereochemical changes in the complexes. The Cu(II) to Cu(I) redox processes are influenced by the coordination number, stereochemistry, and the hard/soft character of the ligand donor atoms.

Table 5. Ligand field parameters of the complexes.

Complex	*Dq* (cm^{-1})	*B* (cm^{-1})	*C* (cm^{-1})	β	LFSE ($kJ\,mol^{-1}$)
$[Mn(L)Cl_2]$	1851.90	613.71	3060.44	0.78	00
$[Mn(L)(NO_3)_2]$	1891.10	518.29	3581.01	0.66	00
$[Co(L)Cl_2]$	1271.62	644.55	—	0.58	121.54
$[Co(L)(NO_3)_2]$	1399.75	574.06	—	0.52	133.79
$[Ni(L)]Cl_2$	1617.80	735.36	—	0.71	231.94
$[Ni(L)](NO_3)_2$	1654.80	752.18	—	0.72	237.25

On comparing the cyclic voltammograms, we observe that the variation in the oxidation and reduction potentials may be due to distortion in the geometry that arises due to different coordinated anions.

Ligand Field Parameters

Various ligand field parameters were calculated for the complexes and are listed in Table 5. The values of *Dq* for the Co(II) complexes were calculated from the transition energy ratio diagram using the ν_3/ν_2 ratios.[18] Our results of ligand field parameters are in agreement with the results reported earlier.[14,15,23] The Nephelauxetic parameter β was readily obtained by using the relation: $\beta = B$ (Complex)$/B$ (Free ion) where B (Free ion) for Mn(II) is 786 cm^{-1}, for Ni(II) is 1041 cm^{-1}, and for Co(II) is 1120 cm^{-1}. The values of β lie in the range of 0.52–0.78. These values indicate appreciable covalent character of the metal–ligand 'σ' bonds.

ACKNOWLEDGMENT

We are thankful to the Principal, Zakir Hussain College, for providing research facilities, the Regional sophisticated Instrumentation Center, Indian Institute of Technology, Mumbai, for recording EPR spectra and the University Grant Commission, New Delhi, for financial assistance.

REFERENCES

1. Laulloo, S.J.; Witvrouw, M. Synthesis and anti-HIV activity of novel macrocyclic benzamides with a disulphide bridge. Ind. J. Chem. **2000**, *39B*, 842–846.

2. Zhang, H.C.; Huang, W.S.; Pu, L. Biaryl-based macrocyclic and polymeric chiral (salophen) Ni(II) complexes: synthesis and spectroscopic study. J. Org. Chem. **2001**, *66*, 481–487.
3. Chandra, S.; Sharma, S.D. Template synthesis of copper(II) complexes of two twelve-membered tetradentate nitrogen donor macrocyclic ligands. J. Ind. Chem. Soc. **2002**, *79*, 495–497.
4. Fryzuk, M.D.; Johnson, S.A.; Rettig, S.J. New mode of coordination for the dinitrogen ligand: a dinuclear tantalum complex with a bridging N_2 unit that is both side-on and end-on. J. Am. Chem. Soc. **1998**, *120*, 11024.
5. Chandra, S.; Gupta, L. Synthesis, ESR and electronic spectral studies on cobalt(II) complexes of semicarbazone and thiosemicarbazones. Synth. React. Inorg. Met. Org. Chem. **1995**, *25* (4), 537–550.
6. Luo, Y.; Zhang, J.; Lu, L.; Qian, M.; Wang, X.; Yang, X. Synthesis and crystal structure of a new dinuclear manganese(II) complex of a macrocyclic ligand with multi-ligating pendant arms. Transition Met. Chem. **2002**, *27*, 469–472.
7. Chandra, S.; Gupta, K. Chromium(III), manganese(II), iron(III), cobalt(II), nickel(II) and copper(II) complexes with a pentadentate, 15-membered new macrocyclic ligand. Transit. Met. Chem. **2002**, *27*, 196–199.
8. Chandra, S.; Gupta, K. Twelve-, fourteen- and sixteen-membered macrocyclic ligand and a study of the effect of ring size on ligand field strength. Transit. Met. Chem. **2002**, *27*, 329–332.
9. Vogel, A.I. *A Textbook of Quantitative Inorganic Analyses*, 4th Ed.; ELBS and Longman, 1978.
10. Köksal, H.; Dolaz, M.; Tümer, M.; Serin, S. Copper(II), cobalt(III), nickel(II), palladium(II) and zinc(II) complexes of the Schiff base ligands derived from 2,6-diacetylpyridine and phthaldialdehyde. Synth. React. Inorg. Met. Org. Chem. **2001**, *31* (7), 1141–1162.
11. Kalsi, P.S. *Spectroscopy of Organic Compounds*, 4th Ed.; New Age International (P) Ltd.: New Delhi, 1999.
12. Shakir, M.; Nasman, O.S.M.; Mohamed, A.K.; Varkey, S.P. Synthesis and characterization of cobalt(II) nickel(II) copper(II) and zinc(II) complexes of N_5, 7,18-membered pentaazamacrocycles with N5 donor sets. Ind. J. Chem. **1996**, *35A*, 710–713.
13. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley Interscience: New York, 1970.
14. Chandra, S.; Sharma, S.D. Chromium(III), manganese(II), cobalt(II), nickel(II), copper(II) and palladium(II) complexes of a 12-membered tetraaza $[N_4]$ macrocyclic ligand. Transition Met. Chem. **2002**, *27*, 732–735.

15. Chandra, S.; Gupta, K.; Sharma, S. Synthesis and spectral studies of transition metal complexes with 5,7,12,14-tetramethyl-1,4,8,11-tetraazacyclotetradeca-4,7,11,14-tetraene, a fourteen-membered tetradentate macrocyclic ligand. Synth. React. Inorg. Met. Org. Chem. **2001**, *31* (7), 1205–1215.
16. Carlin, R.L. ed.; *Transition Metal Chemistry*; Marcel Dekker Inc.: New York, 1965; Vol. I.
17. Chandra, S.; Sangeetika; Tyagi, V.P.; Raizada, S. Synthesis, EPR, electronic and magnetic studies on cobalt(II) complexes of a semicarbazone and thiosemicarbazones. Synth. React. Inorg. Met. Org. Chem. **2003**, *33* (1), 147–164.
18. Lever, A.B.P. *Crystal Field Spectra, Inorganic Electronic Spectroscopy*, 1st Ed.; Elsevier: Amsterdam, 1968; 249–360.
19. Lever, A.B.P. *Inorganic Electronic Spectroscopy*; Elsevier: Amsterdam, 1984.
20. Serin, S. New vic-dioxime transition metal complexes. Transit. Met. Chem. **2001**, *26*, 300–306.
21. Hankare, P.P.; Chavan, S.S. Synthesis and characterization of manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes with 2-[2′-hydroxy-salicylidene 5′-(4″-phenyl, 2″thiazolylazo)] benzoic acid and 2-[2′-hydroxysalicylidene-5′-(4″-phenyl-2″-thiazolylazo)]phenol. Ind. J. Chem. **2003**, *42(A)*, 540–544.
22. Kasprzyk, S.P.; Kolinski, R.A. Direct synthesis, spectral and magnetic properties of trans aniono (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane-7-acetato) copper(II) complexes. Polyhedron **1988**, *7* (12), 1053.
23. Athar, F.; Arjmand, F.; Tabassum, S. New symmetric N_2S_2 macrocycles, their metal chelates and the photokinetics of DNA-complex interaction. Transit. Met. Chem. **2001**, *26*, 426–429.

Received November 14, 2003
Accepted May 6, 2004