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Synthesis and Spectral Characterization of Mn(II) and Co(II) Complexes with Tetradentate Macrocyclic Ligand

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Manganese(II) and cobalt(II) complexes were synthesized with [N_4] tetradentate macrocyclic ligand using different metal salts *i.e.* $MnCl_2$, $Mn(NO_3)_2$, $CoCl_2$ and $Co(NCS)_2$. The ligand was prepared by condensation of glyoxal and carbahydrazide. All these were characterized by elemental analysis, molar conductance measurements, magnetic moment, IR, mass, electronic and EPR spectral studies. Elemental analysis indicates that the complexes have composition MLX_2 where ($X = Cl^-$, NO_3^-, NCS^-). All the complexes were found to be non-electrolytic in nature so can be formulated as [MLX_2]. Infrared spectra of metal complexes suggest that the ligand behaves as tetradentate. On the basis of magnetic moment, electronic and EPR spectral data, all the metal complexes were found to be high spin with octahedral geometry.

Keywords: Macrocyclic ligand, Tetradentate, Glyoxal, Carbahydrazide, Manganese complex, Cobalt complex.

INTRODUCTION

The synthetic macrocyclic metal complexes have gained much significance and attracted interests of synthetic chemists owing to their unusual stability and similarity with naturally occurring macrocycles [1]. The stability of these metal complexes helped scientists to explore many aspects of their reactivity and unusual properties making them learn about the usages and properties of natural and biological macrocycles [2,3]. Therefore, a number of ligand systems have been recognized and used to mimic the naturally occurring carriers in identifying and carrying specific metal ions to understand and reproduce the catalytic activity of metallo-proteins and metalloenzymes [4]. Scientists have made efforts to prepare and characterize metal complexes using macrocyclic ligands [5,6] and as a result variety of these systems starting from simple cyclic compounds to sophisticated systems *viz.* mono, di, tri and macrocycles and calixarines have been prepared and successfully characterized [7]. This led to the development of the novel synthetic routes to prepare large ring compounds. Although there is not much difference between coordination behaviour of macrometallic complexes and open chain polydentate ligands but the kinetic and thermodynamic stability along with some other unusual pro-perties of macro complexes put them into a special class and encourage chemists to understand the reason behind these properties. Macrocyclic ligands belong to polydentate system in which at least three donor atoms are part of a cyclic hydrocarbon skeleton usually comprising of at least nine atoms. The metal ion fits well inside the macrocyclic cavity getting stabilized by making coordination bonds with a few or all of the donor atoms [8]. They provide high stability to complex formation but also a chance to tune the coordination sites through functionalization and modification. They are capable of extending their structure for effective attachment of pendant atoms giving considerable significance to the resulting metal complexes [9-14].

Existence of two or more pendant arms, at appropriate sites on a macrocyclic framework creates a pseudo-enclosed environment appropriate for the genesis of supramolecular, molecular receptor species [15,16]. Macrocyclic chelators, due to their extraordinary binding capacity to metal ions, are emerging as potential chelating agents in various fields such as coordination chemistry, as an anticorrosive and even in biochemical sciences [17-20]. They play significant role in developing an understanding towards the processes such as biochemical, catalytic, hydrometallurgical, extraction of metal, activation, encapsulation and transportation [21-23]. They are found in many anticancer [24-28], antibacterial [26] and antimicrobial [28] activities.

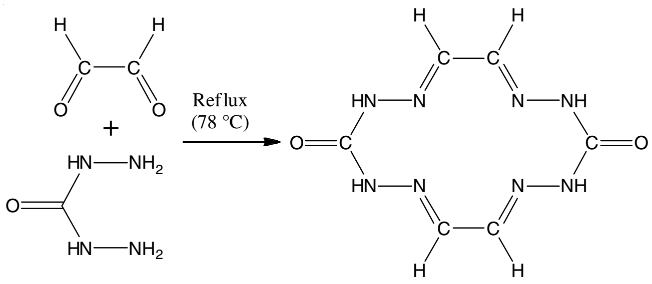
The present work reports the synthesis and characterization of Mn(II) and Co(II) complexes of $[N_4]$ macrocyclic ligand synthesized from glyoxal and carbahydrazide.

EXPERIMENTAL

All the reagents were bought from the chemical traders and used as provided. All Metal salts were purchased from Merck and used without any purification. Solvents used were of the spectroscopic grade.

The elemental analysis of the synthesized ligand and its metal complexes were done on Carlo-Erba EA 1106 elemental analyzer. IR spectra were recorded in the region 4000-400 cm^{-1} on FT-IR SPECTRUM-2000 using KBr pellets. Mass spectra were recorded on Agilant Technologies 6530 Accurate-Mass Q-TOF LC/MS. Molar conductance of the metal complexes were measured in dimethyl sulfoxide at room temperature on ELICO (CM82T) Conductivity Bridge. The magnetic susceptibility of the metal complexes was recorded on a Gouy balance using $CuSO_4{\cdot}5H_2O$ as standard. EPR spectra were recorded as a polycrystalline sample at room temperature on E4-EPR spectrometer using the DPPH as the g-marker.

Synthesis of $[N_4]$ macrocyclic ligand $[L_1]$: The macrocyclic ligand L_1 was synthesized by dissolving glyoxal (0.02 mol) in hot ethanol which was mixed to the solution of carbahydrazide in ethanol (**Scheme-I**). Few drops of conc. HCl were added and the solution was refluxed for 8 h at 78 °C. The contents were cooled, a white solid separated out. The precipitate was filtered, washed with ethanol and dried under vacuum over P_4O_{10}. Table-1 shows the analytical data of L_1.



Scheme-I: Synthesis of $[N_4]$ macrocyclic ligand $[L_1]$

Synthesis of metal complexes of L_1: Ligand L_1 (0.01 mol) was dissolved in minimum quantity of alcohol and with continuous stirring 0.01 mol of corresponding metal salt [$MnCl_2$, $Mn(NO_3)_2$, $CoCl_2$, $Co(NCS)_2$] was added to it. On continuous refluxing the contents for 12-14 h and after cooling, the coloured complexes precipitated out. The complex was filtered, washed and dried oved P_4O_{10}.

RESULTS AND DISCUSSION

Synthesized metal complexes are stable at room temperature and are of type $[MLX_2]$ where ($X = Cl^-$, NO_3^-, NCS^{-1}). The range of molar conductance calculated in DMF indicates the non-electrolytic behaviour of complexes. Table-1 illustrates the physical and analytical data of synthesized complexes.

Mass spectrum: The peak at 221 amu in mass spectrum of L_1 confirms the proposed formula $C_6H_8N_8O_2$ and suggest that a 2+2 cyclization of glyoxal and carbahydrazide. The mass spectrum of L_1 also shows peaks of relative intensities at 172, 138, 112, 84, 54, 43 and 13 amu, respectively. The intensities of different peaks are relative to the stability of the various fragments. Fig. 1 below represents the mass spectrum of macrocyclic ligand L_1.

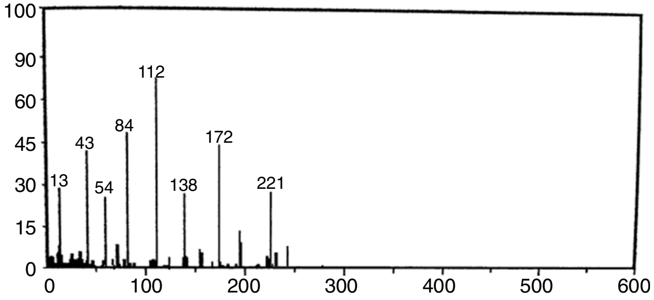


Fig. 1. Mass spectrum of ligand L_1

IR spectra: IR spectrum of L_1 does not exhibit any band around 3400 cm^{-1} suggesting the absence of free primary amine. These bands are not found in the IR spectra of L_1 because of the complete condensation of amino and aldehyde group. Sharp band at 3280 cm^{-1} is due to N-H of the secondary amine group. The structure of the L_1 is well supported by the appearance of characteristic bands due to different functional groups.

In metal complexes, the metal ion binds to azomethine nitrogen and this is supported by shifting of band by 25-30 cm^{-1} after complexation. In the Mn(II) nitrato complex, the band coordination signify that both the nitrate group coordinate to manganese ion in unidentate fashion as the separation between the two high frequency band is of the order 117 cm^{-1}. The 3*d* metals generally form M-N bond in thiocyanato type complexes. The thiocyanato complex of cobalt shows a sharp

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF L_1 AND ITS METAL COMPLEXES [M = Mn(II) AND Co(II)]

Complex	m.f.	m.w. (amu)	Yield (%)	Colour	m.p. (°C)	Elemental analysis (%): Found (calcd.)			
						C	H	N	M
L_1	$C_6H_8N_8O_2$	224	77	White	260	32.12 (32.15)	3.55 (3.60)	49.96 (49.98)	–
$[MnL_1Cl_2]$	$C_6H_8Cl_2MnN_8O_2$	350	60	Light yellow	278	20.55 (20.59)	2.28 (2.30)	31.98 (32.01)	15.66 (15.70)
$[MnL_1(NO_3)_2]$	$C_6H_8MnN_{10}O_8$	403	58	Light yellow	286	17.86 (17.88)	1.97 (2.00)	34.72 (34.75)	13.58 (13.63)
$[CoL_1Cl_2]$	$C_6H_8Cl_2CoN_8O_2$	354	56	Brown	288	20.31 (20.36)	2.23 (2.28)	31.61 (31.65)	16.60 (16.65)
$[CoL_1(NCS)_2]$	$C_8H_8CoN_{10}O_2S_2$	399	65	Dark brown	280	40.27 (24.06)	3.59 (2.02)	8.81 (35.08)	12.35 (14.76)

band at 2076 cm^{-1} which confirms the bonding through N in thiocyanato complex. It also shows that both thiocyanate groups lie in same chemical environment. The IR peaks of other functional groups lie in their expected region and are listed in Table-2. The IR spectra of chloride complex of manganese and thiocyanato complex of cobalt are shown in Figs. 2 and 3.

TABLE-2
IR PEAKS OF L_1 AND METAL COMPLEXES

Compound	ν(NH)	ν(C=N)	ν(C=O)
L_1	3280	1635	1662
[MnL$_1$Cl$_2$]	–	1591	1666
[MnL$_1$(NO$_3$)$_2$]	–	1599	1664
[CoL$_1$Cl$_2$]	–	1620	1650
[CoL$_1$(NCS)$_2$]	–	1610	1658

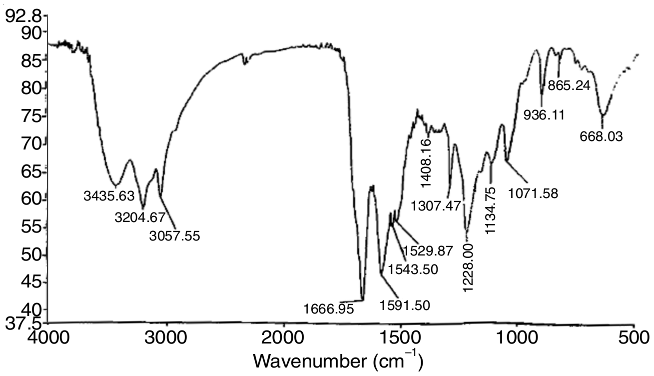


Fig. 2. IR spectrum of [MnL$_1$Cl$_2$]

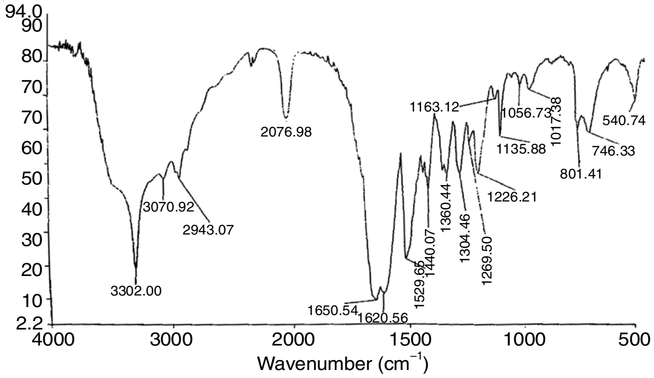


Fig. 3. IR spectrum of [CoL$_1$(NCS)$_2$]

Electronic spectra of metal complexes and ligand field parameter: The electronic spectra of Mn(II) (Fig. 4) complexes revealed a high spin octahedral geometry [29] with $^6A_{1g}$ as ground state. The spectra shows band at 18098-18418 cm^{-1} may be assigned as $^6A_{1g} \rightarrow {}^4T_{1g}(^4G)$, 22254-23215 cm^{-1} band as ^{6}A1g → ^{6}E $^4A_{1g}(^4G)$, around 27000 cm^{-1} band as $^6A_{1g} \rightarrow {}^4E_g(^4D)$ and 30945-30997 cm^{-1} band as 6A$_{1g}$ → $^4T_{1g}(^4P)$ transitions. The observed transitions are used to calculate the values of B, C D$_q$ and β [30,31].

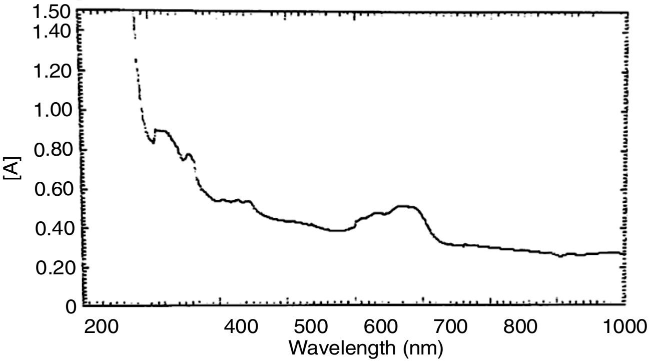


Fig. 4. Electronic spectrum of [MnL$_1$(NO$_3$)$_2$]

Transition due to Co(II) complexes are observed near 9671-9756 cm^{-1} maybe assigned as $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, while for $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, the band appear in the range of 22931-24635 cm^{-1} (Fig. 5). The observed transitions are used to calculate the values of B, C Dq and b.

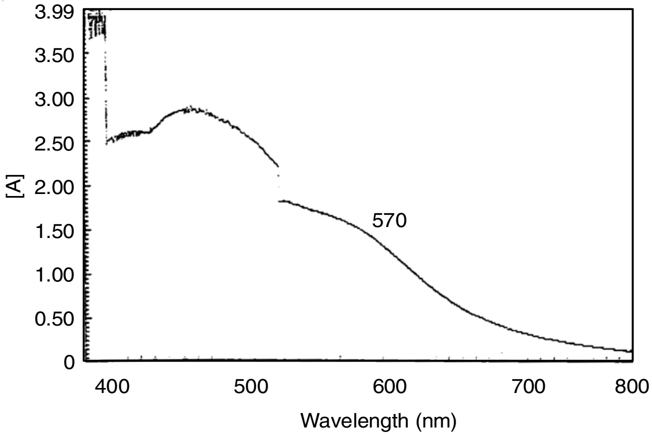


Fig. 5. Electronic spectra of [CoL$_1$(NCS)$_2$]

Electronic spectra data and ligand field parameters for synthesized complexes are listed in Tables 3 and 4.

Electron paramagnetic resonance spectra of Mn(II) and Co(II) complexes: The electron paramagnetic resonance

TABLE-3
ELECTRONIC SPECTRAL DATA OF
Mn(II) AND Co(II) COMPLEXES of L_1

Complex	μ_{eff} (B.M)	λ_{max} (cm^{-1})
[MnL$_1$Cl$_2$]	5.92	18098, 22254, 27021, 30997
[MnL$_1$(NO$_3$)$_2$]	5.95	18418, 23215, 26998, 30945
[CoL$_1$Cl$_2$]	4.92	9756, 24635
[CoL$_1$(NCS)$_2$]	4.96	9671, 22931

TABLE-4
LIGAND FIELD PARAMETERS OF Mn(II) AND Co(II) COMPLEXES OF L_1

Complexes	Dq (cm^{-1})	B (cm^{-1})	β	C (cm^{-1})	F_4	F_2	h_x	ν_2/ν_1	LFSE (KJ/mol)
[MnL$_1$Cl$_2$]	1840	685	0.85	3080	85	1120	2.00	1.14	–
[MnL$_1$(NO$_3$)$_2$]	1810	684	0.83	3070	87	1120	1.85	1.28	–
[CoL$_1$Cl$_2$]	1565	680	0.60	–	–	–	–	–	149
[CoL$_1$(NCS)$_2$]	1690	845	0.75	–	–	–	–	–	160

spectra of Mn(II) complexes have been recorded in DMSO and the electron paramagnetic resonance spectra of Co(II) complexes at low temperatures as polycrystalline sample under the magnetic field strength of 3000G on X band at the frequency of 9.1 GHz (Table-5). The EPR spectra of the chloride complex of manganese and thiocyanato complex of cobalt is shown in Figs. 6 and 7.

TABLE-5
EPR SPECTRAL VALUES OF Mn(II) AND Co(II) COMPLEXES

Complex	$g_{\|}$	$g_{\perp}$	g_{iso}	Å
$[MnL_1Cl_2]$	–	–	1.996	116
$[MnL_1(NO_3)_2]$	–	–	1.988	112
$[CoL_1Cl_2]$	2.58	2.01	2.200	–
$[CoL_1(NCS)_2]$	2.69	2.03	2.250	–

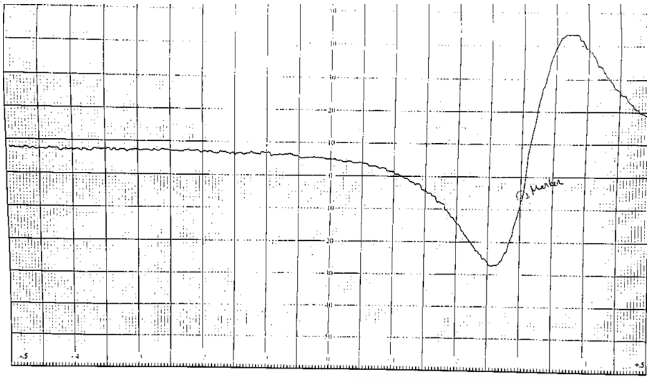


Fig. 6. EPR spectrum of $[MnL_1Cl_2]$

Fig. 7. EPR spectrum of $[CoL_1(NCS)_2]$

Based on the results obtained from various analytical and spectroscopic techniques the proposed structures of metal complexes are shown in Fig. 8.

Conclusion

The novel synthesized ligand L_1 coordinates to metal center through four azomethine nitrogen and the two positions are occupied by anions. The synthesized complexes are non-electrolytic and are of type $[MLX_2]$, where M = Mn(II) or Co(II). All the metal complexes are thermally stable at room temperature. The geometry and the stoichiometry of the complexes are well established by various analytical and spectroscopic techniques. Both metals (manganese and cobalt) bind to ligand in an octahedral fashion. The proposed structures are well supported by spectroscopic data.

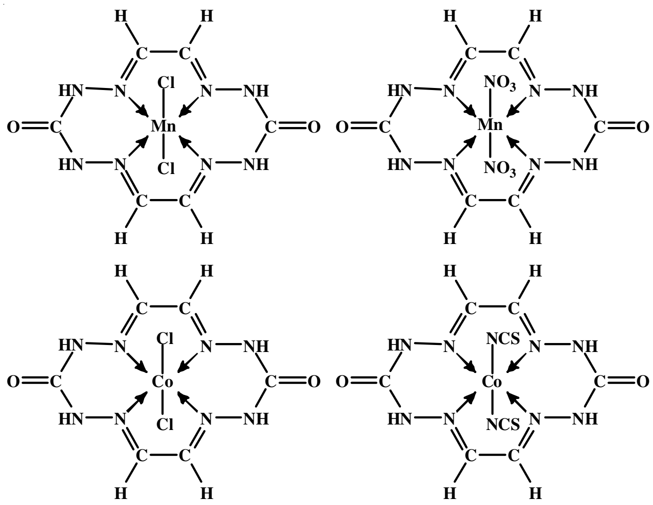


Fig. 8. Proposed structures of metal(II) complexes

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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