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Synthesis and Spectroscopic Study of Mn(II), Co(II), Cu(II) Complexes with 18-Membered Macrocyclic Ligand

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Abstract

Mn(II), Co(II), Cu(II) complexes containing a tetradentate macrocyclic nitrogen ligand *i.e.* 2,7,9,14-Tetraphenyl-1,3,6,810,13-hexaazacyclooctadecane (L) have been synthesized. The complexes have been characterized by the elemental analysis, molar conductance measurement, magnetic susceptibility measurements, IR, electronic and EPR spectral studies. The molar conductance of the complexes in DMSO correspond to non-electrolytic nature for Mn(II), Co(II), Cu(II). Thus, these complexes may be formulated $[M(L)X_2]$ (where M = Mn(II), Co(II), Cu(II) and X=Cl^-, NO_3^-, OAc^-, NCS^-). On the basic of IR, electronic and EPR spectral studies an octahedral geometry has been assigned for Mn(II) and Co(II) complexes and distorted octahedral geometry for Cu(II) complexes. In vitro the complexes were against two pathogenic fungi (i.e. Alternaria alternata and Aspergillus niger) to access growth inhibitor potential.

Key words: Macrocyclic, Coordination Chemistry, IR, UV, EPR

Introduction

Transition metal macrocyclic complexes have received much attention as an active part of metalloenzymes[1] as bio mimic model compounds due to the irresemblance with natural proteins like hemerythrin and enzymes. The tetraaza macrocyclic ligand and their metal complexes have attracted growing interest among the coordination and bioinorganic chemistry[2]. Also, macrocyclic Schiff base ligands have received special attention because of their mixed soft hard donor character versatile coordination behaviour[3-6] and their pharmacological properties i.e. antifungal, antibacterial, anticancerous & antitumor[7-14]. Structural factors, such as ligand rigidity, the type of donor atoms and their disposition have shown to play significant roles to determine the binding features of macrocyclic toward metal ion[15,16]. The importance of macrocylic complexes in coordination chemistry is because of various applications in biological processes such as photosynthesis and dioxygen transport[17-20]. The chemistry of macrocyclic complexes is also important due to its use as dyes and pigments as well as Nuclear Magnetic Resonance (NMR) shift reagents. In view of the above application we report in the present paper the synthesis, characterization and biological application of Mn(II), Co(II), Cu(II) complexes of macrocyclic ligand derived from glutaric anhydride and diethylene tetraamine (Figure 1).

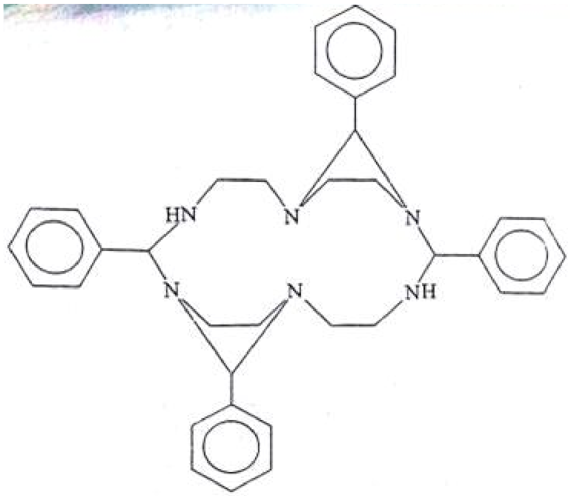

Figure 1. Structure of ligand

Materials :

All the chemicals used were of Anala R grade and purchased from Sigma-Aldrich and Fluka. Metal salts were purchased from E. Merck and were used as received. All solvents used were of standard / spectroscopic grade.

Synthesis of complexes :

The complexes were prepared by template method. Hot ethanolic solution of diethylenetriamine [20 mL] and benzaldehyde (20 mL) was taken in round bottom flask. To this solution an ethanolic solution of the corresponding metal salt (.001 mol) was added. The resulting reaction mixture solution was boiled under refluxed for six hour at 75-80°C. Then the solution was concentrated up to half of its volume under reduced pressure. On cooling the coloured solution complex was precipitated out. The complex was filtered and washed with cold ethanol and dried over P_4O_{10} under vacuum.

Physical measurements :

C, H, and N were analyzed on a Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on the ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using $CuSO_4.5H_2O$ as a calibrant. Electron-impact mass spectra were recorded on JEOL, JMS, DX-303 mass spectrometer. IR spectra (KBr) were recorded on Fourier transform infrared spectroscopy (FTIR) spectrum BX II spectrophotometer. The electronic spectra were recorded in Dimethyl sulfoxide (DMSO) on a Shimadzu UV mini-1240 spectrophotometer. Electron paramagnetic resonance (EPR) spectra of the complexes were recorded as polycrystalline sample and in the Dimethylformamide (DMF) solution, at liquid nitrogen temperature for Co(II) and at room temperature for Mn(II) and Cu(II) complexes on EPR spectrometer using the DPPH as the g marker.

Results and Discussion

On the basis of elemental analysis, the complexes were found to have the composition as shown in Table-1.

The Mn(II), Co(II)and Cu(II) complexes are non-electrolytes with conductance values of 10-19 Ω^{-1} cm^2mol^{-1}. The molar conductance measurement of the complexes in DMSO is corresponding to be non-electrolytic nature for Mn(II), Co(II) and Cu(II). Thus, these complexes may be formulated as $[M(L)X_2]$ (where M=Mn(II), Co(II), and Cu(II) and X = $C1^-$ and NO_3^-). The Important IR bands of the complexes are listed in Table-2. The IR spectrum of the complexes does not exhibit any band corresponding to primary diamine or free keto group[21]. This suggests the complete condensation of the amino group with the keto group[22,23]. The spectrum shows a very strong band at 1600 cm^{-1} which is attributed to the (C=N) stretching vibration. On complexation, the position of

Table-1. Elemental analysis data and molar conductance of complexes

Complexes	Colour	Molar Conductance (Ω^1 cm^2 mol^{-1})	% Yield	Elemental Analysis Data Calculated (Found) %				M. Pt (^{0}C)
				C	H	N	M	
[Mn(L)Cl$_2$]	Light Pink	12.72	77	61.53	8.53	11.96	7.83	288
				(61.05)	(8.52)	(11.95)	(7.81)	
[Mn(L)(NCS)$_2$]	Light Pink	18.63	64	63.59	8.04	15.12	7.36	260
				(63.57)	(8.02)	(15.11)	(7.36)	
[Mn(L)(CH$_3$COO)$_2$]	Light Brown	17.52	69	64.09	8.83	11.22	7.35	276
				(64.08)	(8.81)	(11.21)	(7.36)	
[Co(L)Cl$_2$]	Light Brown	13	64	61.29	8.53	11.93	8.25	280
				(61.27)	(8.51)	(11.91)	(8.22)	
[Co(L)(NO$_3$)$_2$]	Light Brown	13.5	66	58.46	7.93	14.79	7.66	265
				(58.45)	(7.91)	(14.77)	(7.65)	
[Co(L)(CH$_3$COO)$_2$]	Brown	14.4	56	63.85	8.78	11.92	8.38	272
				(63.82)	(8.77)	(11.89)	(8.35)	
[Cu(L)Cl$_2$]	Blue (shiny)	10.5	69	60.95	8.49	11.94	8.92	278
				(60.84)	(8.45)	(11.83)	(8.87)	
[Cu(L)(NO$_3$)$_2$]	Green	10.6	66	56.69	7.94	14.72	8.36	284
				(56.61)	(7.86)	(14.67)	(8.25)	
[Cu(L)(CH$_3$COO)$_2$]	Brown	11.4	65	63.48	8.79	11.18	8.38	269
				(63.40)	(8.71)	(11.09)	(8.32)	

(C=N) band is shifted towards the lower side. This indicates that the nitrogen atoms of the complexes groups are coordinated to the metal ions[24]. The bands at 425-452 and 295-320 cm^{-1} can be assigned to ν(M-N) and ν(MCl), respectively. IR spectra of the complexes and band [ν(N-H)] indicates that amides II and III suggest the coordination takes place through nitrogen of NH group (N$_4$). IR spectra of nitrato complexes display three (N-O) stretching bands at 1410-1426 cm^{-1} ((ν_5), 1303-1315 cm^{-1} (ν_1) and 1003-1017 cm^{-1} (ν_2). The separation of two highest frequency bands (ν_5– ν_1) is 106-113 cm^{-1}. This suggests that both the nitrate groups are coordinated to the central metal ion[25] as a unidentate manner.

Table 2. Infrared absorption frequencies (cm^{-1}) of metal complexes

Complexes	γ (C=N)	γ (M-N)	γ (M-X)	γ (C-H)
[Mn(L)Cl$_2$]	1636	470	359	2929
[Mn(L)(NCS)$_2$]	1636	455	-	2900
[Mn(L)(CH$_3$COO)$_2$]	1637	440	-	2958
[Co(L)Cl$_2$]	1657	435	322	2940
[Co(L)(CH$_3$COO)$_2$]	1627	460	712,625	2929
[Cu(L)Cl$_2$]	1686	440	-	3009
[Cu(L)(NO$_3$)$_2$]	1613	420	1213,1071,842	2923

Table 3. Magnetic moments and electronic spectral data of the complexes

Complexes	λ_{max}(cm^{-1})	μ_{eff} (at room temperature)
$[Mn(L)Cl_2]$	10845-37313	6.01
$[Mn(L)(NCS)_2]$	37453-38314	6.00
$[Mn(L)(CH_3COO)_2]$	24449-32679	5.99
$[Co(L)Cl_2]$	14556-21141	4.72
$[Co(L)(CH_3COO)_2]$	9487-24752	5.11
$[Cu(L)Cl_2]$	17921-22321	1.89
$[Cu(L)(NO_3)_2]$	17821-21321	2.03
$[Cu(L)(CH_3COO)_2]$	16835-24271	1.90

Magnetic Moments and Electronic Spectra

Manganese(II) complex

These complexes show magnetic moment in the range of 5.99-6.01 B.M in Table-3 at room temperature corresponding to five unpaired electrons. The electronic spectrum of the Mn(II) complexes display weak absorption bands at 10845 cm^{-1}, 24449 cm^{-1} and 32679-37453 cm^{-1}. These bands can be assigned to the transitions: $^6A_{1g}\rightarrow{}^4T_{1g}$ (^{4}G), $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}{}^4$ (^{4}G) (10B + 5C), $^6A_{1g}\rightarrow{}^4E_g$ (^{4}D) (17B +5C), and $^6A_{1g}\rightarrow{}^4T_{1g}{}^4$ (^{4}P) (7B + 7C), respectively[26]. The complex may possess an octahedral geometry.

Cobalt (II) complexes :

At room temperature, the magnetic moment of cobalt (II) complexes lay in the range 1.89-2.03 B.M. corresponding to three unpaired electrons as shown in Table-3. The electronic spectra of all the cobalt (II) complexes exhibit absorption in the region 9487-10193, 14556-15723, 21141-24752 cm^{-1}. These bands may be assigned to the transitions: $^4T_{1g}$ (F) – $^4T_{1g}$(F) (v_1), $^4T_{1g}$–$^4A_{2g}$ (v_2) and $^4T_{1g}$(F) – $^4T_{1g}$ (P) (v_3), respectively. The position of bands indicates that these complexes have octahedral geometry around the Co (II) ion[27-30].

Copper (II) complexes :

Magnetic moment of the Cu (II) complexes at room temperature lie in the range 1.90-2.02 B.M. corresponding to one unpaired electron. Electronic spectra of copper (II) complexes show three bands as shown in Table-3, corresponding to the transitions $^2B_{1g}$ – $^1A_{1g}$ ($d_x{}^2$- y^2 – dz^2) v_1, $^2B_{1g}$ – $^2B_{2g}$ (dx^2- y^2– dzy) v_2 and $^2B_{1g}$ – ^2E_g (dx^2- y^2 – dzy, dyz) v_3, respectively[31-33]

EPR :

The EPR spectra of the Mn(II) complexes were recorded as polycrystalline sample and in DMSO solution. The polycrystalline sample give one broad isotropic signal centred at approximately the free electron g-value (g_0 = 2.0023). The broadening of the spectra probably is due to spin relaxation[34]. In DMSO solution the complexes give an EPR spectra containing six lines arising due to hyperfine interaction between the unpaired electrons with ^{55}Mn nucleus (l =5/2). The nuclear magnetic quantum number, M_1 corresponding to the lines are -5/2, -3/2, -1/2, +3/2, +5/2 from low to high field. The EPR spectra of the cobalt (II) complexes were recorded as polycrystalline sample and in the DMSO solution at liquid nitrogen temperature (LNT). The g- values as shown in Table-4 were found to be almost same in both the cases in polycrystalline sample, as well as in the solution. The large deviation in the g values from the free electron value (*g* = 2.0023) is due to large angular momentum contribution.

Table 4. EPR spectral data of the complexes

Complexes	Temperature	g value
$[Mn(L)Cl_2]$	RT	1.93
$[Mn(L)(NCS)_2]$	RT	1.96
$[Mn(L)(CH_3COO)_2]$	RT	1.82
$[Co(L)Cl_2]$	LNT	g_{II}=1.921, g□=1.501
$[Cu(L)(CH_3COO)_2]$	RT	2.251,2.015

Room temperature EPR spectra of Cu(II) complexes were recorded as polycrystalline sample and in DMSO solution of the X-band at frequency 9.5 GHz under the magnetic field strength 3400 G. Polycrystalline spectra exhibit a single broad signal. The analysis of spectra gives the values for g_{11}= 2.251 and $g_{\perp}$ = 2.015. The observed g_{11} values for the complexes are less than 2.3 in agreement with the covalent character of the metal ligand bond. The trend $g_{11} > g_{\perp} > 2.0023$ observed for the complexes indicate that the unpaired electron is localized in $dx^2–y^2$ orbital of the Cu(II) ion and spectral feature are characteristic of axial symmetry. Distorted octahedral structures are confirmed for the Cu (II) complexes.

Antifungal Screening :

In vitro antifungal activities of the complexes were tested using food poison technique[35,36]. *Alternaria alternata* and *Aspergillus niger* were used as test fungi. Test compounds were mixed with Potato Dextrose Agar (PDA) medium and the solution in distilled water were prepared of 500, 250 and 125 ppm concentrations. These were autoclaved at 1000C and then cooled adequately. The medium was dispensed into sterilized petriplates. When the medium in the petriplates was solidified, a mycelia disc of 0.5 cm in diameter cut from the periphery of the 7 days old culture and it was aseptically inoculated upside down in the centre of the petriplates. These treated petriplates were incubated at 26±1°C until fungal growth in the control petriplates was almost complete. Radial growth of colonies was measured at two points along the diameter of the plate and average of these two readings was taken as the diameter of the fungal colony. The % inhibition was measured according to the formula:

$$(C - T) \times 100 / C,$$

Where C and T are the radial diameter of the colony in control and treatment, respectively. The results have shown that complexes used for the experiment exhibited noble activities than the ligand towards the inhibition of test fungi under the test conditions. MIC (Minimum Inhibitory Concentration) of test compounds against both the fungus was 500 ppm and has shown 100% inhibition as shown in Table-5. The complexes of Cu(II) and show nearly the same inhibition but Co(II) complexes show poor inhibition (almost equal to ligand) against both fungal species under study. The compounds have shown fungal inhibition in the following order: Glutaric anhydride < Di ethylene triamine < Mn < Co < Cu.

Table 5. Fungicidal screening data of the complexes

Complexes	*Alternaria alternate*			*Aspergillus niger*		
	500	250	125	500	250	125
Glutaric anhydride	100	58	34	100	50	37
Diethylene triamine	100	52	36	100	47	40
[Mn(L)Cl_2]	100	74	52	100	69	51
[Co(L)Cl_2]	100	79	64	100	83	68
[Cu(L)Cl_2]	100	80	60	100	84	62

Conclusion

Complexes of Mn(II), Co(II), Cu(II) with tetra dentate macrocyclic ligand have been prepared & characterized. On the basis of above spectral studies six coordinated octahedral geometry for Co (II) and Mn(II) and distorted octahedral for Cu(II) complexes. The fungicidal data revels that the complexes are superior to the free ligand. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition, as the concentration increases, the activity increases.

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