Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2013, 5(5):99-104

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

EPR, IR, Mass and electronic spectroscopic studies on newly synthesized 23,24-dioxo-1,6,9,12,17,20-hexaazacyclotracosa-1,5,12,16-tetraene macrocyclic ligand (L) and its transition metal complexes

Sulekh Chandra[a*] and Poonam Pipil[b]

[a]*Department of Chemistry, Zakir Husain Delhi College, University of Delhi, J.L. Nehru Marg, New Delhi, India*
[b]*Department of Chemistry Rajdhani College, University of Delhi, Raja Garden, Ring Road, New Delhi, India*

ABSTRACT

Complexes of manganese (II), cobalt(II), nickel(II) and copper(II) complexes have been synthesized with a new tetradentate ligand viz, 23, 24dioxo1,6,9,12,17,20 hexaazacyclotracosa1,5,12,16tetraene (L) and characterized by the elemental analysis, molar conductance measurement, magnetic susceptibility measurements, Mass, IR, electronic and EPR spectral studies. The molar conductance measurements of the complexes in DMF correspond to be non electrolytic nature for Mn(II), Co(II) and Cu(II) while 1:2 electrolytes for Ni(II) complexes. 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 the basic of IR, electronic and EPR spectral studies an octahedral geometry has been assigned for Mn(II) and Co(II) complexes, square planar geometry for Ni(II) and tetragonal geometry for Cu(II) complexes. In vitro the ligand and its complexes were against two pathogenic fungi (i.e. alternaria alternata and aspergillus niger) to assess their growth inhibiting potential.*

Keywords: Mass, IR, magnetic moment, electronic, EPR and Biological activity

---

INTRODUCTION

Macrocyclic schiff base ligands have received special attention because of their mixed soft hard donor character vessatile coordination behavior **[1-3]** and their pharmacological properties i.e. antifungal, antibacterial, anticancerous & antitumur **[4-10]** Macrocyclic ligands and their metal complexes have attrated much interest among the coordination and bioinorganic chemistry **[11]** the formation of macrocyclic complexes mainly depends on the size of the internal cavity and the rigidity of the macrocycle formed **[12]**. The importance of macrocylic complepes in coordination chemistry is because of various applications in biological processes such as photosynthesis and dioxygen transportant **[13-14]** the chemistry of macrocyclic complexes is also important due to its use as dyes and pigments as well as NMR shift reagents. In the light of above applications in the present paper we report the synthesis and characterization of Macrocyclic ligand 23,24,dioxo1,6,9,12,1720. hexaazacyclotrocosa1,512,16 tetraene **[Fig-1]** with transition metals such as Mn(II) Co(II), Ni(II) and Cu(II)

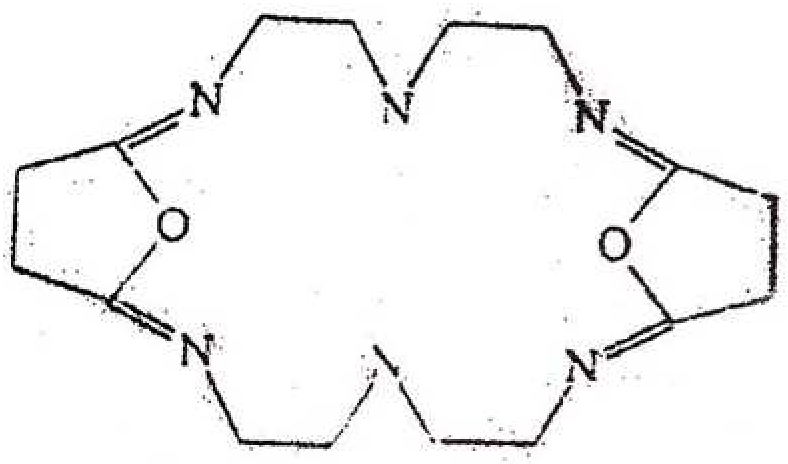


Fig. I Structure of Ligand

EXPERIMENTAL SECTION

Materials

All the chemicals used were of AnalaR grade, and were purchased from Aldrich. Metal salts were purchased from E.Merck and were used as received. All solvents used were of standard/spectroscopic grade.

Synthesis of complexes

All the complexes were prepared by template method. An ethanolic solution of diethylenetriamine [10 mL] and glutaric anhydride (10 mL) was taken in round bottom flask. To this solution an ethanolic solution of the corresponding metal salt (.001 mol) was added. The resulting solution was boiled under refluxed for six hour. Then the solution was concentrated upto half of its volume under reduced pressure. On cooling the solution coloured complex was precipitated out. It was filtered washed with cold ethanol and dried over P_4O_{10} under vacuum.

Physical Measurements

The 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 were recorded on a Perkin-Elmer 137 instrument in KBr pellets EPR spectra of the complexes were recorded as polycrystalline sample and in the DMF solution, at liquid nitrogen temperature for Co(II) and at room temperature for Mn(II) and Cu(II) complexes on E_4-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**.

Table -1: Molar Conductance and elemental analysis data of Complexes

Complex	Colour	Molar Conductance (Ω^1 cm^1 mol-^{1})	% Yield	Elemental Analysis Data Calculated (Found) %				M. Pt (^{0}C)
				C	H	N	Metal	
$[Mn(L)Cl_2]$	Cream	02	66	45.0 (45.0)	4.00 (3.92)	11.00 (10.05)	10.90 (10.85)	280
$[Mn(L)(NO_3)_2]$	Cream	01	61	40.0 (40.8)	3.45 (3.58)	14.95 (15.00)	9.95 (9.83)	289
$[Co(L)Cl_2]$	Pink	10	67	44.7 (44.6)	3.93 (3.90)	11.05 (10.96)	11.65 (11.55)	292
$[Co(L)(NO_3)_2]$	Pink	08	60	10.0 (9.7)	3.45 (3.50)	15.00 (14.95)	10.34 (10.45)	>300
$[Ni(L)Cl_2]$	Red	158	62	11.1 (47.02)	3.80 (3.91)	10.85 (10.92)	10.49 (10.55)	>300
$[Ni(L)(NO_3)_2]$	Orange red	146	65	42.53 (42.60)	3.62 (3.53)	14.82 (14.90)	10.55 (10.48)	>300
$[Cu(L)Cl_2]$	Green	06	59	46.68 (46.60)	3.92 (3.85)	11.02 (10.85)	12.50 (12.46)	288
$[Cu(L)(NO_3)_2]$	Shiny Blue	09	63	42.15 (42.20)	3.62 (3.55)	14.90 (14.75)	11.13 (11.25)	292

The molar conductance measurement of the complexes in DMF is corresponding to be nonelectrolytic nature for Mn(II), Co(II) and Cu(II) while 1:2 electrolytes for Ni(II) complexes. 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=$C1^-$ and NO_3^-). IR spectra of the complexes and band [v(N-H)] indicates that amides II and III suggest the coordination takes place through nitrogen of NH group (N_4).

IR bands due to anions

IR spectra of nitrato complexes display three (N-O) stretching bands at 1410-1426 cm^{-1} ((v_5), 1303-1315 cm^{-1} (v_1) and 1003-1017 cm^{-1} (v_2). The separation of two highest frequency bands (v_5 - v_I) is 106-113 cm^{-1}. This suggests that both the nitrate groups are coordinated to the central metal ion **[15]** as an unidentate manner.

However, nitrate complex of Ni(II) displays a sharp and strong band at 1393 cm^{-1} which suggests that the nitrate group is uncoordinated.

Manganese (II) complexes

At room temperature complexes of manganese(II) show magnetic moment in the range 5.80-5.94 B.M corresponding to five unpaired electrons. Electronic spectra of Mn(II) complexes, exhibit four weak intensity absorption bands in the range 18507-18915, 22552-23102, 29342-19729 and 37575-38120 cm^{-1} **(Table 2).**

Table – 2: Magnetic moments and electronic spectral data of the complexes

Complex	λ Max (cm^{-1})	μEff (B.M.)
$[Mn(L)Cl_2)$	18506, 22552, 29342, 37575	5.80
$[Mn(L)(NO_3)_2$	18915, 23102, 29729, 32120	5.94
$[Co(L)Cl_2]$	10170, 14625, 18690, 26593	4.83
$[Co(L)(No_3)_2]$	11195, 14798, 18656, 32678	4.90
$[Ni(L)Cl_2)$	16176, 22085, 29540,	Diamagnetic
$[Ni(L)(No_3)_2)$	16546, 21305, 29820,	Diamagnetic
$[Cu(L)Cl_2]$	10903, 11247, 16443, 27930	1.90
$[Cu(L)(No_3)_2]$	11182, 11220, 16259,	2.02

These bands may be assigned to the transitions: $^4A_{1g}$ – $^4T_{1g}$ (^{4}G), $^6A_{1g}$ – ^4E_g $^4A_{1g}$(^{4}G) (10B+5C), $^6A_{1g}$ – ^4E_g (^{4}D) (17B + 5C) and $^6A_{1g}$ – $^4T_{1g}$ (7B+7C), respectively.

EPR spectra were recorded at room temperature as polycrystalline sample and in solution of DMF. The polycrystalline spectra were isotropic and exhibit the ‘g’ value in the range 2.0050-2.0094 **(Table 3).**

Table – III: EPR spectral data of the complexes

Complex	Date as polycrystalline sample					Date in DMF solution			
	Temperature	g_{11}	G_1	g_{iso}	G	g_{11}	g_1	g_{iso}	G
$[Mn(L)Cl_2]$	RT	--	--	2.0052	--	--	--	2.0015	--
$[Mn(L)(NO_3)_2]$	RT	--	--	2.0094	--	--	--	2.0018	--
$[Co(L)Cl_2]$	LNT	2.3265	2.0096	2.1153	--	2.3255	2.0175	2.1206	--
$[Co(L)(NO_3)_2]$	LNT	2.3385	2.0170	2.1243	--	2.3296	2.0050	2.1130	--
[Cu(L)Cl2]	RT	2.0830	2.0596	2.0680	1.4285	2.1325	2.0700	2.0908	1.8955
$[Cu(L)(NO_3)_2]$	RT	2.1180	20.665	2.0838	1.7665	2.0830	2.0686	2.0735	1.2040

In DMF solution, Mn(II) complexes give EPR spectra containing the six lines arising due to the hyperfine interaction between the unpaired electron with the ^{55}Mn nuclear (l=5/2). The nuclear magnetic quantum number M_1, corresponding to these lines are -5/2, -3/2 – ½, ½, +3/2 and 5/2 from low to the high field.

The parameters Band C were calculated from the second and third transitions because these transitions are free the crystal field splitting and depend on Band C parameters **[16,17].** The calculated values of the ligand field parameters are given in **(Table 4).**

Table – IV: Ligand Field Parameters of the complexes

Complex	Dq (cm^{-1})	B (cm^{-1})	C (cm^{-1})	β	LFSE (kJ mol^{-1})
$[Mn(L)Cl_2)$	1851.85	613.70	3060.40	0.75	
$[Mn(L)(NO_3)_2$	1891.08	518.25	3581.00	0.61	
$[Co(L)Cl_2]$	1271.55	644.53		0.53	121.50
$[Co(L)(No_3)_2]$	1399.70	574.01		0.50	133.75
$[Ni(L)Cl_2)$	1617.75	735.32		0.66	231.90
$[Ni(L)(No_3)_2]$	1654.74	752.16		0.80	237.23

Cobalt(II) complexes

At room temperature the magnetic of cobalt(II) complexes lie in the range 4.83-4.90 B.M. corresponding to three unpaired electrons **(Table 2).**

The electronic spectra of all the cobalt(II) complexes exhibit absorption in the region 10170-11195, 14625-14798, 18656-18690 and 26593-32678 cm^{-1}. These band 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, and the fourth band may be due to charge transfer. The position of bands indicates that these complexes have distorted octahedral geometry **[18-19]**.

EPR spectra of cobalt(II) complexes were recorded as polycrystalline sample and in DMF solution at LNT. 'g' Values are found to be almost same in both cases in polycrystalline sample as well as in the solution **(Table 3).**

Nickel(II) complexes

At room temperature these complexes show the diamagnetic behavior. Indicating the square planar environment around the Ni(II) ion.

The electronic spectra of the Ni(II) complexes, exhibit three absorption bands in the range 16176-16546, 21305-22085 and 29540 -29820 cm^{-1}. An examination of these bands indicates that the complexes have square planar geometry.**[20]** These bands may be assigned to the three spin allowed transitions:

$^1A_{1g}$ (D)- $^1A_{2g}$ (G) (v_1), $^1A_{1g}$ (D)- $^1B_{2g}$ (G) (v_2) and $^1A_{1g}$ (D)- $^1E_{1g}$ (G) (v_3), respectively.

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 **(Table 2),** corresponding to the transitions $^2B_{1g}$ – $^1A_{1g}$ ($d_{x^2-y^2} – d_{z^2}$) v_1, $^2B_{1g}$ – $^2B_{2g}$ ($d_{x^2-y^2} – d_{zy}$) v_2 and $^2B_{1g}$ – ^2E_g ($d_{x^2-y^2} – d_{zy,}\, d_{yz}$) v_3, respectively **[21, 22**]

Room temperature EPR spectra of Cu(II) complexes were recorded as polycrystalline sample and in DMF 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} = 2.0830 – 2.1326 and $g_\perp$ = 2.05962.0700. 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 $d_{x^2-y^2}$ orbital of the Cu(II) ion and spectral feature are characteristic of axial symmetry. Tetragonaly elongated structure are confirmed for the Cu(II) complexes.

Ligand field parameters

Various ligand field parameters were calculated for the complexes and are listed in **(Table 4).** The value of Dq in Co(II) complexes were calculated from transition energy ratio diagram using the v_3/v_2 ratio **[16].** Our results are in agreement with the complexes reported earlier **[17]**. The Nephelauxetic parameter β was readily obtained by using the relation : β = B (complex)/B(Free ion)

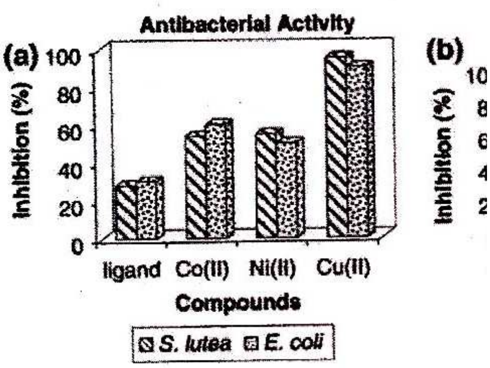
Where B (free ion) for Mn(II) is 786 cm^{-1}, for Ni(II) is 1041 cm^{-1} and for Co(II) is 1120 cm^{-1} **[16,17]**. The values of β lie in the range of 0.53-0.80. These values indicate the appreciable covalent character of metal ligand 'σ' bond.

Biological study

The ligand (L), ligand free metal ions and its complexes were evaluated against different species of bacteria and fungi as per the procedure reported earlier **[23-26]**. In both, antibacterial and antifungal studies ligand free metal ions in solution show inhibition capacity slighty more than the ligand but much less than complexes against all the species under study.

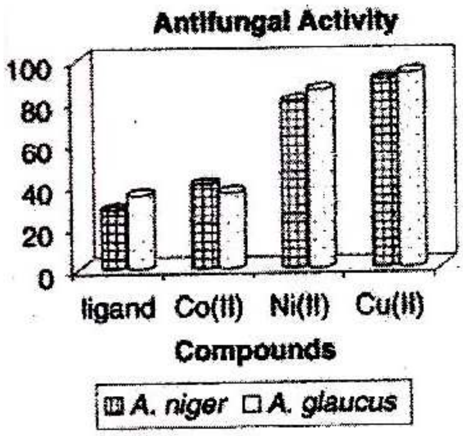
Antibacterial screening

The compounds were screened against Sarcinalutea (gram-positive) and Escherchiacoli (gram-negative) bacteria, as growth inhibior by disc diffusion technique **[23-24].** The results of the antibacterial screening show the maximum inhibition by the Cu(II) complexes while Co(II) and Cu(II) complexes show approximately equal activity to the metal free ligand, presented in **Graph 1(a)**



Antifungal screening

Aspergillus-niger and Aspergillus-glaucus fungi were used as the test organism for all the newly synthesized compounds for the purpose of antifungal screening by agar plate technique **[25-26]**. The results are shown in **Graph 1(b).** The complexes of Cu(II) and Ni(II) show nearly the same inhibition but Co(II) complexes show poor inhibition (almost equal to ligand) against both fungal species under study.



CONCLUSION

Complexes of Mn(II), Co(II), Cu(II) & Ni(II) with tetra dentate macrocyclic ligand have been prepared & charaterzied. On the basis of above spectral studies six cordinated octahedral geometry for Co(II) and Mn(II) and squre planar geometry for Ni(II) and tetragonal geometry for Cu(II) complexes. Various ligand field and bonding parametres have been calculated and discussed. The gungicidal data revels that the complexes are superior than the free ligand. It has also been proposed that concentration plays a vital role in increasing the degree of inhibition, as the consentration increases, the activity increases

Acknowledgement

Authors are thankful to UGC New Delhi for financial assistance and I.I.T. Bombay for recording EPR spectra.

REFERENCES

[1] P. Comba, M. Kersches, Y.D. Lampeka, L.L. Lotzbeyer, M. Prizkow, L.V. Tsymbal. *Inor. Chem.* **2003**, 42, 3387.
[2] G. Pushibhai. S. Vasudhevan, S. Kulti Rani, G. Rajago, *Spectsochim. Acta A,* **2009**,72, 687.
[3] P. Sengupta, R. Dinda, S. Ghosh, W.S. Sheldrick, *Polyhedron*, **2003**, 22, 477.
[4] S. Chandra, Sangetika, *Spectrochim, Acta A*, **2004**, 60, 147.
[5] S. Chandra K. Gupta, *Trans Met. Chem.* **2002**, 27, 196.
[6] S. Chandra, L.K. Gupta, *Spectrochim Acta* A **2005**, 61, 2169.
[7] U. Hiiseyin, H.Zelira, *Spectrochim Acta* A, **2010**, 75, 782.
[8] S. Chandra, Ruchi, *Spectrochim Acta A, molecular and biomolecular spectro scopy* **2013**, 103, 338-348.
[9] S. Chandra, A. Kumar, *Spectrochim Acta* A, *molecular and biomolecular spectro scopy* **2013**, 102, 250-253.

[10] S. Chandra, S. Barguljar, R. Nirwal etal, Spectrochim Acta A, *molecular and biomolecular spectro scopy* **2013**, 106, 91-98.
[11] E, Tos. A. Kilic,. M. Durgun, L.Kupeeik, I. Yilmaz, S.Asslam, *Spectrochim Acta* A **2010**, 75, 811.
[12] N. Raman. *Journal of Indian Chem. Soci*. **2009**, 86, 1143-1149.
[13] D.P. Singh, R. Kumar, J. Singh, *Euro. J. of Medicinal chemistry* **2008**, 3, 7.
[14] D.P. Singh, R. Kumar, V Malik, K. Kumar, *Rasayan J. of Chemistry* **2008** 1(2) 349 – 354.
[15] S. Chandra. L.K. Gupta, *Spectrochim; Acta*, **2004**, 60A, 1563; M. Shakir S.P. Varkey. P.S. Hameed, *Polyhedron*, **1993**, 12, 2775; S. Chandra. S.D. Sharma, *Trans. Met Chem*., **2002**, 27, 732; S. Chandra L.K. Gupta. *Spectrochim; Acta*, **2004**, 60A, 2004, 3079; S. Chandra L.K. Gupta, Spectrochim Acta **2005**, 62A, 1125 1130.
[16] S. Chandra, K. Gupta, *Trans. Met. Chem* **2002**, 27, 329.
[17] S. Chandra, Sangeetika, *Ind. J. Chem*. **2002**, 41A, 1629. E.Q. Gao, H.Y. Sun, D.Z. Liao, Z.H. Jiang, S.P. Yan, Polyhedron **2002**, 21, 359.
[18] S. Chandra, R. Kumar, *Spectochim Acta A.* **2005**, 61 (3, 14) 437-446.
[19] S. Chandra, Sangeetika, *Ind. J. of Chem*. **2002**, 41A, 1629-16933.
[20] (a) M. Shakir, A.K. Mohamad OSM, Nasma, *Polyhedron* **1996**,15 3490-3497.
(b) S Chandra, L.K. Gupta, *Spectrochim Acta* A **2004**, 60 2411 – 2417.
(c) S. Chandra, R. Gupta, *Trans. Met. Chem*. **2002,** 27, 329-332.
(d) V.V. Pavlishchak, S.P. Kulotilov, A.W. Addison, R.J. Butcher, E. Sinn., *J. of Chem. Soc. Dalton Trans* **2007**, 335-341.
[21] S. Chandra, A.K. Jhaima, *Spectrochim Acta A* **2009,** 72 (4) 851-857.
[22] G.G. Mohammed, M.M. Omar, A.M. Hindy, *Spectrochim Acta A* **2005**, 62, 1140-1150.
[23] S. Chandra, and L.K. Gupta *Spectrochim Acta A* **2004**, 60, 1563.
[24] S. Chandra, and L.K. Gupta & Sangeetika, *Synth React. Inorg. met org. chem*. **2004**, 34, 1591.
[25] A. Bansal and R.V Singh, *Ind. J. Chem*. **2001**, 40 A, 989.
[26] W.G. Hanna & M.M. Mohamad *Trans Met Chem*. **2001**, 26, 644.