

Synthesis and spectral studies of nitrogen-oxygen donor macrocyclic metal complexes of Mn^{II}, Cu^{II}, Zn^{II}, Pd^{II} and Pt^{II}

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Abstract : The complexes of Mn^{II}, Cu^{II}, Zn^{II}, Pd^{II} and Pt^{II} with a nitrogen-oxygen donor macrocyclic ligand, viz. 5,6,13,14-dibenzo[1,4,8,11]dioxadiaza-5,7,11,13-cyclotetradecin have been synthesized and characterized by elemental analysis, molar conductance, magnetic susceptibility measurements, spectral and electrochemical studies. The molar conductance measurements of the complexes in DMF solution correspond to non electrolytic nature for M(L)X₂ complexes and 1 : 2 electrolytes for M'(L)X₂ complexes [where M = Mn^{II}, Cu^{II}; M' = Zn^{II}, Pd^{II} and Pt^{II}; X = Cl⁻, NO₃⁻ and L = ligand]. Thus, the complexes may be formulated as [M(L)X₂] and [M'(L)X₂] respectively. Mn^{II}, Cu^{II} complexes were of the high-spin type whereas the complexes of Zn^{II}, Pd^{II} and Pt^{II} were diamagnetic. On the basis of spectral studies an octahedral geometry has been assigned for Mn^{II}, tetragonal for Cu^{II}, tetrahedral for Zn^{II} complexes whereas square planar for Pd^{II} and Pt^{II} complexes.

Keywords : Macrocyclic, Mn^{II}, Cu^{II}, Zn^{II}, Pd^{II}, Pt^{II}.

Introduction

Since the first report of the Schiff reaction¹, the synthesis of tetradentate Schiff bases as ligands and of their complexes, has been widely described². The interaction of transition metals ions with oxygen-nitrogen donor macrocycles has been the subject of a range of studies. A number of these investigations have been involved in synthetic³, kinetic⁴, thermodynamic⁵ and structural aspects⁶ of complex formation with a range of metal ions. The capacity of transition metal to bind both hard and soft donor ligands allows its coordination chemistry to encompass a variety of geometries, coordination numbers and oxidation states with its reactivity in biological to organometallic chemistry⁷. The value of these tetradentate N₂O₂ ligands and their transition metal complexes has attracted significant attention as catalyst⁸, recent interest have been stimulated by the diagnostic and therapeutic medical applications^{9,10}. A number of publications describing the preparation of nitrogen and oxygen donor ligands, using various derivatives of salicylaldehyde has been reported^{11,12}.

In the present paper we report the synthesis,

spectroscopic characterization and electrochemical studies of Mn^{II}, Cu^{II}, Zn^{II}, Pd^{II} and Pt^{II} complexes with a nitrogen-oxygen donor macrocyclic ligand (L) (Fig. 1).

Experimental

All the chemicals used were of AnalaR grade, and were used as received. All solvents used were of standard/spectroscopic grade.

Synthesis of ligand :

Ligand (L) (Fig. 1) was prepared as cited in literature¹³

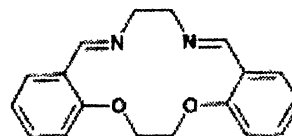


Fig. 1. Structure of the ligand (L).

Synthesis of complexes :

A hot ethanolic solution of ligand (L) (0.40 g, 0.001 mol) and hot ethanolic solution (20 mL) of corresponding metal salts (0.001 mol) were mixed together with

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

Complexes and Empirical formula	Molar conductance ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)	Colour	m.p. ($^{\circ}\text{C}$)	Yield (%)	Elemental analysis (%):			
					Found (Calcd.)			
					Metal	C	H	N
[Mn(L)Cl ₂] C ₁₈ H ₁₈ MnN ₂ O ₂ Cl ₂	8	White	290	68	13.20 (13.12)	51.56 (51.55)	4.20 (4.29)	6.85 (6.68)
[Mn(L)(NO ₃) ₂] C ₁₈ H ₁₈ MnN ₄ O ₈	10	White	278	66	11.74 (11.62)	46.02 (45.66)	3.94 (3.80)	6.12 (5.91)
[Cu(L)Cl ₂] C ₁₈ H ₁₈ CuN ₂ O ₂ Cl ₂	9	Bluish green	284	73	15.06 (14.95)	51.10 (50.46)	4.28 (4.20)	6.86 (6.54)
[Cu(L)(NO ₃) ₂] C ₁₈ H ₁₈ CuN ₄ O ₈	11	Shiny green	>300	69	13.85 (13.27)	44.92 (44.81)	3.56 (3.73)	5.98 (5.80)
[Zn(L)Cl ₂] C ₁₈ H ₁₈ ZnN ₂ O ₂ Cl ₂	262	White	290	68	15.26 (15.34)	50.65 (50.23)	4.22 (4.18)	6.85 (6.51)
[Zn(L)(NO ₃) ₂] C ₁₈ H ₁₈ ZnN ₄ O ₈	254	White	278	66	13.56 (13.63)	44.82 (44.62)	3.86 (3.71)	6.10 (5.78)
[Pd(L)Cl ₂] C ₁₈ H ₁₈ PdN ₂ O ₂ Cl ₂	245	Coffee	295	58	22.74 (22.55)	46.25 (45.95)	4.32 (3.82)	6.22 (5.95)
[Pt(L)Cl ₂] C ₁₈ H ₁₈ PtN ₂ O ₂ Cl ₂	236	Orange	>300	55	33.45 (34.88)	39.26 (38.64)	2.86 (3.22)	5.35 (5.00)

constant stirring. The mixture was refluxed for 4 h at 80–85 $^{\circ}\text{C}$. On cooling the complex was formed. It was filtered, washed with cold EtOH and dried under vacuum over P₄O₁₀.

Physical measurements:

The C, H and N were analysed on Carlo-Ebra 1106 elemental analyser. Molar conductance was measured on a ELICO (CM82T) conductivity bridge. Magnetic susceptibility was measured at room temperature on a Gouy balance using CuSO₄·5H₂O as a calibrant. IR spectra (KBr) were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer IR 598 FT-IR spectrophotometer. The electronic spectra were recorded in DMSO on Shimadzu UV mini-1240 spectrophotometer. EPR spectra of the

complexes were recorded at room temperature for the Mn^{II} and Cu^{II} complexes on an EPR-JEOL JM FE₃ spectrometer using DPPH as a *g*-marker. Cyclic voltammograms were made with a Autolab PGSTAT30 with GPES software in Ar atmosphere. The solvent was DMF with supporting electrolyte LiClO₄ (0.1 M) for the studied species, the working electrode was a Pt disk (diam. 1.5 mm), the counter electrode was a Pt foil, and the reference electrode was Pt wire.

Results and discussion

On the basis of elemental analysis, the complexes were found to have the composition as shown in Table 1. The molar conductance measurements of the complexes in DMF solution correspond to non electrolytic nature for

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

Complexes	μ_{eff} (B.M.)	UV-Visible
		λ_{max} (cm^{-1}), (ϵ) ($\text{L mol}^{-1} \text{ cm}^{-1}$)
[Mn(L)Cl ₂]	5.84	18150 (38); 24700 (64); 29620 (96); 31800 (132)
[Mn(L)(NO ₃) ₂]	5.96	18264 (34); 25644 (66); 29756 (98); 32685 (126)
[Cu(L)Cl ₂]	1.91	10172 (49); 18522 (56); 30384 (156)
[Cu(L)(NO ₃) ₂]	1.98	11192 (45); 18756 (52); 31142 (158)
[Zn(L)Cl ₂]	Diamagnetic	23529 (58); 27027 (85)
[Zn(L)(NO ₃) ₂]	Diamagnetic	22682 (62); 26832 (96)
[Pd(L)Cl ₂]	Diamagnetic	22946 (42); 32447 (67); 37636 (112)
[Pt(L)Cl ₂]	Diamagnetic	24580 (56); 28512 (72)

$M(L)X_2$ complexes and 1 : 2 electrolytes for $M'(L)X_2$ complexes [where $M = Mn^{II}, Cu^{II}$; $M' = Zn^{II}, Pd^{II}$ and Pt^{II} ; $X = Cl^-, NO_3^-$ and $L =$ ligand]. Thus, the complexes may be formulated as $[M(L)X_2]$ and $[M'(L)]X_2$ respectively.

Infrared spectra : In the IR spectrum of ligand L , appearance of strong bands at 1642, 1460, 1226 and 1264 cm^{-1} are assignable to the $\nu(C=N)_{imine}$, $\nu(C=C)$, $\nu(C-O)$ groups respectively. On complexation the position of $\nu(C=N)$ bands shift by 18–34 cm^{-1} toward lower side. In the mean time the position of $\nu(C-O)$ bands shift to higher wave number. Conclusive evidence of the bonding is also shown by the observation that new bands in the IR spectra of the metal complexes appear at 463–545 cm^{-1} and 370–496 cm^{-1} assigned to $\nu(M-O)$ and $\nu(M-N)$ stretching vibrations¹⁴. IR spectra of nitrate complexes display three (N–O) stretching bands at ~1412–1464 (ν_5), 1307–1315 (ν_1) and 1005–1044 cm^{-1} (ν_2). The separation of two highest frequency bands ($\nu_5 - \nu_1$), Δ is 103–130 cm^{-1} , suggest that both the nitrate groups are coordinated as unidentate manner¹⁵. However, the IR spectrum of Zn^{II} complex displays a sharp and strong band at 1379 cm^{-1} indicating uncoordinated behaviour of nitrate groups¹⁶.

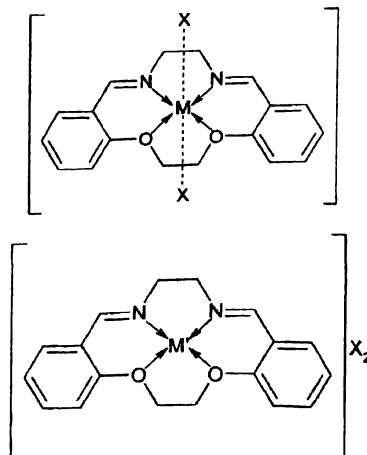
Magnetic moments : Mn^{II} complexes show magnetic moment in the range 5.84–5.96 B.M. at room temperature corresponding to five unpaired electrons. Cu^{II} complexes show magnetic moment in the range 1.91–1.98 B.M. at room temperature corresponding to one unpaired electron (Table 2).

Electronic spectra : Electronic spectra of Mn^{II} complexes display weak absorption bands in the ranges 18150–18264, 24700–25644, 29620–29756 and 31800–32685 cm^{-1} corresponding to an octahedral geometry (Table 2). These bands may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4G), ${}^6A_{1g} \rightarrow {}^4E_{2g}$, ${}^4A_{1g}$ (4G), ${}^6A_{1g} \rightarrow {}^4E_{2g}$ (4D) and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ (4P) transitions respectively¹⁷. Cu^{II} complexes display absorption bands in the ranges 10172–11192, 18522–18756 and 30384–31142 cm^{-1} . First two bands may be assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ($d_{x^2-y^2} \rightarrow d_{z^2}$) (ν_1), ${}^2B_{1g} \rightarrow {}^2B_{2g}$ ($d_{x^2-y^2} \rightarrow d_{xy}$) (ν_2) transitions respectively and third band may be due to charge transfer. The complexes may have tetragonal geometry¹⁸. Zn^{II} complexes exhibit bands in the ranges 22529–22682 and 26832–27027 cm^{-1} which may be assigned due to ligand to metal charge transfer¹⁹. Palladium(II) complex shows bands at 22946, 32447 and 37636 cm^{-1} . First two bands may be assigned to ${}^1A_{1g} \rightarrow$

${}^1A_{2g}$ (ν_1) and ${}^1A_{1g} \rightarrow {}^1B_{1g}$ (ν_2) transitions respectively and the third band may be due to charge transfer spectra. The complex may be considered to possess a low spin square planar geometry²⁰. Platinum(II) complex shows two bands at 24580 and 28512 cm^{-1} . First band may be assigned to ${}^1A_{1g} \rightarrow {}^1B_{1g}$ transition and second band is due to charge transfer spectra. The complexes may be considered to possess square planar geometry²¹.

EPR spectra : The EPR spectra of Mn^{II} complexes were recorded at room temperature as polycrystalline samples and in DMSO solution. The polycrystalline spectra were isotropic and exhibit the 'g' value in the range 2.0052–2.0096 (Table 3). In DMSO solution the complexes give well resolved six lines spectra due to hyperfine interaction between the unpaired electrons with the Mn nucleus ($I = 5/2$). The nuclear magnetic quantum number M_I , corresponding to these lines are $-5/2, -3/2, -1/2, +1/2, +3/2$ and $+5/2$ from low to high field²². The EPR spectra of Cu^{II} complexes were recorded at room temperature as polycrystalline samples and in DMSO solution, on the x-band at 9.3 GHz under the magnetic field strength 3400G. Polycrystalline spectra show a well resolved anisotropic broad signal. The analysis of spectra give $g_{||} = 2.0853$ – 2.1182 and $g_{\perp} = 2.0597$ – 2.0669 (Table 3). The trend $g_{||} > g_{\perp} > 2.0023$, observed for the complexes, under study, indicate that the unpaired electron is localized in $d_{x^2-y^2}$ orbital of the Cu^{II} ion²³.

Cyclic voltammetry : Fig. 3(a) shows the cyclic voltammogram of the $[Cu(L)Cl_2]$ complex at a potential sweep rate of 100 mV/s superimposed on the blank DMF. Two sets of peaks – one reversible couple centered at -0.1 V vs Pt QRE (Quasi reference electrode) ($E_{pc1} = +0.72$



[$M = Mn^{II}, Cu^{II}$; $M' = Zn^{II}, Pd^{II}, Pt^{II}$] [$X = Cl^-, NO_3^-$]
Fig. 2. Suggested structure of the complexes.

Table 3. EPR spectral data of the complexes

Complexes	Temp.	As polycrystalline				In DMSO solution			
		g_{\parallel}	g_{\perp}	g_{iso}	G	g_{\parallel}	g_{\perp}	g_{iso}	G
[Mn(L)Cl ₂]	RT	–	–	2.0052	–	–	–	2.0014	–
[Mn(L)(NO ₃) ₂]	RT	–	–	2.0096	–	–	–	2.0022	–
[Cu(L)Cl ₂]	RT	2.0853	2.0597	2.0672	1.4288	2.1382	2.0702	2.0922	1.8956
[Cu(L)(NO ₃) ₂]	RT	2.1182	2.0669	2.0842	1.7668	2.0834	2.0690	2.0737	1.2049

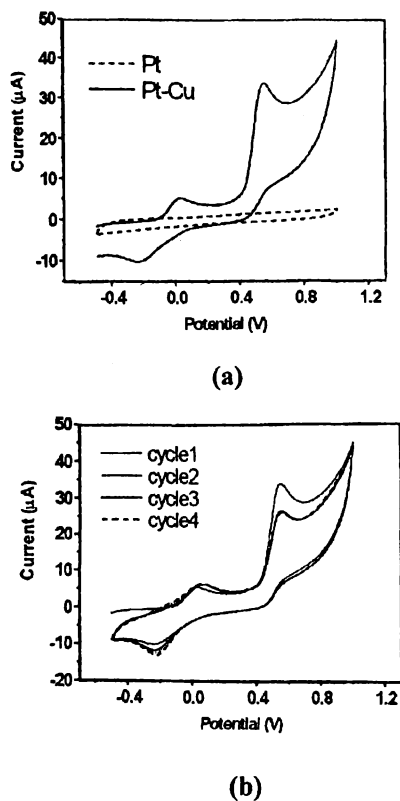


Fig. 3. Cyclic voltammetry of [Cu(L)Cl₂] in DMF in presence of LiClO₄ (0.1 M) at various scan rates.

V, $E_{\text{pal}} = +0.50$ V, $E^{0'} = +0.61$ V) could be assigned to Cu⁺/Cu couple²⁴ and another irreversible centered at +0.5 V ($E_{\text{pc1}} = -0.10$ V, $E_{\text{pal}} = -0.34$ V, $E^{0'} = -0.22$ V) could be assigned to Cu²⁺/Cu⁺ couple and another possibility is that it could be a reaction of imine nitrogen or oxygen ligands/capping molecules with the supporting electrolyte at the applied potential. To analyze these possibilities, variation in the voltammetric features with potential cycles and sweep rates are investigated. Accordingly, Fig. 3(b) shows the cycle dependence of CVs at a sweep rate of 100 mV/s. While there is a considerable difference between the first and the second cycles (which most often occurs due to instrumental artifacts), there are no further changes in the subsequent cycles. This indicates that

the second set of peaks may not be due to ligand dissociation in which case there should be continuous cycle dependence until the ligands go away²⁵. Metal-bound imine functions are difficult to be reduced electrochemically at least within the electrochemical window of dimethylformamide/LiClO₄ system²⁶.

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References

1. H. S. Schiff, *Ann. Chim. (Paris)*, 1864, **131**, 118.
2. L. F. Lindoy, *Inorg. Chem.*, 1976, **15**, 1724.
3. D. Esteban, R. Bastida, A. Blas, A. Rodriguez, T. Rodriguez-Blas, D. E. Fenton, H. Adams and J. Mahia, *Inorg. Chem.*, 1999, **38**, 1937.
4. A. Ekstrom, L. F. Lindoy and R. J. Smith, *Inorg. Chem.*, 1980, **19**, 724.
5. G. Anderegg, A. Ekstrom, L. F. Lindoy and R. J. Smith, *J. Am. Chem. Soc.*, 1980, **102**, 2670.
6. K. R. Adam, L. F. Lindoy, H. C. Lip, J. H. Ria, B. W. Skelton and H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 74.
7. A. Berkessel, M. Bolte, T. Newmann and L. Seidel, *Chem. Ber.*, 1996, **129**, 1183.
8. R. T. Roy, M. Chaudhary, S. K. Mondal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1984, 1681.
9. P. S. Pan, F. A. Curtius, C. L. Carroll, I. Medina, L. A. Liotta, G. J. Sharpless, S. R. Mcalpine and R. Shelli, *Bioorganic & Medicinal Chemistry*, 2006, **14**, 4731.
10. Y. S. Tsantrizos, J. M. Ferland, A. McClory, M. Poirier, Y. Vittorio, K. Nathan, X. J. Wang, N. Haddad, X. Wei, J. Xu and L. Xang, *J. Organometallic Chem.*, 2006, **691**, 5163.
11. (a) L. G. Armstrong and L. F. Lindoy, *Inorg. Chem.*, 1975, **14**, 1322; (b) L. G. Armstrong, P. G. Grimsley, L. F. Lindoy, R. C. Lip, V. A. Norris and R. J. Smith, *Inorg. Chem.*, 1978, **17**, 2350; (c) L. F. Lindoy, H. C. Lip, L. F. Power and J. R. Rea, *Inorg. Chem.*, 1976, **15**, 1724.
12. D. M. Boghaei and S. Mohebi, *Tetrahedron*, 2002, **58**, 5357.

13. A. Simion, C. Simion, T. Kanda, S. Nagashima, Y. Miltoma, T. Yamada, K. Mimura and M. Tashiro, *J. Chem. Soc., Perkin Trans.*, 2001, 2071.
14. P. S. Kalsi, "Spectroscopy of Organic Compounds", 4th ed., New Age International (P.) Ltd., New Delhi, 1999.
15. S. Chandra and L. K. Gupta, *Trans. Met. Chem.*, 2006, **31**, 368.
16. S. Chandra and L. K. Gupta, *Spectrochimica Acta (A)*, 2004, **60**, 3079.
17. S. Chandra and L. K. Gupta, *Spectrochimica Acta (A)*, 2004, **60**, 1563.
18. S. Chandra, L. K. Gupta and D. Jain, *Spectrochimica Acta (A)*, 2004, **60**, 2411.
19. S. Chandra, L. K. Gupta and Sangeetika, *Synth. React. Inorg. Metal-Org. Chem.*, 2004, **34**, 1591.
20. R. S. Lal, A. Kumar and J. Chakarabarty, *Indian. J Chem., Sect. A*, 2001, **40**, 422.
21. A. Singh and P. Singh, *Indian J Chem., Sect. A*, 2000, **39**, 874.
22. S. Chandra and L. K. Gupta, *Spectrochimica Acta (A)*, 2005, **61**, 269.
23. S. Chandra and L. K. Gupta, *J. Indian Chem. Soc.*, 2005, **82**, 454.
24. A. J. Bard and L. R. Faulkner, "Electrochemical Methods : Fundamental and Applications", 2nd ed., Wiley Interscience, New York, 2001.
25. N. Deligonul and M. Tumer, *Trans. Met. Chem.*, 2006, **31**, 920.
26. Shirley *et al.*, *J. Inorg. Biochem.*, 2002, **89**, 54.