J. Indian Chem. Soc.,
Vol. 86, March 2009, pp. 220-224

Spectroscopic studies and characterization of Ni^{II} and Cu^{II} complexes with a nitrogen donor new azamacrocyclic ligand with pendent arms

Sulekh Chandra[a]*, Deepali Jain[b], Anjana Sarkar[c] and Anupama[a,b]

[a]Department of Chemistry, Zakir Husain College (University of Delhi), JLN Marg, New Delhi-110 002, India

E-mail : schandra_00@yahoo.com

[b]Department of Chemistry, D. N. College, Meerut, Uttar Pradesh, India

E-mail : deepali 101@yahoo.com

[c]NSIT (University of Delhi), Sector-3, Dwarka, Uttar Pradesh, India

Manuscript received 17 June 2008, revised 23 September 2008, accepted 12 November 2008

Abstract : The newly synthesised azamacrocyclic ligand L [2,6,12,16,21,22-hexaaza-3,4,5,13,14,15-hexamethyltricyclo-[15,3,1,1^{7-11}]-docasa-1(2,10,2,5,7,9,11(22),12,15,17,19-decene] was prepared by the reaction of 3-methyl-2,4-pentadione and 2,6-diaminopyridine. The complexes of Cu^{II} and Ni^{II} were synthesised with the new macrocyclic ligand. All the complexes were characterized by the molar conductance measurements, magnetic susceptibility measurements, mass, IR, electronic and EPR spectral studies. The molar conductance measurement of the complexes in DMF solution is corresponding to non-electrolytic nature. Thus these complexes may be formulated as $[M(L)X_2]$ (where, M = Ni^{II} and Cu^{II} and X = Cl^- and NO_3^-]. On the basis of spectral studies, an octahedral geometry for Ni^{II} complexes and tetragonal for Cu^{II} complexes is assigned. The biological activity of the ligand and complexes were screened *in vitro* against different pathogenic fungi and several bacteria to study their comparative capacity to inhibit the growth.

Keywords : Spectroscopic, EPR, 2-6-diaminopyridine, 3-methyl-2,4-pentadione, Ni^{II} and Cu^{II} complexes.

Introduction

The intense interest in the synthetic macrocycles and their metal complexes depends on the fact that they mimic naturally occurring macrocyclic molecule in their structural and functional features[1-4]. In addition to this, the study of metal complexes of macrocyclic ligands appears to be interesting in view of the possibility of obtaining coordination compounds of unusual structures and stability. The formation of macrocyclic complexes depends on the size of the macrocycle, the nature of its donor atoms and complexing behaviour of the anions, involved in coordination[5]. The multifarious roles of transition metals in chemistry and biochemistry suggest that considerable potential exists for the development of a new chemistry with these metals, ligands and their complexation reactions represent an important beginning in this direction[6-11]. Schiff base macrocyclic ligands display very important and interesting biological properties such as anti-tumor[12], anti-bacterial[13] and anti-fungal[14]. Coordination of these compounds with transition metal ions often enhances their activity[15]. In view of the above applications, in this paper, we report the synthesis, spectroscopic characterization of macrocyclic complexes of Ni^{II} and Cu^{II} and their biological screening.

Experimental

All the chemicals used were of AnalaR grade and procured from Fluka and Sigma Aldrich. Metal salts were purchased from E. Merck.

Preparation of ligand :

The hot ethanolic solution (20 ml) of 2,6-diaminopyridine (2.18 g, 0.02 mol) and the hot ethanolic solution (20 ml) of 3-methyl-2,4-pentadione (2.28 ml, 0.02 mol) were mixed slowly with constant stirring. This mixture was refluxed at (70–80 °C) for 6–8 h (pH 4–5) in the presence of few drops of concentrated hydrochloric acid. On cooling, light brown colored precipitate was formed, which was filtered, washed with cold EtOH and dried under vacuum over P_4O_{10}. The scheme for the synthesis of ligand is given in Fig. 1.

Yield : 55%, m.p 122 °C. The elemental analysis (atomic mass 371.6 amu), C, 70.24; H, 6.48 and N,

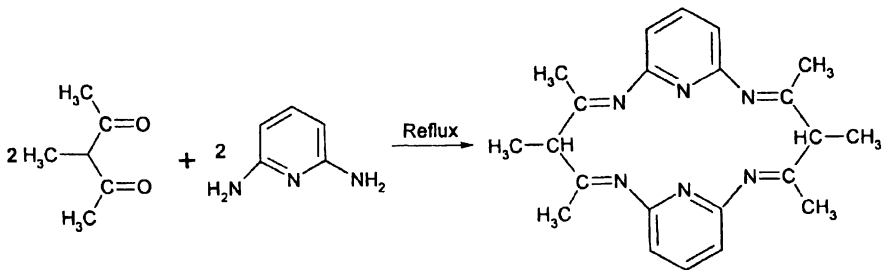


Fig. 1

22.45%. Calcd. for $C_{22}H_{26}N_6$ (calcd. atomic mass 374 amu), C, 70.58; H, 6.95 and N 22.45%.

Preparation of complexes :

Hot ethanolic solution (20 ml) of ligand (0.001 mol) and hot ethanolic solution (20 ml) of corresponding metal salt (0.001 mol) were mixed together with constant stirring. The mixture was refluxed for 5-7 h at 70-90 °C. On cooling, colored complex was precipitated out. It was filtered washed with cold EtOH and dried under vacuum over P_4O_{10}.

Physical measurements :

The C, H and N were analyzed on a Carlo-Erba 1106 elemental analyzer. Molar conductance was measured on an 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 spectrum was recorded on Joel-MS Route mass spectrometer. IR spectra (KBr) were recorded on Hitachi FTIR spectrum BX-II spectrophotometer. The electronic spectra was recorded in DMSO solution on Shimadzu UV mini-1240 spectrophotometer.

EPR spectra of the complexes were recorded as polycrystalline sample at room temperature for Cu^{II} complexes on E_4-EPR spectrometer using the DPPH as the *g*-marker.

Results and discussion

Characterization of the ligand (L) :

The electron impact mass spectrum of ligand (L) confirmed the proposed formula by showing a peak at 371.6 amu corresponding to the macrocyclic moiety [$(C_{22}H_{26}N_6)^+$, calculated atomic mass 374 amu]. It also shows a series of peaks corresponding to various fragments. Their intensities give an idea of the stability of the fragments.

IR spectrum of the ligand does not exhibit any band corresponding to free primary diamine and keto group[15] which suggests the complete condensation of the amino group with keto group. The infrared spectral bands corresponding to ν(C=C) and ν(C=N) skeleton are present in the region 1640-1370 cm^{-1}.

IR spectrum of the ligand show the band appearing in the region 1456 cm^{-1} corresponding to the N atom pyridine ring. The band appearing in the region 1635-1590 cm^{-1} may be assigned to symmetric or asymmetric ν(C=N) vibration. On complexation the position of $\nu_{C=N}$ band is shifted towards lower side. This indicates that the coordination takes place through the nitrogen of ν(C=N) group. Thus ligand behaves as tetradentate.

Characterization of the complexes :

On the basis of elemental analysis, the complexes are assigned to possess the composition as shown in Table 1.

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

Complexes	Color	Molar conduc.	Yield (%)	M.p. (°C)	Elemental analysis (%) : Found (Calcd.)			
					M	C	H	N
$[Cu(L)Cl_2]$	Black	13.28	65	292	11.66	48.54	4.76	15.44
$[CuC_{22}H_{26}N_6Cl_2]$					(11.68)	(48.57)	(4.78)	(15 45)
$[Cu(L)(NO_3)_2]$	Dark brown	11.80	59	>300	10.26	42.84	4.20	13.66
$[CuC_{22}H_{26}N_8O_6]$					(10.31)	(42.88)	(4.22)	(13.64)
$[Ni(L)Cl_2]$	Light green	6	64	248	9.58	43.11	4.25	13.73
$[NiC_{22}H_{26}N_6Cl_2]$					(9.59)	(43.13)	(4.24)	(13.72)
$[Ni(L)(NO_3)_2]$	Light green	3	62	240	8.81	39.70	3.94	12.66
$[NiC_{22}H_{26}N_8O_6]$					(8.83)	(39.71)	(3.91)	(12.64)

The molar conductance measurements of the complexes in DMF are corresponding to non-electrolytic nature. Thus complexes may be formulated as $[M(L)X_2]$ [M = Ni^{II} and Cu^{II}, X = Cl^- and NO_3^-]. On complexation, the position of band appearing at 1456 cm^{-1} corresponding to Py-N is not shifted. It indicates non-involvement of pyridine nitrogen in coordination[16]. In the infrared spectra of the nitrate complexes, three medium intensity bands in the region 1440–1460, 1301–1323 and 1000–980 cm^{-1} are present which are corresponding to the ν_3, ν_2 and ν_1, respectively[17,18]. The position of these bands indicates that nitrate is coordinated to the metal ion as an unidentate manner.

Magnetic moment and electronic spectral studies :

Nickel(II) complexes :

The measured magnetic moment of Ni^{II} complexes at room temperature lie in the range 2.95–2.98 B.M. These values are in agreement with a high spin configuration. The electronic spectra of the complexes exhibit three absorption bands in the range of 10449–11223, 18518–18578 and 22471–22675 cm^{-1}. The position of these bands indicates that the complexes have an octahedral geometry[19]. The ground state of Ni^{II} in an octahedral coordination is $^3A_{2g}$. Thus these bands may be assigned to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions[20–22], respectively.

Copper(II) complexes :

Cu^{II} complexes show magnetic moment at room temperature in the range 1.96–2.00 B.M., corresponding to one unpaired electron.

Electronic spectra of six coordinated copper complexes display bands in the range 10672–11112, 16318–17331 and 24300–26110 cm^{-1}, corresponding to $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively (Table 2).

EPR spectra of Cu^{II} complexes were recorded, at room temperature, as polycrystalline samples and in DMSO solution. Polycrystalline spectra show a well resolved anisotropic broad signal[23]. The analysis of spectra gives $g_\parallel$ = 2.0773–2.1480 and $g_\perp$ = 2.0382–2.0445. The observed $g_\parallel$ values for the complexes are less than 2.3 which is 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 $d_{x^2-y^2}$ orbital of the Cu^{II} ion. Tetragonally elongated structures are confirmed for Cu^{II} complexes. $G = (g_\parallel - 2)/(g_\perp - 2)$, which measures the exchange interaction between the metal centers in a polycrystalline solid has been calculated. According to Hathaway[13], if the value of G is more than 4, then exchange interaction is negligible, but the value of G less than 4 indicates considerable exchange interaction in the solid complexes. In the present complexes, value of G is less than 4 therefore there is exchange interaction in the solid complexes (Table 3).

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

Complexes	μ_{eff} (B.M.)	λ_{max} (cm^{-1})
$[Cu(L)Cl_2]$	2.00	10672, 16318, 24300
$[Cu(L)(NO_3)_2]$	1.96	11112, 17331, 26110
$[Ni(L)Cl_2]$	2.98	10449, 18518, 22675
$[Ni(L)(NO_3)_2]$	2.95	11223, 18578, 22471

Table 3. EPR spectra of Cu^{II} complexes

Complexes	$g_\parallel$	$g_\perp$	g_{iso}	G
$[Cu(L)Cl_2]$	2.1480	2.0445	2.0786	3.3258
$[Cu(L)(NO_3)_2]$	2.0773	2.0382	2.0512	2.0235

Ligand field parameters :

Various ligand field parameters have been calculated for Ni^{II} complexes. The value of B for a given complex can be calculated as :

$$B = (\nu_2 + \nu_3 - 3\nu_1)/15$$

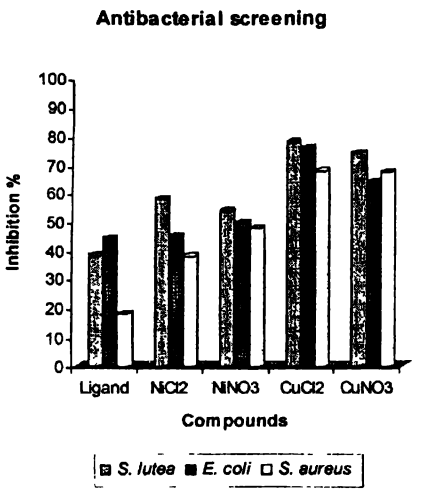
In the complexes value of Racah parameter B is found less than the value of free ion i.e. 1041 cm^{-1}. The Nephelauxelic parameter β has been calculated by the help of relation $\beta = B_{complex}/B_{free\ ion}$. The value of β for Ni^{II} complexes under study, lie in the range 0.47–0.63 (Table 4). These values indicate the appreciable covalent character of metal ligand σ bond.

Table 4. Ligand field parameters of Ni^{II} complexes

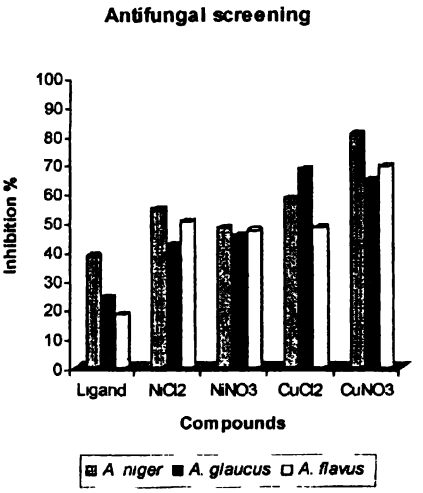
Complexes	Dq (cm^{-1})	B (cm^{-1})	β	LFSE (kJ mol^{-1})
$[Ni(LA)Cl_2]$	1044	656	0.63	150
$[Ni(LA)(NO_3)_2]$	1122	488	0.47	161

Biological activity :

The ligand (L) and its complexes were evaluated against different species of bacteria and several plant pathogenic fungi. The antimicrobial data reveals that the complexes are more active than free ligand. The ligand and its complexes were directly mixed at different concentration as



Graph 1A



Graph 1B

Antibacterial and antifungal screening of the ligand and its complexes.

250, 125, 63.5 μg ml^{-1}. At concentration 250 μg ml^{-1}, ligand and its complexes show better antibacterial and antifungal screening (Graph 1A and 1B).

Antibacterial screening :

Sarcina lutea (gram-positive), *Escherichia coli* (gram-negative) and *S. aureus* bacteria were used as the test organism in antimicrobial study, for 24–36 h at 36 °C. The bacterial growth was checked by disc diffusion techniques[24-27] (Graph 1A). Whatmann No. 4 filter paper having 8.00 mm was soaked in the solution of compounds in DMSO solution. After drying, it was placed on nutrient agar plates. The inhibition areas were observed after 40 h. DMSO solution was used as a control and Gentamycin as a standard drug. The bacterial growth inhibition capacity of the ligand and complexes follow the order :

Ligand < Ni^{II} complexes < Cu^{II} complexes

Antifungal screening :

The antifungal activity of the ligand and its complexes was checked by Agar-Agar plate technique for the *Aspergillus niger, Aspergillus glaucus* and *Aspergillus flavus* fungi. The ligand and the complexes were directly mixed to the medium in different concentrations. All the complexes show inhibition of fungal growth. The growth of fungus was measured by recording the diameter of fungal colony.

The following relation was used to calculate to the fungal growth inhibition,

Fungal growth inhibition (%) = $(A - B) \times 100/A$,

where, A is the diameter of fungal colony in control plate and B is the diameter of fungal colony in test plate. The results of antifungal activity are shown in Graph 1B. In all the complexes studied here, Cu complexes show best inhibition.

Cu^{II} complexes > Ni^{II} complexes > ligand

Acknowledgement

We are thankful to the Principal of D. N. College, Meerut and Zakir Husain College, Delhi for providing laboratory facilities. We are also thankful to IIT Mumbai for recording EPR spectra and UGC (New Delhi) for financial support.

References

1. L. F. Lindoy, "The Chemistry of Macrocyclic Ligand Complexes", Cambridge University Press, UK, 1989.
2. P. Dietrich, P Viout and J. M. Lehn, "Macrocyclic Chemistry", VCH Publishers Inc, New York, 1993.
3. R. M. Izatt, K. Powak and J. S. Bradshaw, *Chem. Rev.*, 1999, **91**, 1721.
4. F. Lions, *Pure Appl. Chem.*, 1969, **19**, 777.
5. (a) T. A. Kaden, *Topics Curr. Chem.*, 1984, **121**, 54; (b) P. V. Bernhardt and G. A. Lawrance, *Coord. Chem. Rev.*, 1990, **104**, 297.
6. T. A. Kaden, *Pure Appl. Chem.*, 1998, **60**, 1117.
7. F. C. J. M. Van Veggel, W. Verboom and D. N. Reinhoudt, *Chem. Rev.*, 1994, **94**, 279.
8. K. R. Adam, M. Antolovich, D. S. Baldwin, L. G Brigden

and P. A. Duckworts, *J. Chem. Soc., Dalton Trans.*, 1992, 1869.

9. K. Y. Choi, H. Y. Lee, β. B. Park, J. H. Kim, M. W. Kim, J. W. Ryu, M. Sub and H. Hwan suh, *Polyhedron*, 2001, **20**, 2003.
10. T. W. Hambley, L. F. Lindoy, J. R. Reimers, P. Turner, G. Wei and A. N. W. Cooper, *J. Chem. Soc., Dalton Trans.*, 2001, 614.
11. E. Q. Gao, H. Y. Sun, D. Z. Liao, L. H. Jiang and S. P. Van, *Polyhedron*, 2002, **21**, 359.
12. M. Das and S. E. Livingstone, *Inorg. Chim. Acta*, 1976, **19**, 5.
13. M. Mohan, A. Agarwal and N. K. Jha, *J. Inorg. Biochem.*, 1988, **34**, 41.
14. A. Bansal and R. V. Singh, *Indian J. Chem., Sect. B*, 2001, **40**, 989.
15. N. K. Singh and S. K. Kushawaha, *Transition Met. Chem.*, 2001, **26**, 140.
16. (a) S. V. Rosokha, Y. D. Lampeka and I. M. Matoshtan, *J. Chem. Soc., Dalton Trans.*, 1993, 631; (b) S. Chandra and L. K. Gupta, *Spectrochim. Acta*, 2004, **60A**, 1563.
17. P. S. Kalsi, "Spectroscopy of Organic Compounds", 4th ed. New Age International (P) LTd., New Delhi, India, 1999.
18. K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiely Interscience, New York, 1970.
19. A. B. P. Lever, "Inorganic Electronic Spectroscopy", 1st ed., Elsevier, Amsterdam, 1968, 249.
20. M. Shakir, O. S. M. Nasman, A. K. Mohamed and S. P. Varkey, *Indian J. Chem., Sect. A*, 1996, **25**, 710
21. F. Athar, F. Arjmand and S. Tabassum, *Transition Met. Chem.*, 2001, **26**, 426.
22. S. Chandra, K. Gupta and S. Sharma, *Synth. React. Inorg. Metal-Org. Chem.*, 2001, **31**, 1205.
23. W. G. Hanna and M. M. Moawad, *Transition Met. Chem.*, 2001, **26**, 644.
24. M. Sakai, A. Hara, S. Anjo and M. Nakamura, *J. Pharm. Biomed. Anal.*, 1999, **18**, 1057.
25. P. Kopel, Z. Travnicek, J. Marek, M. Korabik and J. Mrozinski, *Polyhedron*, 2003, **32**, 411.
26. S. Chandra, D. Jain and L. K Gupta, *Spectrochim. Acta*, 2004, **60**, 2411.
27. S. Chandra and S. Sharma, *Transition Met. Chem.*, 2007, **32**, 150.