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SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY OF TETRAAZAMACROCYCLIC COMPLEXES

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ABSTRACT

Novel tetraazamacrocyclic complexes of Cu (II), Co (II), Ni (II) and Zn (II) has been synthesized from the reaction of ethylenediamine/*o*-phenylenediamine/4-nitro-*o*-phenylenediamine, with acetylacetone/acetonyl acetone/dimedone/Meldrums acid and divalent metal ions using solid-supported perchloric acid ($HClO_4$-SiO_2) as a catalyst. The complexes were characterized by IR, ^{1}H NMR, EPR spectra, magnetic moments, conductances, thermal analysis (TGA and DTA), and powder X-ray analysis (XRD). The antimicrobial studies of these complexes against *Staphylococcus typhi*, *Staphylococcus aurieus*, *Escherichia coli* and *Bacillus subtilis* species by Minimum Inhibitory Concentration (MIC) method revealed that these complexes possess potent antibacterial activity.

Key words: Cu (II), Ni (II), Zn (II), Complexes, Tetraazamacrocycle.

INTRODUCTION

The diversified role played by the naturally occurring macrocycles in biological systems is well known. Several macrocyclic complexes have been reported to possess remarkable antibacterial, antifungal and anti-inflammatory activities[1,2] and are used as dyes and pigments, MRI contrast agents, and models for naturally occurring macrocycles[3-6]. In addition, macrocyclic nickel complexes find use in DNA recognition and oxidation[7] while copper complexes find use in DNA binding and cleavage[8]. Generally, macrocyclic complexes of type.

$[M(C_{16}H_{28}N_4)X_2]$, where M = Cu (II), Co (II), Ni (II), Zn (II) and X = Cl^-, NO_3^-, CH_3COO^- are prepared by refluxing ehylenediamine, acetonyl acetone and metal salt in methanol or ethanol (template method)[9].

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EXPERIMENTAL

Material and methods of analysis

IR spectra (400–4000 cm^{-1}) were recorded on Shimadzu FTIR spectrophotometer using KBR discs, and the absorption bands are expressed in cm^{-1}. ^1H NMR spectra were recorded in DMSO-d_6 with tetramethyl silane as an internal standard. Molar conductivity of 10^{-3} M solution in DMSO was obtained on C-100 Elico digital conductivity meter at room temperature. Magnetic susceptibilities were recorded on Guoy balance using AR grade $CuSO_4$ and $FeSO_4$ as standards. EPR spectra of complexes are performed in solid state at room temperature on Varian-E-4X band EPR spectrophotometer. TG/DTA scans were recorded on Mettler-Toledo-851 TGA-DTA instrument at linear heating rate of 10^o per minute under nitrogen atmosphere in a temperature range 25-1000^{o}C. X-ray powder diffraction patterns of complexes were recorded in the 2 θ range of 10-80^o on Bruker X-D-8 advanced diffractometer and XRD scans with the help of powder X-programme. Analytical grade chemicals brought from Sigma-Aldrich, Inc. were used throughout this work.

Present work

Herein attempts have been made to synthesize novel macrocyclic complexes of type $[M(C_{16}H_{28}N_4)X_2]$ by non-template method utilizing solid-supported perchloric acid ($HClO_4$-SiO_2) as a catalyst at room temperature (**Scheme 1 and 2**). The investigated complexes were characterized and evaluated for their antimicrobial activity against four bacterial strains.

Typical procedure for the synthesis of $[Cu(C_{16}H_{28}N_4)Cl_2]$

A mixture of ethylenediamine (10 mmol), copper chloride (5 mmol) and acetonyl acetone along with 10 mol % solid-supported perchloric acid in ethanol (50 mL) was stirred at room temperature for 80 min. The resulting colored complex along with insoluble catalyst was dissolved in DMSO (2 x 15 mL) and then filtered. The filtrate was then concentrated under reduced pressure to afford shiny blue colored copper complex, which was dried over calcium chloride (67% yield).

Chemistry

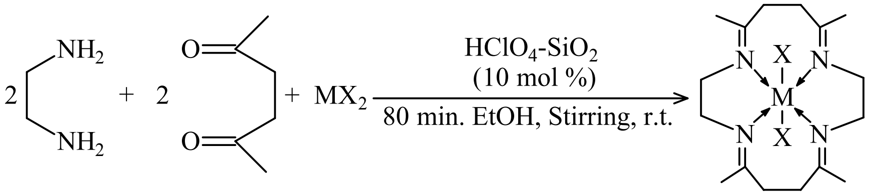
The analytical data suggest the formula of macrocylic complexes as $[M(C_{16}H_{28}N_4)X_2]$ where M = Co (II), Ni (II), Cu (II), Zn (II) and X = Cl^-, NO_3^- and CH_3COO^-. The anion test is positive after decomposing the complexes with concentrated HNO_3, indicating their presence inside the coordination sphere.[9] Conductivity measurements in DMSO indicate them to be non-electrolytic in nature (10-20 ohm^{-1} cm^2 mol^{-1})[10]. The melting point of all complexes were above 200^{o}C and all complexes are intensively colored. Magnetic movement values suggest octahedral environment around metals (Table 1)[11].

Table 1: Analytical data of complexes of type [M($C_{16}H_{28}N_4$)X_2]

S. No.	Mol. Form. of complex	Mol. wt.	Colour	Melting point (°C)	Elemental analysis % Calcd. (Found) % C	% H	% N	$\lambda M_{ohm^{-1}cm^2}$	M. M. μ_B
1	[Cu($C_{16}H_{28}N_4$)Cl_2]	410.874	Blue	215	46.772 (46.005)	6.869 (6.005)	13.636 (12.940)	17	1.76
2	[Cu($C_{16}H_{28}N_4$)$(NO_3)_2$]	463.976	Dark blue	220	41.419 (40.995)	6.869 (5.725)	18.113 (17.639)	19	1.78
3	[Cu($C_{16}H_{28}N_4$)$(CH_3COO)_2$]	458.056	Blue	215	52.443 (51.935)	7.482 (6.998)	12.231 (11.735)	19	1.76
4	[Co($C_{16}H_{28}N_4$)(Cl_2)]	406.367	Brown	235	47.302 (46.840)	6.947 (6.001)	13.79 (12.995	20	4.86
5	[Co($C_{16}H_{28}N_4$)$(NO_3)_2$]	559.369	Dark brown	230	41.834 (41.001)	6.144 (5.842)	18.295 (17.807)	19	4.84
6	[Co($C_{16}H_{28}N_4$)$(CH_3COO)_2$]	453.449	Black	225	52.976 (52.151)	7.558 (6.935)	12.355 (11.975)	19	4.82
7	[Ni($C_{16}H_{28}N_4$)Cl_2]	406.044	Light green	220	47.328 (46.935)	6.95 (6.025)	13.798 (13.005)	18	2.81
8	[Ni($C_{16}H_{28}N_4$)$(NO_3)_2$]	459.146	Green	225	41.855 (41.000)	6.147 (5.835	18.303 (17.895)	20	2.82
9	[Ni($C_{16}H_{28}N_4$)$(CH_3COO)_2$]	453.226	Green	230	53.00 (52.519)	7.561 (6.915)	12.362 (12.00)	19	2.82
10	[Zn($C_{16}H_{28}N_4$)Cl_2]	412.704	Buff	240	46.565 (45.735	6.838 (5.995)	13.575 (12.995)	18	-
11	[Zn($C_{16}H_{28}N_4$)$(NO_3)_2$]	465.806	Buff	244	41.256 (40.687)	6.059 (5.530)	18.042 (17.741)	15	-
12	[Zn($C_{16}H_{28}N_4$)$(CH_3COO)_2$]	459.886	Buff	255	52.234 (51.539)	7.452 (6.895)	12.183 (11.635)	19	-

Infrared spectra

The infrared spectra of complexes (Table 2) do not exhibit broad peak in the region 3230-3260 cm^{-1} for ν (NH_2) and strong peak in the region 1700-1720 cm^{-1} for ν (C=O) group. This confirms the condensation of acetyl acetone/acetonyl acetone and amino groups of ethylene diamine[12,13]. The appearance of two new peaks in the region 1575-1606 cm^{-1} and 1000-1310 cm^{-1} for ν (C=N) and ν (C-N) respectively supports the formation of macrocyclic frame[14]. Further, the presence of peak in the region 420-460 cm^{-1} for ν (M-N) indicates coordination of azomethine nitrogen[15,16].



M = Cu (II), Co (II), Ni (II), Zn (II)
X = Cl^-, NO_3^-, CH_3COO^-

Complexes = 12

Scheme 1

Table 2: IR spectra of complexes

Compound	ν (C = N)	ν (C − N)	ν (M − N)
[$Cu(C_{14}H_{24}N_4)Cl_2$]	1575-1606	1000-1310	420-460
[$Zn(C_{16}H_{28}N_4)(NO_3)_2$]	1575-1606	1000-1310	420-460

NMR Spectra

The ^1H NMR spectrum of [$M(C_{16}H_{28}N_4)X_2$] type complexes shows signal of $-NCH_2CH_2N-$ protons (8H) at δ = 2.90 ppm, $-CCH_2CH_2C-$ protons (8H) at δ = 2.65 ppm, while $-CH_3$ protons (12H) appeared at δ = 2.40 ppm (Table 3).

Table 3: ^1H NMR spectra of complexes

Compound	$-CH_3$	$-NCH_2CH_2N-$	$-CCH_2C-$	$-CCH_2CH_2C-$
[$Zn(C_{14}H_{24}N_4)(NO_3)_2$]	2.40	3.15	2.65	-
[$Zn(C_{16}H_{28}N_4)(NO_3)_2$]	2.40	2.90	-	2.65

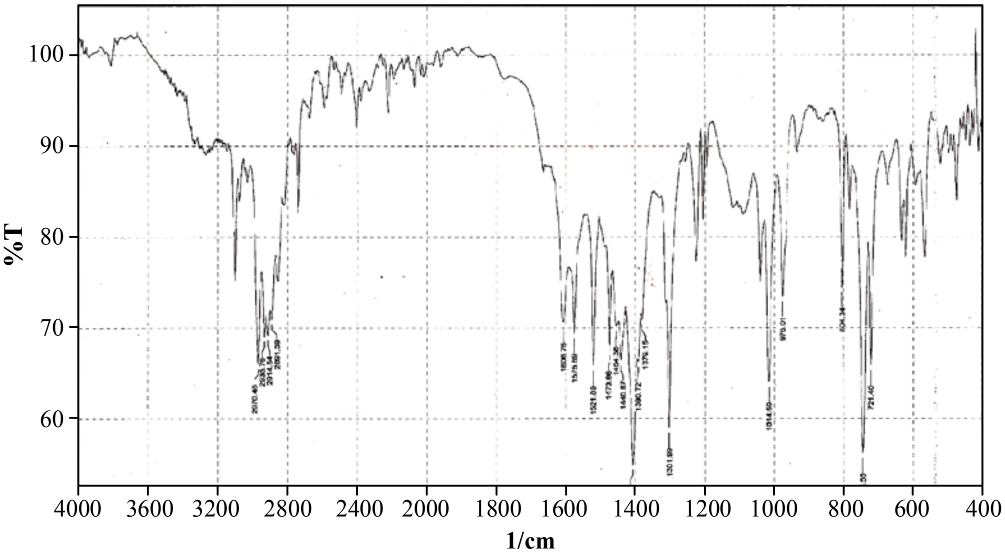
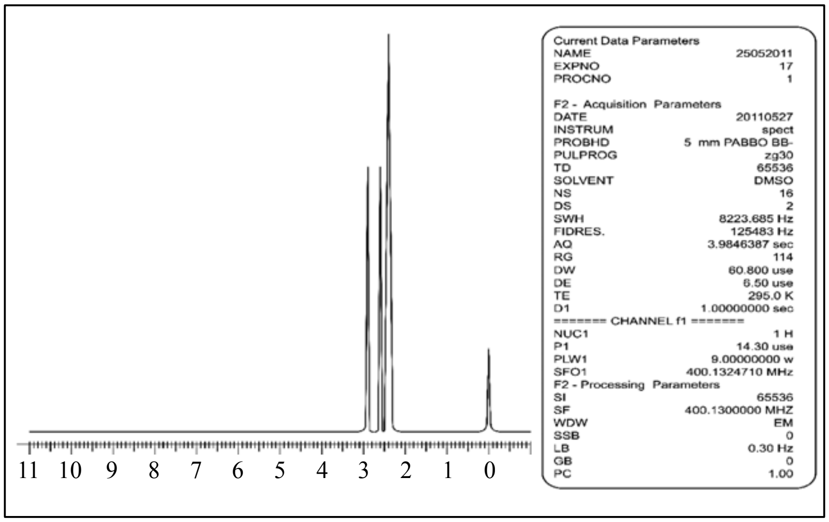


Fig. 1: Infra red spectrum



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FIDRES.	125483 Hz
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RG	114
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DE	6.50 use
TE	295.0 K
D1	1.00000000 sec
======= CHANNEL f1 =======	
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P1	14.30 use
PLW1	9.00000000 w
SFO1	400.1324710 MHz
F2 - Processing Parameters	
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SF	400.1300000 MHZ
WDW	EM
SSB	0
LB	0.30 Hz
GB	0
PC	1.00

Fig. 2: ^{1}H NMR Spectrum

EPR Spectra

The EPR spectra of the $[Cu(C_{16}H_{28}N_4)Cl_2]$ complex in powder form at room temperature shows anisotropic signals with $g_\parallel = 2.0029$, $g_\perp = 1.9973$, and $g_{iso} = 1.9991$, $A_\parallel = 0.83$ *G*, $A_\perp = 10.00$ *G*, $A_{iso} = 5.208$ *G* and exchange coupling interaction constant G = 0.1914. This finding indicates that the observed 'g' values for the complex are less than

2.3 in agreement with the covalent character of the metal ligand bond[17-20]. The trend $g_{\parallel} > g_{\perp} > 2.0023$ observed for the Cu (II) complex indicated that unpaired electron is localized in the dx^2-y^2 orbital and spectral features are characterstic of axial symmetry. Tetragonal elongated structure is confirmed for the complex[21-23].

Table 4: EPR parameters for metal complexes

Complex	Gyromatric ratio (g)	A (Gauss)	G	e/gm × 10^{21}
$[Ni(C_{22}H_{22}N_6O_4)Cl_2]$	g‖= 2.0005 g ⊥ = 1.9989 gav = 1.9994	A ‖ = 4.09 A ⊥ = 8.19	0.6595	1.5078
$[Cu(C_{24}H_{26}N_6O_4)(NO_3)_2]$	g ‖= 2.0015 g ⊥ = 1.9995 gav = 2.0001	A ‖ = 3.33 A ⊥ = 6.66	0.200	1.5073

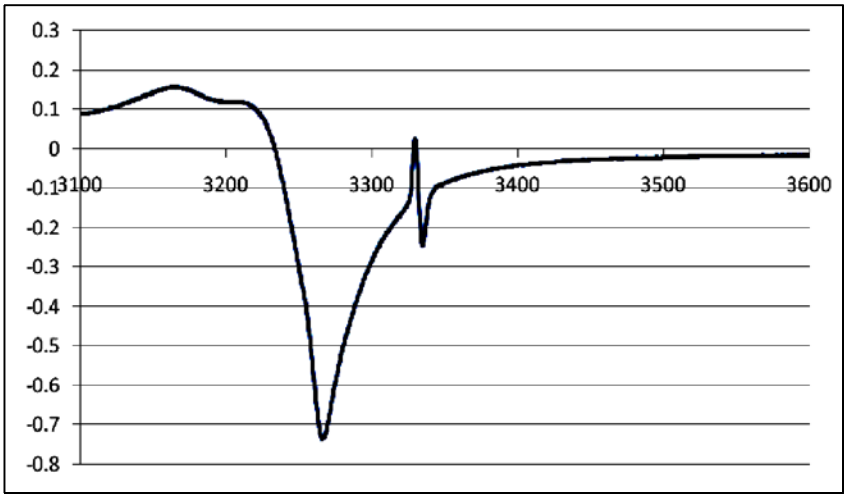

Fig. 3: EPR Spectrum

Powder X-ray analysis

Powder XRD diffractogram of Cu (II) complexes were recorded in the range 20-80° at wavelength 1.5447 Å. The diffractogram and associated data (Table 5) depict the 2θ value for each peak, relative intensity and inter-planar spacing (d-values). Major refluxes were used to determine corresponding interplaner distances. The unit cell of $[Cu(C_{16}H_{28}N_4)Cl_2]$ yielded values of lattice constants a = 9.130711, b = 8.659392, c = 7.325985 and unit cell volume 476.29°A^3. Also, in association with these cell parameters, the conditions such as a≠ b ≠c and $\alpha = \gamma = 90^\circ \neq \beta$ required for sample to be monoclinic were tested and found satisfactory. In conclusion the complexes Cu (II) have monoclinic crystal system[24-30].

Table 5: Millar indices and interprener distances

Complex	h k l	2θ observed	2θ observed	d
$[Cu(C_{14}H_{24}N_4)Cl_2]$	1 0 1	23.590	23.597	3.7684
	-1 0 2	24.776	24.788	3.5906
	-2 0 2	25.250	25.252	3.5242
	-2 1 2	27.300	27.301	3.2641
	2 2 0	31.497	31.517	2.8381
	3 0 0	35.846	35.852	2.5031
$[Cu(C_{16}H_{28}N_4)Cl_2]$	-3 2 1	36.479	36.475	2.4611
	-4 2 2	44.939	44.931	2.0155
	-4 2 3	48.919	48.402	1.8785
	-4 3 2	51.028	51.036	1.7884
	-4 2 4	56.326	56.328	1.6321
	-4 3 4	61.624	61.620	1.5038
	3 2 2	64.075	64.073	1.4521

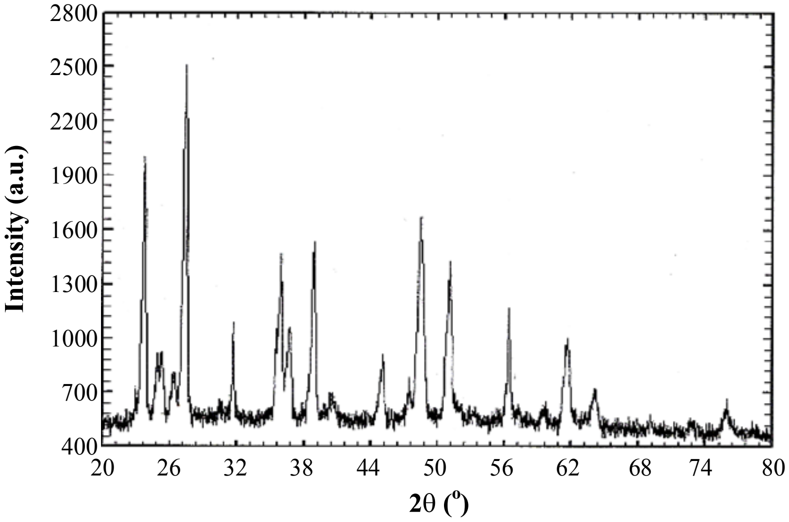

Fig. 4: XRD Pattern

The experimental density values of complexes were determined using specific gravity method and found to be 0.8590 g cm^{-3} for the Cu (II) complexes. Using the experimental density values ρ, the molecular weight of the complexes (M), Avogadro's number (N), and the volume of unit cell (V) and the number of molecules per unit cell (n) were calculated using the equation ρ = nM/NV and they were found to be one. With these values, the theoretical densities were computed and found to be 0.8619 g cm^{-3} for respective complexes. Comparison of experimental and theoretical density value shows good agreement within the limits.

Thermal analysis

On the TG curve of $[Cu(C_{16}H_{28}N_4)(NO_3)_2]$ complex, the mass loss of 6% (calculated 6.69%) in the range of 30-250°C indicates the removal of non-coordinated partial part of nitrate. An endothermic peak on DTA curve also corresponds to dehydration and partial loss of nitrate. The second step of the decomposition between 260-650°C with 80% mass loss (calcul. 80.81%) is attributed to the removal of the coordinated nitrate and organic moiety of the complex. The mass loss continued with slow decomposition of the remaining part upto 750°C corresponding to final residue of copper oxide.

Kinetic data

The kinetic and thermodynamic parameters viz, order of reaction (n), energy of activation (E_a), pre exponential factor (Z) etc. for non-isothermal decomposition of metal complexes were determined by the Metzer-Horowitz approximation method. The data obtained are given in Table 7. The calculated values of the activation energy of the complexes are relatively low, indicating the autocatalytic effect of the metal ion on the thermal decomposition of the complex. The negative activation entropy values suggest that the activated complex were more ordered than the reactants and that the reaction were slow. The more ordered nature may be due to polarization of bonds in activated state.

Antimicrobial activity

The *in vitro* antibacterial activities of synthesized complexes have been studied by disc diffusion method. The antibacterial activities were done at 100 µg /mL concentrations in DMF solvent using four bacterial strains (*S. typhi, S. aureus, E. coli and B. subtilis*) by the minimum inhibitory concentration (MIC) method[41]. These bacterial strains were incubated for 72 h at 27°C. Standard antibacterial (Cefodox and Linazoid) were used for comparison under similar conditions. Activity was determined by measuring the diameter of the zone of inhibition (mm) (Table 7 and 8).

Table 6: Thermal decomposition and kinetic parameters

Complex	DTA peak (°C)	Temp. range (°C)	Mass loss (%) observed (calculated)	Nature of decomposition	Order of reaction	ΔE Kg/mole	ΔS JK/mole	GKJ/ mole	Frequency factor Z
[$Cu(C_{14}H_{24}N_4)Cl_2$]	90	0-200	19.2 (19.5)	Water & chloride	1.9	16.804	-250.029	30.889	8.549×10^{-1}
	300	200-450	63.2 (63.92)	Ligand & chloride	0.5	153.80	-9.902	154.537	3.92×10^{12}
[$Cu(C_{16}H_{28}N_4)NO_3)_2$]	-	0-250	6 (6.69)	Nitrate	1.9	45.031	-194.584	55.830	6.63×10^{2}
	260	250-650	80 (80.81)	Nitrate & ligand	1.95	128.205	-16.673	129.243	1.45×10^{12}

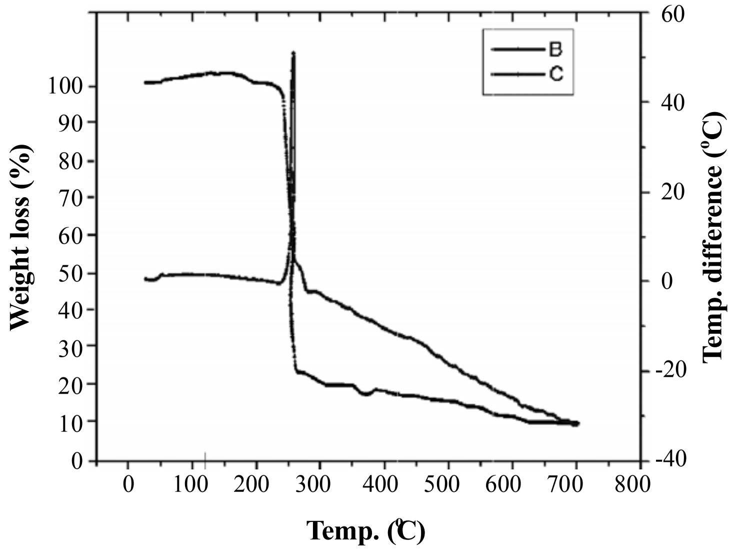

Fig. 5

Table 7: Antibacterial activity of complexes of type [$M(C_{16}H_{28}N_4)X_2$]

S. No.	Complex	Inhibition zone (mm)			
		S. typhi	***S. aureus***	***E. coli***	***B. subtilis***
1	$[Cu(C_{16}H_{28}N_4)Cl_2]$	10	10	11	8
2	$[Cu(C_{16}H_{28}N_4)(NO_3)_2]$	10	9	11	9
3	$[Cu(C_{16}H_{28}N_4)(CH_3COO)_2]$	12	8	9	8
4	$[Co(C_{16}H_{28}N_4)Cl_2]$	19	27	17	11
5	$[Co(C_{16}H_{28}N_4)(NO_3)_2]$	17	16	13	10
6	$[Co(C_{16}H_{28}N_4)(CH_3COO)_2]$	16	14	12	11
7	$[Ni(C_{16}H_{28}N_4)Cl_2]$	17	14	16	15
8	$[Ni(C_{16}H_{28}N_4)(NO_3)_2]$	16	15	12	11
9	$[Ni(C_{16}H_{28}N_4)(CH_3COO)_2]$	23	19	16	18
10	$[Zn(C_{16}H_{28}N_4)Cl_2]$	15	11	13	10
11	$[Zn(C_{16}H_{28}N_4)(NO_3)_2]$	13	11	11	8
12	$[Zn(C_{16}H_{28}N_4)(CH_3COO)_2]$	11	13	9	8
13	Cefodox	22	27	22	20
14	Linazoid	25	28	22	20

Table 7 indicated that Ni (II) and Co (II) complexes are more active against the bacterial strains *S. aureus* and *S. typhi* as compared to other bacterial strains. Cu (II) and Zn (II) complexes were found to be moderately active against all bacterial strains.

CONCLUSION

(i) Macrocyclic ligand complexes of transition metal ions are tetradentate in nature.

(ii) Macrocyclic ligand complexes decompose above 200°C suggesting good thermal stability.

(iii) Macrocyclic ligand complexes are insoluble in organic solvents, freely soluble in DMSO/DMF. Molar conductivity of complexes in DMSO suggests non electrolytic nature.

(iv) Magnetic moments suggest octahedral environment around metal ion.

(v) Infrared spectra suggest involvement of nitrogen in coordination.

(vi) Solid state EPR spectral studies indicate isotropic and anisotropic behavior, suggesting the line, width is independent of temperature. Ni (II) complexes shows sharp peaks where as Cu (II) complexes shows broad peaks indicating distortion and g value indicate sufficient covalent nature of metal ligand bond. Small G value of exchange interaction coupling constant suggest strong exchange interaction and local tetragonal axes are misaligned.

(vii) Thermal analysis of complexes gives information regarding decomposition pattern of metal ligand ratio and also suggests presence of lattice water molecules. Decomposition of complexes at higher temperature suggests thermal stability. Non-isothermal kinetic parameter suggests that decomposition process follow second order kinetics and activated complex is more ordered.

(viii) Powder X-ray diffraction studies of complexes reveal monoclinic system and lattice type P2/M.

(ix) From above observations, it is concluded that macrocyclic ligand complexes has undergone structural rearrangement to acquire stability and coordinated to metal through free donor atoms.

REFERENCES

1. D. P. Singh, R. Kumar, V. Malik and P. Tyagi, J. Enz. Inhib. Med. Chem., **22**, 177 (2007).
2. R. V. Singh and A. Chaudhary, J. Inorg. Biochem., **98**, 1712 (2004).
3. L. F. Lindoy, The Chemistry of Macrocyclic Ligand Complexes, Cambridge University Press, Cambridge (1989).
4. E. C. Constable, Coordination Chemistry of Microcyclic Compounds, Oxford University Press, Oxford (1999).
5. D. P. Singh, R. Kumar, V. Malik and P. Tyagi, Transition Met. Chem., **32**, 1051 (2007).
6. A. D. Watson and S. M. Rockladge, in C. B. Higgins (Ed.), Magnetic Resonance Imaging of the Body, Raven Press, New York (1992).
7. J. G. Muller, X. Chen, A. C. Dadiz, S. E. Rokita and C. J. Burrows, Pure and Appl. Chem., **65**, 545 (1993).

8. J. Liu, T. B. Lu, H. Deng, L. N. Ji, L. H. Qu and H. Zhou, Transition Met. Chem., **28**, 116 (2003).
9. D. P. Singh, R. Kumar, M. Kamboj and K. Jain, Acta Chim. Slov., **56**, 780 (2009).
10. A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam (1984).
11. R. N. Prasad and M. Mathur, J. Indian Chem. Soc., **83**, 1208 (2006).
12. Q. Zeng. J. Sun, S. Gou, K. Zhou, J. Fang and H. Chen, Transition Met. Chem., **23**, 71 (1998).
13. A. K. Singh, R. Singh and P. Saxena, Transition Met. Chem., **29**, 867 (2004).
14. L. K. Gupta and S. Chandra, Transition Met. Chem., **31**, 368 (2006).
15. D. Singh, K. Kumar, R. Kumar and J. Singh, J. Serb. Chem. Soc., **75(2)**, 217 (2010).
16. O. S. M. Nasman, Asian. J. Chem, **19**, 1231 (2007).
17. O. S. M. Nasman, Transition Met. Chem., **33**, 285 (2007).
18. N. Raman and J. Joseph, Russian J. Inorg. Chem., **55(7)**, 1064 (2010).
19. R. K. Ray and G. R. Kauffman, Inorg. Chim. Acta, **173**, 207 (1990).
20. N. E. Wakiel, Y. E. Sayed and M. Gaber, J. Mol. Struct., **1**, 1001 (2011).
21. K. K. Narang and V. P. Singh, Transition Met. Chem., **21**, 507 (1996).
22. R. S. Joseyphus and M. Sivasankaran Nair, Arab. J. Chem., **3**, 195 (2010).
23. A. S. El-Tabl, Transition Met. Chem., **21**, 428 (1996).
24. D. Kivelson and R. Neiman, J. Chem. Phys., **35**, 149 (1961).
25. V. A. Shelke, S. M. Jadhav, V. R. Patharkar, S. G. Shankarwar, A. S. Munde and T. K. Chondhekar, Arab. J. Chem. (2010).
26. A. S. Munde, A. N. Jagdale, A. N. Jadhav and T. K. Chondhekar, J. Korean, Chem. Soc., **53**, 4 (2009).
27. C. S. Dilip, V. Thangaraj and A. Paul Raj, Arab. J. Chem. (2011).
28. A. Lehleh, A. Beghidja, C. Beghidja, O. Mentre, R. Welter and C. R. Chimie., **14**, 462 (2011).
29. A. C. Kathalikkattil, K. K. Bisht, P. S. Subramanian and S. Eringathodi, Polyhedron, **29**, 1801 (2010).
30. A. Beghidja, R. Walter, P. Rabu and G. Rogez, Inorg. Chem. Commun., **11**, 1088 (2008).

31. A. S. Munde, A. N. Jagdale, S. M. Jadhav and T. K. Chondhekar, J. Serbian Chem. Soc., **75(3)**, 349 (2010).
32. A. S. El-Tabl, F. A. El-Saied, W. Plass and A. N. Al-Hakimi, Spectrochimica Acta Part A, **(71)**, 90 (2008).
33. A. Lehleh, A. Beghidja, C. Beghidja, O. Mentre, R. Welter and C. R. Chimie, **14**, 462, 70 (2011).
34. S. M. Abdullah, M. A. Zayed and G. G. Mohamed, Arab. J. Chem., **3**, 103 (2010).
35. R. A. Shaikh, M. Y. Wani, S. Shaikh, L. A. Khan and A. A. Hashmi, Arab. J. Chem. (2011).
36. A. S. El-Tabl and S. M. Imam, Transition Met. Chem., **22**, 259 (1997).
37. M. Gaber and M. M. Ayad, Thermochimica Acta, **176**, 21 (1991).
38. H. H. Horowitz and G. Metzger, Anal. Chem., **35**, 1464 (1963).
39. K. N. Thimmaiah, W. D. Lioyd and G. T. Chandrappa, Inorg. Chim. Acta, **106**, 81 (1985).
40. M. M. Omar, G. G. Mohamed and A. A. Ibrahim, Spectrochimica Acta, **73**, 358 (2009).
41. A. K. Sadana, Y. Mirza, K. R. Aneja and O. Prakash, Eur. J. Med. Chem., **38**, 533 (2003).

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