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Spectral Characterization and In Vitro Screening of cyclam based Unsymmetrical Binuclear Copper (II) and Nickel (II) Complexes

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ABSTRACT Macrobicyclic binuclear copper (II) and nickel (II) complexes were synthesized and characterized by elemental and spectral analysis. ‘Red shift’ in λ_{\max} value is observed due to increase in the chain length of imine compartment. ESR spectrum confirms the anti ferromagnetic interaction between the two ligands copper ions with nickel ions. This macrocyclic compound further applies for antimicrobial study. For testing, In-vitro studies have been done for antimicrobial properties using the different human pathogenic bacteria Staphylococcus aureus, Bacillus subtilis, Pseudomonas aeruginosa and Escherichia coli. Also, Antifungal activity of all the complexes test against the phytopathogenic fungus Candida albicans and Aspergillus niger show some antifungal activity, comparable with N-substituted tetraazamacrocycles. Both, antifungal and antimicrobial test given significant result for the macrobicyclic binuclear copper (II) and nickel (II) complexes.

KEYWORDS: Copper and nickel complexes, spectral and In vitro screening, Antifungal test, antimicrobial test.

I. INTRODUCTION

Macrocyclic complexes bearing pendant-arm have amassed interest in recent past. Compared to unsubstituted macrocycles, addition of pendant functional groups significantly alter the properties of complex [1-2]. These complexes have focused on applications to MRI contrasting agents, DNA cleavers, luminescent probes, radioisotopes and medicines [3]. Modern reviews have inspected pendant-arm macrocycles as prototype for biological molecules which increases the selectivity of the ligand for a given ion and also modulates the property of the complex [4]. The trans-dioxocyclam was recognized recently as a useful trans-‘autodiprotected’ macrocycle for the synthesis of 1, 8-disubstituted cyclam derivatives [5-7]. The present study is focused on the preparation of macrobicyclic binuclear copper (II) and nickel (II) complexes. Their spectral characteristics and antimicrobial activity of the complexes are rationalized.

II. METHODOLOGY

MATERIALS: 5-methylsalicylaldehyde [8], 3-chloromethyl-5-methylsalicylaldehyde [10] and 1,4,8,11-tetraazacyclotetradecane 5,12-dione [9-10], 1,8,[(N,Nbis(3-formyl-2-hydroxy-5-methyl)benzyl)]-5,12-dioxo 1,4,8,11-tetraazacyclotetradecane [11] (PC-1) were prepared by literature methods. Acetonitrile, methanol and DMF were purchased from Qualigens.

III. SYNTHESIS OF THE MACROBICYCLIC BINUCLEAR COMPLEXES

1. Macrobicyclic binuclear copper(II) complexes

A methanolic solution of PC-1 (0.188 g, 0.00036 mol), copper(II) perchlorate hexahydrate (0.133 g, 0.00036 mol), 1,2-diaminoethane (0.022 g, 0.00036 mol) and triethylamine (0.072 g, 0.00072 mol) were refluxed. After an hour copper (II) perchlorate (0.133 g, 0.00036 mol) was added and refluxed in water bath for 24 h. The solution was filtered and evaporated to get the product.



[Cu₂L^{1a}] Dark green compound .Yield: 0.27 g (55%), Analytical data for C₃₀H₃₆N₆O₄Cu₂, Calculated (%): C,53.64; H,5.40; N,12.51; Cu,18.92,Found (%): C,53.62; H,5.37; N,12.49; Cu,18.90,FAB mass (m/z (%): [Cu₂L^{1a}] 745 ,Conductance (Λ_m, S cm² mol⁻¹) in DMF: 17, IR (KBr) (ν/cm⁻¹): 1618 [s, ν(C=N)],λ_{max}, nm (ε, M⁻¹ cm⁻¹) in DMF: 990 (45), 600 (114), 410, 345 (10 7400), 260 (14 320). ,g: 2.01, μ_{eff}: 1.47 B.M.

The complexes [Cu₂L^{1b}], [Cu₂L^{1c}], [Cu₂L^{1d}], and [Cu₂L^{1e}] were synthesized by following the above procedure using 1,3-diaminopropane(0.071g,0.00036mol),1,4-diaminobutane (0.084 g, 0.00036 mol), 1,2-diaminobenzene (0.22 g, 0.00036 mol) and 1,8-diaminonaphthalene (0.15 g, 0.00036 mol) respectively, instead of using 1,2-diaminoethane.

[Cu₂L^{1b}]: Dark green compound. Yield: 0.033 g (55%), Analytical data for C₃₁H₃₈N₆O₄Cu₂: Calculated (%): C,54.30; H, 5.58; N,12.25; Cu, 18.53,Found (%) : C,54.28; H, 5.57; N,12.23; Cu, 18.52, Conductance (Λ_m, S cm² mol⁻¹) in DMF: 11. IR(KBr)(ν/cm⁻¹): 1623 [s ν(C=N)] ,λ_{max}, nm (ε, M⁻¹ cm⁻¹) in DMF: 1000 (32), 610 (128) 380 (10 400), 280 (15 650), 260 (22 100). g: 2.03, μ_{eff}: 1.45 B.M.

[Cu₂L^{1c}]: Dark green compound. Yield: 0.03 g (52%) , Analytical data for C₃₂H₄₀N₆O₄Cu₂: Calculated (%): C,54.92; H, 5.76; N,12.01; Cu, 18.16, Found (%): C,54.91; H, 5.74; N,12.00; Cu, 18.14, Conductance (Λ_m, S cm² mol⁻¹) in DMF: 13, IR(KBr)(ν/cm⁻¹): 1620 [s, ν(C=N)], λ_{max}, nm (ε, M⁻¹ cm⁻¹) in DMF: 1050 (28), 650 (224), 395 (12 130), 340 (15 680), 300 (19 200) ,g: 2.10, μ_{eff}: 1.31 B.M.

[Cu₂L^{1d}]: Dark green compound. Yield: 0.19 g (53%) , Analytical data for C₃₄H₃₆N₆O₄Cu₂: Calculated (%): C,58.73; H,5.04; N,11.68; Cu, 17.65, Found (%): C,58.71; H,5.02; N,11.66; Cu, 17.64, Conductance (Λ_m, S cm² mol⁻¹) in DMF: 15, IR(KBr) (ν/cm⁻¹): 1629 [s, ν(C=N)], λ_{max}, nm (ε, M⁻¹ cm⁻¹) in DMF: 682 (168), 375 (12 860), 275 (17 420), g: 2.11, μ_{eff}: 1.47 B.M.

[Cu₂L^{1e}]: Dark green compound. Yield: 0.42 g (49%), Analytical data for C₃₈H₃₈N₆O₄Cu₂., Calculated (%): C,59.29; H, 4.97; N,10.92; Cu, 16.51 ,Found (%): C,59.27; H, 4.95; N,10.91; Cu, 16.49, FAB mass (m/z (%): [Cu₂L^{5e}] 769 , Conductance (Λ_m, S cm² mol⁻¹) in DMF: 19, IR (KBr) (ν/cm⁻¹): 1625 [s, ν(C=N)],λ_{max}, nm (ε, M⁻¹ cm⁻¹) in DMF: 718 (179), 383 (13 600), 276 (17 800), g: 2.10, μ_{eff}: 1.53 B.M.

2. Macrobicyclic binuclear nickel(II) complexes

[Ni₂L^{1a}]: A methanolic solution of PC-1 (0.188 g, 0.00036 mol) ,nickel(II) perchlorate hexahydrate (0.131 g, 0.00036 mol) ,1,2-diaminoethane (0.022 g, 0.00036 mol) and triethylamine (0.072 g, .00036 mol) were refluxed. One equivalent of nickel (II) perchlorate (0.131 g, 0.00036 mol) was added after an hour and refluxed for 24 h. The solution was filtered and evaporated to get the product.

Dark green compound: Yield: 0.10 g (58%) , Analytical data for C₃₀H₃₆N₆O₄Ni₂: , Calculated (%): C,54.42; H,6.02.; N,12.69; Ni, 17.73, Found (%): C,54.40; H,6.01; N,12.66; Ni, 17.71, Conductance (Λ_m, S cm² mol⁻¹) in DMF: 13 , IR (KBr) (ν/cm⁻¹): 1630 [s, ν(C=N)],λ_{max}, nm (ε, M⁻¹ cm⁻¹) in DMF: 1045 (25), 750 (78), 655 (127),

The complexes [Ni₂L^{1b}], [Ni₂L^{1c}], [Ni₂L^{1d}], and [Ni₂L^{1e}] were synthesized by following the above procedure using 1,3-diaminopropane (0.15 g, 0.002 mol), 1,4-diaminobutane (0.18 g, 0.002 mol), 1,2-diaminobenzene (0.22 g, 0.002 mol) and 1,8-diaminonaphthalene (0.32 g, 0.002 mol) respectively, instead of using 1,2-diaminoethane.



[Ni₂L^{1b}]: Dark green compound, Yield: 0.015 g (63%), Analytical data for C₃₁H₃₈N₆O₄Ni₂: Calculated (%): C,55.07; H, 5.66; N,12.43; Ni, 17.37, Found (%): C,55.05; H, 5.64; N,12.41; Ni, 17.35, Conductance (Λ_m, S cm² mol⁻¹) in DMF: 18 ,IR (KBr) (ν/cm⁻¹): 1634 [s, ν(C=N)], λ_{max}, nm (ε, M⁻¹ cm⁻¹) in DMF: 1000 (34), 750 (168), 394 (12 200), 305 (17 300)

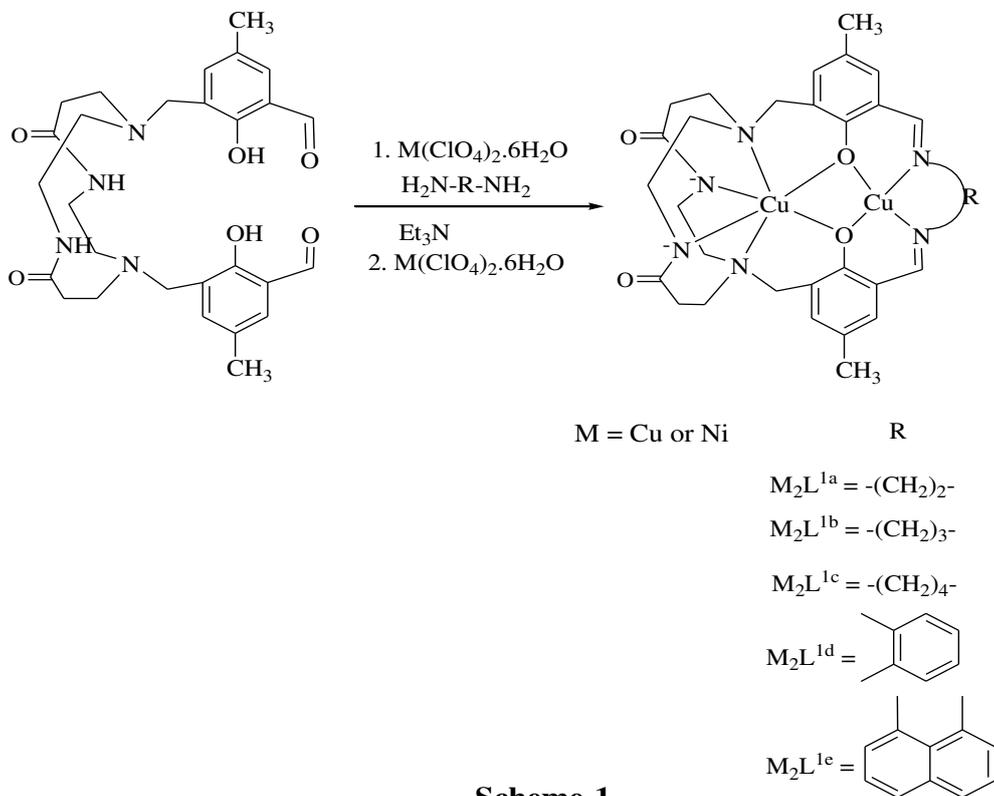
[Ni₂L^{1c}]: Dark green compound, Yield: 0.43 g (52%), Analytical data for C₃₂H₄₀N₆O₄Ni₂: Calculated (%): C,55.69; H, 5.84; N,12.18; Ni, 17.01, Found (%): C,55.67; H, 5.82; N,12.17; Ni, 17.00, FAB mass (m/z) (%): [Ni₂L^{1c}] 664, Conductance (Λ_m, S cm² mol⁻¹) in DMF: 15, IR (KBr) (ν/cm⁻¹): 1637 [s, ν(C=N)], λ_{max}, nm (ε, M⁻¹ cm⁻¹) in DMF: 1060 (32), 820 (85), 670 (120), 410 (11 800), 342 (21 100)

[Ni₂L^{1d}]: Dark green compound, Yield: 0.1 g (57%), Analytical data for C₃₄H₃₆N₆O₄Ni₂: Calculated (%): C,57.51; H,5.10; N,11.83; Ni,16.53 , Found (%): C,57.49; H,5.09; N,11.81; Ni, 16.52, Conductance (Λ_m, S cm² mol⁻¹) in DMF: 16, IR (KBr) (ν/cm⁻¹): 1643 [s, ν(C=N)], λ_{max}, nm (ε, M⁻¹ cm⁻¹) in DMF: 1030 (117), 742(163), 605 (180), 375 (12,800), 277 (17,000).

[Ni₂L^{1e}]: Dark green compound ,Yield: 0.17 g (59%), Analytical data for C₃₈H₃₈N₆O₄Ni₂·, Calculated (%): C,60.04; H,5.57; N,11.05; Ni, 15.45, Found (%): C,60.02; H,5.56; N,11.03; Ni, 15.43, Conductance (Λ_m, S cm² mol⁻¹) in DMF: 17, IR (KBr) (ν/cm⁻¹): 1650 [s, ν(C=N)], λ_{max}, nm (ε, M⁻¹ cm⁻¹) in DMF: 1037 (123), 754 (169), 613 (187), 383 (13, 600), 277 (17, 800).

IV. RESULTS AND DISCUSSION

Macrobicyclic binuclear copper(II) and nickel(II) complexes were prepared by Schiff base condensation of the precursor compound with aliphatic or aromatic diamines.



Scheme-1



1. Spectral studies

The IR spectrum of (PC-1) shows a sharp band at 1664 cm⁻¹ indicating CHO group. The band at 2918 cm⁻¹ is an indicative of νN-H stretching in the ligands. The OH group in the ligand shows a broad peak at 3417 cm⁻¹ which is shown in Fig 1. The disappearance of peak around 3390 cm⁻¹ show that the OH group is deprotonated due to complexation with metal ion. All the complexes show a sharp band in the region of 1610-1637 cm⁻¹ due to the presence of ν(C=N) in the complexes. The complete disappearance of C=O (aldehyde group) peak and the appearance of new strong C=N peak indicates the effective Schiff-base condensation between the aldehyde group of (PC-1) and appropriate diamines [12]. Further, the appearance of bands in the region of 1530-1537 cm⁻¹ in all the complexes suggests phenoxide bridging with the metal ions [13] as shown in Fig 2.

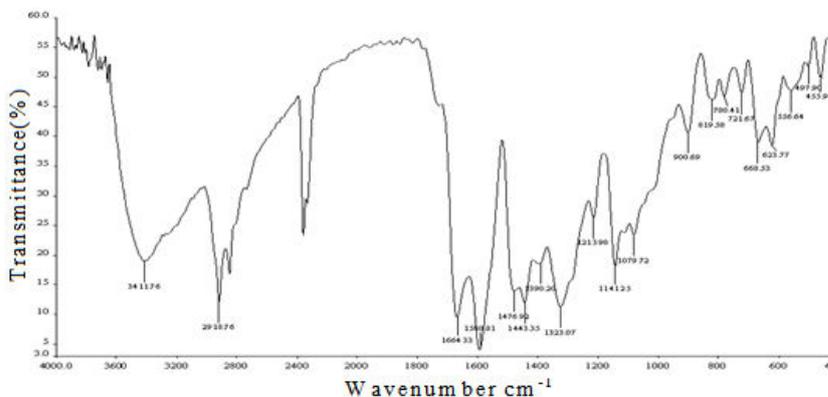
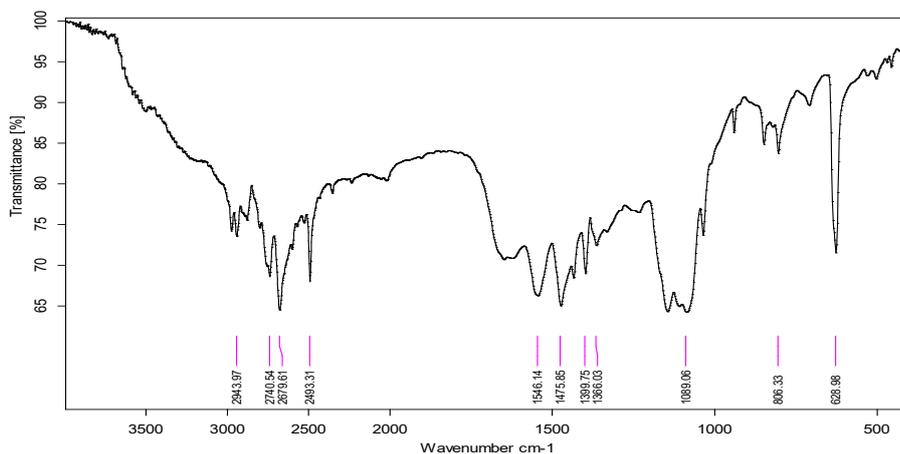


Fig 1. FT IR Spectrum of PC-1



The FAB mass spectrum recorded for complex [Cu₂L^{1c}] shows the presence of dicopper core in the complex. A molecular ion peak at m/z = 769 are assignable to the [Cu₂L^{1c}]⁺ ion .The appearances of many peaks are due to presence of isotopic atoms. The electronic spectra of the complexes exhibit peaks in the range of 250-340nm attributed to (π-π*) transition. An intense peak in the range of 380-420 nm is due to ligand-to-metal charge transition. The binuclear copper (II) complexes show the d-d transition in the range of 600-615 nm and a solder around 1050 nm. The d-d transition for the binuclear nickel(II) complexes show three main bands in the region of 550-1100 nm, which is characteristic of Ni²⁺ in the 6/4 coordination environment [14]. An increase in λ_{max} (red shift) of the d-d transition of



copper (II) ion in the complexes of the ligands L^{1a} to L^{1c} and L^{1d} to L^{1e} indicates that the coordination geometry around the copper atom is more distorted. This may be due to the flexibility of the macrocyclic ring on increasing the chain length of the imine compartment, which causes more distortion of the geometry [15]. The same trend was also observed for the nickel (II) complexes. The ESR spectra of the binuclear copper (II) complexes were obtained. A broad spectrum with no hyperfine splitting was obtained for the binuclear copper (II) complexes with $g=2.10-2.13$ indicating the presence of an antiferromagnetic interaction [16] between the two copper ions as shown in the Fig 3.

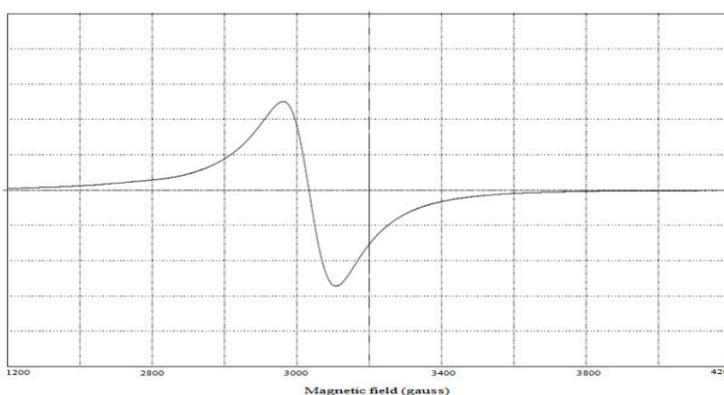


Fig 3. ESR spectrum of $[Cu_2L^{1a}]$

2. In vitro studies

In vitro activities of the complexes were tested by the cup plate method using nutrient agar. The complexes have been screened for antibacterial activity against the humanpathogenic bacteria Staphylococcus aureus, Bacillus subtilis, Pseudomonaas aeruginosa and Escherichia coli. All the complexes show reliable potency against the tested pathogenic bacteria, comparable with N- substituted tetraazamacrocycles [24]. Antifungal activity of all the complexes against the phytopathogenic fungus Candida albicans and Aspergillus niger show some antifungal activity, comparable with N-substituted tetraazamacrocycles²⁵. Complexes containing aromatic diimines show higher activity than complex containing aliphatic diimines. The presence of cyclam unit in the molecule apparently improves the activity of the complexes. The screening data of the inhibition of the bacteria and fungi are given in Fig 4 & Table 1.

Table 1: Antimicrobial activity of binuclear complexes

Antibacterial activity	Antifungal activity (zone of inhibition diameter in nm)						
	Complex	S.a	B.s	P.a	E.c	C.a	A.n
	$[Cu_2L^{1a}]$	14	15	16	13	10	11
	$[Cu_2L^{1b}]$	16	16	17	14	11	12
	$[Cu_2L^{1c}]$	17	16	17	14	11	11
	$[Cu_2L^{1d}]$	18	18	18	15	12	13
	$[Cu_2L^{1e}]$	19	20	19	16	13	13
	$[Ni_2L^{1a}]$	16	15	14	12	11	10
	$[Ni_2L^{1b}]$	17	16	16	14	12	11
	$[Ni_2L^{1c}]$	17	18	17	13	12	11
	$[Ni_2L^{1d}]$	19	19	19	14	13	12
	$[Ni_2L^{1e}]$	20	20	21	15	13	13

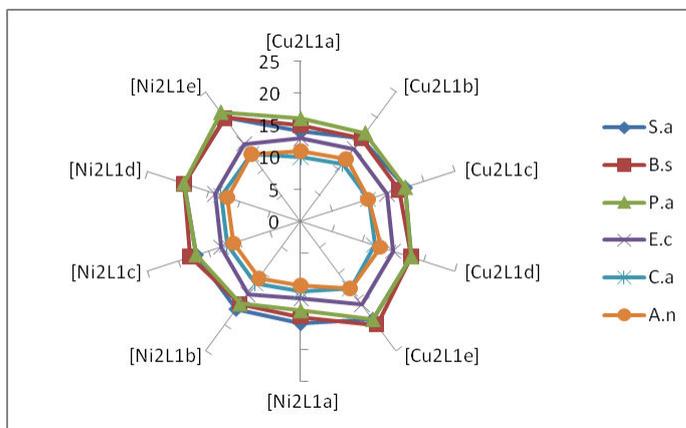


FIG.4. ANTIMICROBIAL ACTIVITY OF BINUCLEAR COMPLEXES

V. CONCLUSION AND FUTURE WORK

The reduction potential of all the binuclear complexes decreases while increasing the chain length and N-alkylation due to the distortion in the geometry. Based on the conclusion, it is inferred that a small variation in the ligand framework such as changing the chain length of the imine compartment and increasing N-alkylation of the amine compartment affects the spectral and In vitro screening of the complexes.

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