

**SYNTHESIS AND CHARACTERISATION OF Co(II), Ni(II) AND Cu(II)
COMPLEXES OF 12-MEMBERED MACROCYCLIC LIGANDS**

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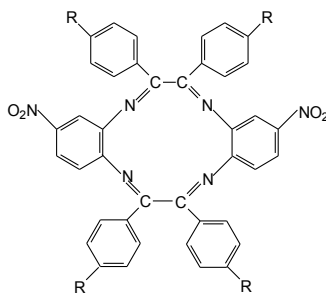
ABSTRACT: Complexes of Co(II), Ni(II) and Cu (II) with two 12-membered tetradentate macrocyclic ligands derived from the condensation of diketones with diamines have been prepared. All the complexes have been characterized by elemental analyses, conductance measurements, magnetic moment, infrared, ESR and electronic spectral studies. The complexes were found to have composition $MLCl_2$. On the basis of spectral and magnetic studies octahedral geometry have been assigned for these complexes. These complexes have been screened *in vitro* for their possible antimicrobial activity.

Keywords: Synthesis, Copper, Nickel, Cuprous and Macrocyclic ligands

INTRODUCTION

The tetraaza macrocyclic ligands and their metal complexes have attracted much interest of the coordination chemists, followed by many works on the controlled template and metal free template synthesis of macrocyclic species¹. Macrocyclic complexes of the transition metals are studied as models for the active sites of the certain naturally occurring enzymes². Macrocycles with delocalized structures have also attracted attention as components of molecular electronics devices as building blocks of electro active networks and for their molecular recognition properties³.

A large number of synthetic macrocyclic complexes have been obtained by the condensation of di or polyamines with aldehydes or ketones^{4,6}. In this paper we wish to report the synthesis and spectral studies of Co(II), Ni(II) and Cu(II) complexes of 12-membered tetra dentate macrocyclics ligands di-(2-nitrobenzo)-(b,h)-2,3,8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene (L₁) and di-(2-nitrobenzo)-(b,h)-2,3,8,9-tetra(methoxyphenyl)-1,4,7,10-tetraazacyclo do deca-1,3,7,9-tetraene (L₂).



L₁: R=H, L₂: R= OCH₃

Experimental

All the chemicals and solvents used were of AR grade. Salicylaldehyde was obtained from Siscochem. Industries. The metal salts were purchased from commercial sources. Metal contents were estimated using standard methods⁷.

IR spectra of the compounds were recorded on a Beckman IR-20 spectrophotometer in the region 4000-250cm⁻¹. ¹H NMR spectra were recorded on a Perkin-Elmer 90 MHz spectrometer. The electronic spectra were recorded on an Elico SL 159 spectrophotometer in the 200-1000nm ranges in DMF solution (10⁻³). Elemental analyses were obtained HERAEUS C, H, N-O rapid analyzer. E.S.R measurements were carried out on a VARAN E-109 GHz. The experiment was carried by taking DPPH as the reference with the field set at 3200 Gauss. Magnetic susceptibilities were determined by the faraday method using a Model 300 Lewis Coil Force Magnetometer of one tesla field strength at room temperature. The instrument being calibrated with Hg [Co (SCN)₄]⁸.

Preparation of ligands

The ligands were prepared by the condensation of diketone with diamines in methanol. A mixture of 2-nitro-p-phenylenediamine (0.01mol) in methanol (25ml) and the methanol solution of 1,2-diphenoldione / 1,2-di(methoxyphenyl)-1,2-dione (0.01mol) and few drops of acetic acid (because the reaction was taking place in acidic medium) was refluxed for 8 hours. The resulting solution was kept overnight at room temperature. A yellow solid was separated out, this was filtered, washed with methanol and dried over P₄O₁₀ in *vacua*.

For L₁, found: C, 69.92, N, 12.22, H, 3.75%

Calculated: C, 69.97, N, 12.24, H, 3.79%

Yield: 1.87g (80%); mp: 132-133°C

For L₂, found: C, 65.50, N, 19.85, H, 3.421%

Calculated: C, 65.47, N, 19.79, H, 4.19%

Yield: 1.75g (79%); mp: 147-148°C

Preparation of complexes:

A mixture of hot ethanol solution (50ml) of the metal chloride salts (0.002mol) and the ethanol solution of L₁ / L₂ (0.002mol) was refluxed for 8 hours. The contents were cooled at room temperature for a day after reducing the volume of the solution to half, which lead to the precipitation of the complexes. The complexes were filtered, washed with hot ethanol and dried in air

RESULTS AND DISCUSSION

The analytical and physical data of the compounds are given in Table-1. The results of elemental analyses of the complexes (Table-1) correspond to stoichiometry for metal:ligand in 1:1 molar ratios. Molar conductance measurements of these complexes in DMF correspond to nonelectrolytes. The band in the region 1640-1590cm⁻¹ is assigned to HC=N group, indicates that the condensation between amino group of o-phenylenediamine and diketones. The band due to ν_(C=N) appears in the region of 1620-1590cm⁻¹ as a high intensity band in the complexes, indicating that the C=N group is involved in coordination of metal ions through nitrogen. In complexes the bands due to C=N group are shifted to lower frequency by 30-20cm⁻¹. The magnetic moment of the Co(L₁), Ni(L₁) and Cu(L₁) are 4.82, 3.15 and 1.80 B.M respectively. The μ_{eff} values are well within the range known for six coordinate octahedral geometry (Table-1).

Similarly magnetic moment for the Co (L₂), Ni (L₂) and Cu(L₂) are 4.75 3.25 and 1.82 B.M. respectively⁹⁻¹². The electronic spectra of the complexes recorded in DMF display three bands at 11760-15620cm⁻¹(v₁), 15600-19230cm⁻¹(v₂) and 20830-22720cm⁻¹ (v₃) (Table 2). Six coordinate complexes with Oh symmetry show three spin allowed bands. These bands are due to ⁴T_{1g}(F)→⁴T_{2g}(F) (v₁), ⁴T_{1g}(F)→⁴A_{2g}(F)(v₂) and ⁴T_{1g}(F)→⁴T_{1g}(P)(v₃) for cobalt complexes, ³A_{2g}→³T_{2g}(v₁), ³A_{2g}→³T_{1g}(F) (v₂) and ³A_{2g}→³T_{1g}(P)(v₃) for nickel complexes and ²B_{1g}→²A_{1g}(v₁), ²B_{1g}→²B_{1g}(v₂) and ²B_{1g}→²E_g(v₃) for copper complexes¹³. Various ligand field parameters have been evaluated for cobalt and nickel complexes (Table2).

Table-1 : Physical data, elemental analyses, magnetic measurements and molar conductance of metal complexes with ligands HL¹, HL²and HL³

Ligands/ Complexes ^a	Colour M.P(°C)/ Yield(%)	Metal (%) Found/ (Calcd),M	μ _{eff} (B.M)	Molar Cond. mho cm ² mol ⁻¹
Co(L ₁)Cl ₂ Co(C ₄₀ H ₂₆ N ₆ O ₄)Cl ₂	Brown 192(65)	8.87 (8.81)	4.82	40.00
Ni(L ₁)Cl ₂ Ni(C ₄₀ H ₂₆ N ₆ O ₄)Cl ₂	Pink 195(62)	8.83 (8.77)	3.15	32.20
Cu (L ₁)Cl ₂ Cu(C ₄₀ H ₂₆ N ₆ O ₄)Cl ₂	Yellow 204(65)	9.39 (9.43)	1.80	43.40
Co (L ₂)Cl ₂ Co(C ₄₄ H ₃₈ N ₆ O ₈) Cl ₂	Brown 215(68)	8.41 (8.45)	4.75	30.85
Ni(L ₂)Cl ₂ Ni(C ₄₄ H ₃₈ N ₆ O ₈) Cl ₂	Brown 225(62)	8.37 (8.43)	3.25	45.30
Cu(L ₂)Cl ₂ Cu(C ₄₄ H ₃₈ N ₆ O ₈) Cl ₂	Yellow 220(65)	9.12 (9.06)	1.82	35.20

^aAll the ligands and their complexes showed satisfactory C, H and N analysis.

Table-2 : Electronic spectra and ligand field parameters of complexes

Complex	v ₁ (Cm ⁻¹)	v ₂ (Cm ⁻¹)	v ₃ (Cm ⁻¹)	D _q (Cm ⁻¹)	B ₁ (Cm ⁻¹)	β	LFSE
Co(H ₂ L ¹)	12425	17650	21515	5223	1562.05	1.60	18.00
Ni(H ₂ L ¹)	11762	15875	22225	4112	1715.00	1.64	12.99
Cu(H ₂ L ¹)	12030	15622	22740	-	-	-	-
Co(H ₂ L ²)	13510	19235	20836	5714	1520.10	1.59	15.40
Ni(H ₂ L ²)	14715	16133	22720	1427	2310.75	2.23	5.85
Cu(H ₂ L ²)	15622	17235	21745	-	-	-	-

The nephelauxetic parameter, β is readily obtained using the relation β=B(complex)/B(free ion), indicate that complex under study have appreciable covalent character. The value of D_q could be evaluated with the help of the curve transition energies versus D_q by Orgel using the energy level due to transitions ⁴T_{1g}(F) →⁴A_{2g}(F) and ³A_{2g}→³T_{1g}(P) respectively. The parameter B was evaluated by using the methods reported earlier¹⁴⁻¹⁵.

The ESR spectra of the copper complexes as polycrystalline sample have been recorded at room temperature, (ESR chart was calibrated with DPPH). The polycrystalline samples gives one broad isotropic signal centered approximately at 2.023 and 2.040 for the complex Cu (L₁). The observed g values of the Cu (L₁) complex as follows $g_{\parallel}=2.058$, $g_{\perp}=2.014$, $g_{av}=2.028$ and $G = 4.19$. While for Cu ((L₂), $g_{\parallel} = 2.052$ $g_{\perp} = 2.024$ $g_{av} = 2.030$ and $G = 4.22$. The isotropic g values have been calculated Kneubuhl's methods¹⁶ and methods reported earlier. $G = (g_{\parallel}-2)/(g_{\perp}-2)$ which measures the exchange interaction between copper centers in a polycrystalline solid has been calculated. According the Hathaway¹⁷ if the G value is greater than 4, the exchange interaction is negligible, while a value of G less than 4 indicates a considerable exchange in the solid complexes. As $G=4.13$ and $G= 4.20$ for Cu (L₁) and Cu (L₂) respectively, indicates the exchange interaction is negligible.

Antimicrobial Activity:

The antimicrobial activity of the ligands L₁ and L₂ and their metal complexes were determined by agar cup-plate method¹⁸⁻¹⁹. The antibacterial activity against *Escherichia coli* and *Pseudomonas aeruginosa* and antifungal activity against *Aspergillus niger* and *Candida albicans*, were screened by the ligands and their metal complexes. The medium was prepared as per the instructions of the manufacturer of dry Mueller Hinton agar powder (Hi-Media). The test ligands and their metal complexes were dissolved in dimethylsulphoxide (DMSO) at a concentration of 100µg/ml. Ciproflaxacin (100µg/ml) in DMSO was used as reference standard for antibacterial and flucanazole (100µg/ml) in DMSO was used as reference standard for antifungal activity. The solvent control (only DMSO) was also maintained throughout the experiment. The zones of inhibition are reported in Table-3

Table-3: Antibacterial and antifungal activity data of the ligands and their complexes (Zone of inhibition in mm*)

Ligands/ Complexes	Antibacterial		Antifungal	
	E.coli	P.aeruginosa	A.niger	C.albicans
HL1	12	14	11	09
Co(L1)2	14	17	13	12
Ni(L1)2	15	18	14	12
Cu(L1)2	20	19	18	16
HL2	11	13	10	10
Co(L2)2	14	16	14	13
Ni(L2)2	14	17	13	14
Cu(L2)2	21	22	17	17
HL3	12	14	12	01
Co(L3)2	13	16	14	13
Ni(L3)2	15	15	14	15
Cu(L3)2	22	23	18	18
Ciproflaxacin	27	30	—	—
Flucanazole	—	—	24	23
DMSO	00	00	00	00

*Diameter of cup is 6 mm.; *E.coli*: *Escherichia coli*, *P.aeruginosa*: *Pseudomonas aeruginosa*, *A.niger*: *Aspergillus nige*, *C.albicans*: *Candida albicans*

From the Table-2, it is clear that all the ligands L_1 and L_2 show moderate activity against all the antibacterial and antifungal microorganisms. But all the metal complexes show moderate to high active against all the organisms²⁰⁻²⁴. Among the complexes, all copper complexes $Cu(L_1)Cl_2$ and $Cu(L_2)Cl_2$ were found to be most active against all the microbes tested, as compared to their ligands, which due to the faster diffusion of the $Cu(II)$ complexes. Even though the test compounds are less active with reference to the standard drug *ciproflaxacin* and *flucanazole*, the data reported in this article may be a helpful guide for the medicinal chemists who are working in the area²⁵⁻²⁶.

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