

Electronic, magnetic and biological properties of mono and homobinuclear Co(II) Complexes

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Abstract: A series of 20 memberd macrocyclic metal(II) complexes have been synthesised by template condensation of 1,3 diamino propane with thio diglycolic acid .The bonding and stereochemistry of the complexes have been characterized by elemental analysis, Magnetic susceptibility, conductivity measurements, IR, Electronic spectral studies and EPR. Their biological properties have also been studied. The complexes of the type $[ML]X_2$ have been found to have distorted octahedral configuration. The binuclear complexes $[M_2LX_2]X_2$ were found to have square planar configuration.

Key Words: Macrocyclic, Magnetic susceptibility, conductivity, octahedral.

Introduction: Macrocyclic complexes are those which contain transtion metal ions and macrocyclic ligand which in living systems work as enzymes or carriers in macrocyclic ligand field environments. Massoud. et al, 2017. Therefore meaningful research in this direction might generate simple models for biologically occurring metalloenzymes. Malik. et al, 2013. Metal template condensation reaction often provides selective routes toward products that are not obtainable in absence of metal ions. Prashanthi. et al, 2012. Especially, template reaction involving thiodiglycolic acid and amines facilitates the preparation of multi dentate macrocyclic complexes. Singh. et. al 2014. The reactions are simple “one-pot reactions” which are cheap and high yielding. Keeping the above view in mind we report the synthesis and characterization of Co(II) and Cu(II) complexes of a twenty membered hexadentate macrocyclic ligand i.e. 6,10,16,20-tetraketo-8,18-dithia-1,5,11,15-tetraazacycloeicosane $[N_4S_2L]$ (Fig. 1.)

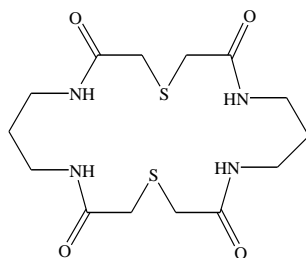


Fig1. Structure of macrocyclic ligand L

EXPERIMENTAL

Preparation of complexes: A mixture of metal salts (1mmol) and 1,3 diamino propane (2mmol) dissolved in 30mL ethanol. The mixture was stirred with gentle heating for about 10 min and was followed by addition of an ethanolic solution of thiodiglygolic acid (2mmol). The resultant mixture was refluxed on water bath at 78^o C for about 4-6 hours. On cooling the reaction mixture overnight at 0^o C the coloured crystals of the complexes precipitated out. They were filtered, washed with

ethanol and dried over silica gel. Binuclear complexes were prepared by using the same method which is adopted for the synthesis of mononuclear except 2mmol of metal salt solution were used.

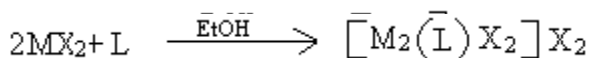
Physical Measurements: Carlo- Erba 1106 was used as Microanalyser (C, H and N) of these complexes. KBr pellets or Nujol mulls was used to record IR spectra on a Perkin Elmer 137 instrument Spectrophotometer-1240 UVmini Shimadzu was used to record the electronic spectra. Elico CM82T Conductivity meter was used for molar conductance measurement. CuSO₄.5H₂O callibrant at room temperature was used for Magnetic susceptibility measurements on Guoy balance. E-4 EPR spectrometer using g-marker (DPPH) at room temperature was used for recording EPR of the complexes. Paper disc diffusion method was used for antimicrobial, (antibacterial) activities of these complexes. The chosen strains were G(+) Streptococcus fecalis and G(-) Escherichia coli. The bacterial subcultures was autoclaved at 15 lb pressure for 20 min at 121°C before inoculation. The bacteria were cultured at 36°C for 24 h in an incubator. Nutrient agar was poured onto a plate and allowed to solidify. The test compounds (DMSO solutions) were added dropwise to a 10mm diameter filter paper disc placed at the center of each agar plate. The plates were then kept at 5°C for 1h and transferred to an incubator maintained at 36°C. The width of the growth inhibition zone around the disc was measured after 24 h incubation. Four replicas were made for each treatment.

RESULTS AND DISCUSSION

Metal ion and ligand were condensed in 1:1 and 2:1 for the preparation of mono and binuclear complexes respectively. The reaction sequences were given below:

(M = Co, Cu and X = NO₃)

A new series of mononuclear [ML]X₂ and binuclear complexes [M₂LX₂]₂ ((M = Co, Cu and X =NO₃)

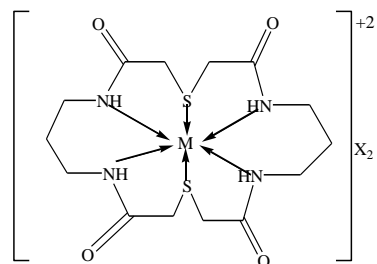


have been prepared. The complexes were stable in atmosphere. All the complexes have high melting point (>250°C). The results of elemental analysis (table1) supports the proposed macrocyclic structure. Sharma. et.al, 2015. The molar conductance values of all the complexes in DMSO solution suggest that the complexes are 1:2 electrolyte. Infrared spectra of complexes under study do not exhibit any bands characteristic for the free -NH and -OH groups and the appearance of four new bands corresponding to amide groups are seen in the regions 1638-1647, 1553-1582, 1380-1385 and 698-779 cm⁻¹ and these bands amide I [ν(C=O)], amide II [ν(C-N) + δ(N-H)], amide III [δ(N-H)] and amide IV [δ(C=O)], respectively. A single sharp band observed in the region 3334-3534 cm⁻¹ may be assigned to ν(N-H) of a secondary amino group. The unidentate NO₃ group exhibits three NO stretching bands at 1420 cm⁻¹ (ν₅)^s(NO₂), 1305 cm⁻¹ (ν₁)^a(NO₂) and 1008 cm⁻¹(ν₂)(NO). Our complexes show IR bands at 1430-1435cm⁻¹ (ν₁), 1374-1377 cm⁻¹(ν₃), 1209-1203 cm⁻¹ (ν₅), 1010-1013 cm⁻¹(ν₂) and 839-835 cm⁻¹(ν₆). Nakamoto, 1970. The absence of a broad band at 1390 cm⁻¹ indicates the coordination of both nitrate groups. The separation between ν₁ and ν₅ of ~125 indicates that both nitrate groups are unidentate in these complexes.

Cobalt(II) Complexes: The electronic spectra of the mononuclear cobalt complexes exhibit absorptions in the range 14,794-15,597 and 18,621-20,516 cm⁻¹ which may be assigned to ⁴T_{1g}(F) → ⁴A_{2g}(F) and ⁴T_{1g}(F) → ⁴T_{1g}(P) transitions, suggesting an octahedral environment around the cobalt

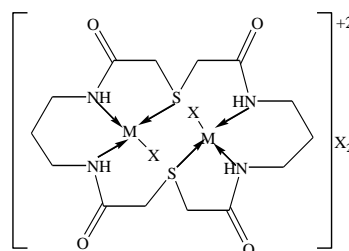
ion. Lever, 1968. Magnetic moment value in the range 4.7-5.2 B.M support the octahedral geometry. The electronic spectra of the homobinuclear cobalt complexes display characteristic absorptions in the regions of 10,121-11,025 cm^{-1} and 22,141-22,624 cm^{-1} suggesting low-spin square-planar geometry, which was further supported by magnetic moment values of 1.88-1.94 B.M. The EPR spectra of the complexes were recorded at liquid nitrogen temperature Because the rapid spin lattice relaxation of Co(II) broadened the lines at higher temperatures ($g_{11} = 2.84-3.10$ and $g_{\perp} = 1.89-2.61$). The large deviation of the g values from the spin-only value ($g = 2.0023$) is due to the large angular momentum contribution.

Copper(II) complexes: The electronic spectra of mononuclear complexes show two bands in the regions 18750-19170 and 15928-16583 cm^{-1} which can be assigned to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions respectively. Therefore, it, may be concluded that the complexes are distorted octahedral which is further confirmed by magnetic moment of 1.82 B.M corresponding to one unpaired electron and C_{4v} symmetry. The electronic spectra of dinuclear copper complexes show three bands in the regions 9737-12790, 14049-17667, 19727-21540 cm^{-1} which can be assigned to the ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions, corresponding to square planer geometry around the copper ions. The effective magnetic moment lie in the range 0.98-1.5BM corresponding to one unpaired electron in square planar environment. The low value of μ_{eff} indicates some antiferromagnetic interactions in these complexes. Therefore, metal-metal interaction must be present in the complexes which confirms the binuclear nature of the macrocyclic complexes. The e.p.r spectra of all copper(II) binuclear complexes show a single broad band with g_{11} and g_{\perp} values at 2.16– 2.19 and 2.09-2.13 respectively. The absence of hyperfine splitting may be due to strong dipolar and exchange interactions between the copper(II) ions in the unit cell. The observed g values indicate the presence of an unpaired electron in the $dx^2 - y^2$ orbital. The magnitude of the ratio $G = (g_{11}-2)/(g_{\perp}-2)$ reveals the possibility of an exchange interaction in these complexes. In the present case the G values were found in the range 1.46–1.77 ($G > 4$) range indicates considerable interactions. Wilkinson, 1988. The G values of the copper(II) complexes provides information about the covalent character of the metal ligand bond. The g_{11} value is greater than 2.3, indicates an ionic environment. In copper(II) complexes $g_{11} < 2.3$ indicates their covalent character. On the basis of IR, EPR, electronic, magnetic susceptibilities values studies the following structures (Fig 2 & 3) are suggested for the mononuclear (1) and binuclear (2) complexes respectively.



M = Co(II), Cu(II) and X = NO_3

Fig.2. Structure of $[\text{M}(\text{L})]\text{X}_2$



(M = Co(II), Cu(II) and X = NO_3)

Fig.3. Structure of $[\text{M}_2(\text{L})\text{X}_2]\text{X}_2$

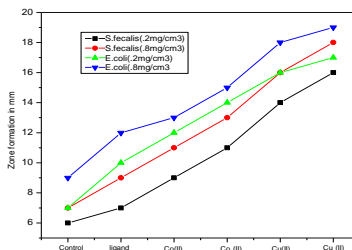


Fig 4. Antibacterial activity of ligands and Complexes

Table I Analytical and Physical Data of the Complexes

Complexes Molecular formula	Melting Point (°C)	Mol. Wt. Found (calc.)	Colour	Yield (%)	Molar Cond. (Ω^{-1} cm ² mol ⁻¹)	Found(calculated%)			
						M	C	H	N
[Co(L)](NO ₃) ₂ CoC ₁₄ H ₂₄ N ₆ O ₁₀ S ₂	278	560 (559.50)	Lotus pink	55	219	10.71 (10.76)	30.00 (30.07)	4.28 (4.34)	15.00 (15.07)
[Co ₂ (L)](NO ₃) ₂ (NO ₃) ₂ Co ₂ C ₁₄ H ₂₄ N ₈ S ₂ O ₁₄	217	712 (711.79)	Dark pink	59	228	16.85 (16.89)	23.59 (23.72)	3.37 (3.45)	15.73 (15.79)
[Cu(L)](NO ₃) ₂ CuC ₁₄ H ₂₄ N ₆ O ₁₀ S ₂	214	564 (563.72)	Blue	65	225	11.35 (11.39)	29.78 (29.85)	4.25 (4.32)	14.89 (14.93)
[Cu ₂ (L)](NO ₃) ₂ (NO ₃) ₂ Cu ₂ C ₁₄ H ₂₄ N ₈ O ₁₄ S ₂	204	720 (719.72)	Dark blue	68	230	17.78 (17.83)	23.34 (23.39)	3.34 (3.38)	15.56 (15.62)

Table II. Magnetic Moments, Electronic and e.p.r spectral bands of the Complexes

Complexes	μ_{eff} (B.M.)	Electronic spectral bands (cm^{-1}) and $\epsilon(\text{Lmol}^{-1}\text{cm}^{-1})$	g_{\parallel}	g_{\perp}
[Co(L)](NO_3) ₂ CoC ₁₄ H ₂₄ N ₆ O ₁₀ S ₂	4.70	14,927,19,831 88,103	2.899	2.098
[Co ₂ (L)](NO_3) ₂](NO_3) ₂ Co ₂ C ₁₄ H ₂₄ N ₈ S ₂ O ₁	1.67	10,959,22,095 81,107	2.88	1.88
[Cu(L)](NO_3) ₂ CuC ₁₄ H ₂₄ N ₆ O ₁₀ S ₂	1.72	16,145,18,792 125,47	-	-
[Cu ₂ (L)](NO_3) ₂](NO_3) ₂ Cu ₂ C ₁₄ H ₂₄ N ₈ O ₁₄ S ₂	1.74	12,749,16,512 21,594	-	-

Table III Antibacterial activity of Ligands and Complexes . (Zone formation in mm)

S.No.	Compounds	S.aureus (0.2mg/cm ³)	S.aureus (0.2mg/cm ³)	E.coli (0.2mg/cm ³)	E.coli (0.2mg/cm ³)
1	Control	5	6	7	7
2	Ligand	6	8	10	11
3	Co(II)	7	10	11	12
4	Co ₂ (II)	10	11	13	14
5	Cu(II)	13	15	15	16
6	Cu ₂ (II)	15	16	15	17

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