



Synthesis, Characterisation and Electrochemical studies of Transition Metal complexes with bis-(macro-cyclic) Ligands

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ABSTRACT

The new macrocyclic ligand 5,5'-ethane bis-(10,14-dihydroxo 12-thio,1,5,9-triazacyclotetradeca 1,9-diene) has been prepared and characterised. Its transition metal complexes have been prepared and characterised by Melting point, elemental analyses, molar conductance, electronic and IR spectral studies. Based on these studies, probable structures have been proposed for these complexes

Key words : Macrocyclic, Ligand and Transition metal.

INTRODUCTION

The vast family of macrocyclic ligands and their complexes has now been established as an integral part of coordination chemistry. The preference for macrocyclic ligand over unidentate and bidentate ligands has arisen from being close to the biological system¹⁻³, the greater stability and inertness of their complexes^{4,5} and often the extreme physical properties in their complexes due to strong ligand field.

Keeping these facts in view, new bis (macrocyclic) ligands having unique and unusual features has been prepared, characterised and its transition metal complexes have been prepared.

EXPERIMENTAL

All the chemicals and reagents used were of A.R. grade or equivalent purity. The ligand and its complexes were subjected to elemental analyses for C, H & N at CDRI, Lucknow, melting points molar conductance and gravimetric estimation of the metals were carried out in the college lab. Magnetic susceptibility was determined by Gouy's balance using $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ as calibrant.

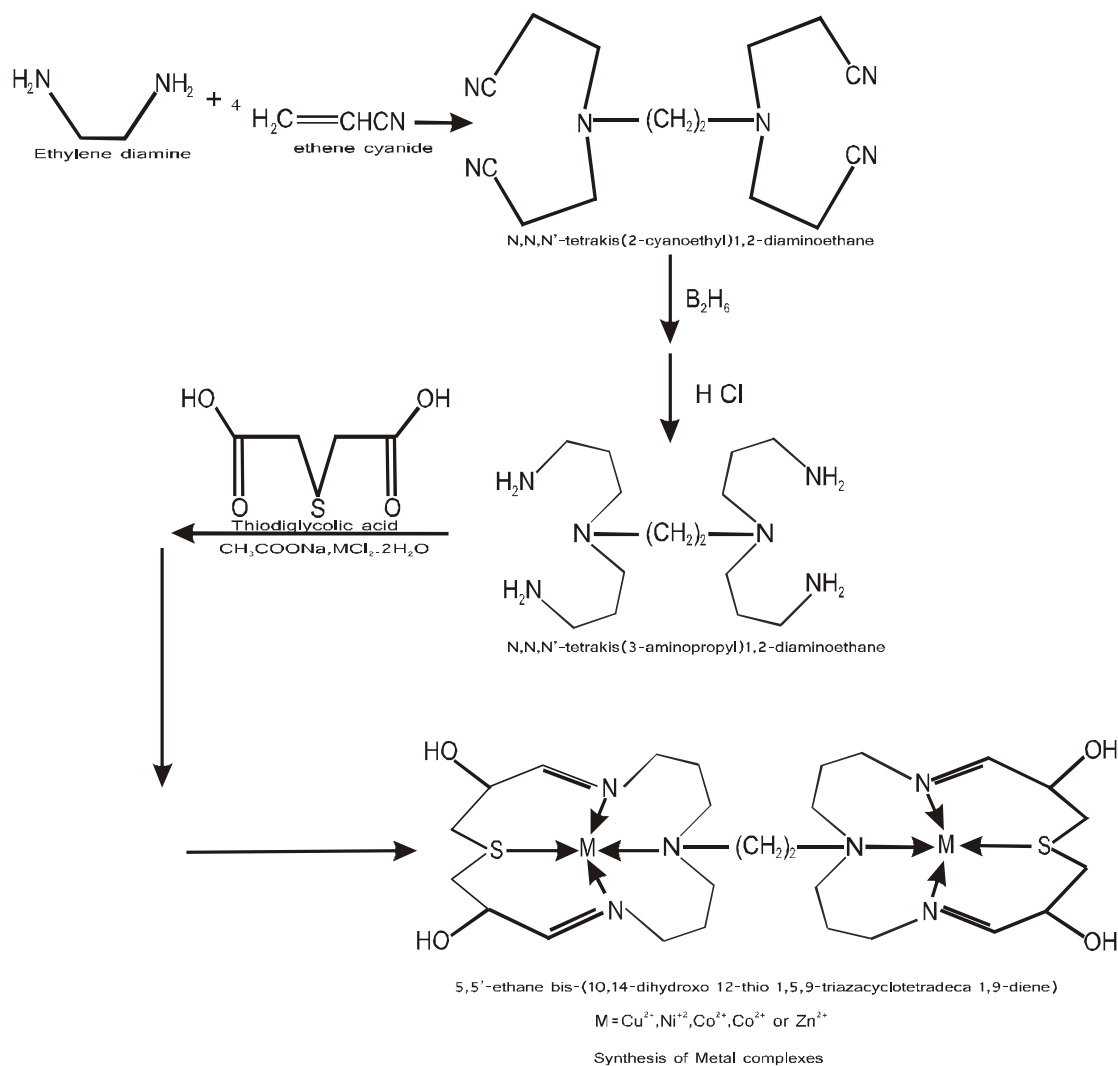
Electronic spectra of the complexes were recorded by Beckmann-Du spectrometer. IR spectra were recorded in KBr phase at CDRI, Lucknow.

Preparation of Ligand and Metal Complexes

Ethylene diamine and cyanoetheno were treated by reflux to N,N,N',N'-tetrakis(2-cyanoethyl)-

1,2-diaminoethane, which on successive treatment with diborane and HCl gave N,N,N',N'-tetrakis(3-aminopropyl)-1,2-diaminoethane. This on treatment with thiodiglycolic acid, CH₃COONa and the

respective metal salt gave the desired complexes. The chemical reactions involved may be represented as:



RESULTS AND DISCUSSION

The colours of the complexes were noted and are given in the table. The solubility of the complexes was checked in various solvents. The melting points of the ligand and the corresponding metal complexes were determined by open capillary method and are uncorrected (Table 1). The measurement of molar conductance at 10^{-3} M dilution

and 25°C suggested 1:4 electrolytic nature for all the synthesised complexes.

The magnetic susceptibility was determined at room temperature by Gouy's method. The value of magnetic moment values of the complexes are given in Table 1. The values suggested expected paramagnetic nature for the synthesised complexes.

The IR spectra of the ligand and its metal complexes were compared in order to find out the possible coordination sites. The comparison revealed that the ligand has coordinated through sulphur atoms and azomethine nitrogen atoms. The IR peaks of the ligand due to these groups show downward shifts of about 10-15 cm^{-1} and 20-25 cm^{-1} in the IR spectra of the complexes. The IR spectra respectively of the complexes show bands in the 1597-1621 cm^{-1} region attributed to C=N⁶. The bands due to coordinated C-S groups appeared in the region of 1060 cm^{-1} ¹⁷. Together with these results, the most important feature is that the spectra of bis(macrocylic)complexes have no bands assignable to carbonyl group stretching modes. A band in the 1172-1182 is assigned to C-N vibration in all complexes⁸. The absorption bands in the 2800-2850 cm^{-1} and 1445-1455 cm^{-1} region correspond to (C-H) and (C-H) respectively. The O-H bands appeared in the region of 3280-90 cm^{-1} and remained unaffected in the complexes, excluding the possibility of coordination of these groups with the metal.

The non ligand bands in the far IR region of the complexes at 445-466 cm^{-1} and 360-365 cm^{-1} may be assigned to (M-N) and (M-S) vibrations respectively⁹. This further supported the coordination sites mentioned above.

The electronic spectrum of the copper(II) complex shows broad band at 17000 cm^{-1} with a shoulder at 14100 cm^{-1} , which may be assigned to 2B1g2Eg and 2B1g2A1g transitions respectively in square planar configuration¹⁰. The electronic spectrum of Ni(II)complex shows two absorption bands at 15385 and 25975 cm^{-1} assignable to $^3A_{2g} \rightarrow ^3T_{1g}(f)$ and $^3A_{2g} \rightarrow ^3T_{1g}(p)$ transitions (II). The electronic spectrum of cobalt(II) complex also shows two bands at 14080 and 17090 cm^{-1} . These bands may be assigned to 1A1g1B1g and charge transfer transitions respectively¹². These are characteristic of square planar geometry¹². The electronic spectrum of Mn(II)complex shows absorption bands at 14950, 24690,31950 cm^{-1} assignable to $^6A_{1g} \rightarrow ^4T_{1g}(G)$, $^6A_{1g} \rightarrow ^4A_{1g}$ and $^6A_{1g} \rightarrow ^6A_{1g}(G)$ charge transfer respectively¹³. The magnetic moments of Cu(II)complex is 1.79B.M. that of Co(II)complex is 3.29B.M. Ni(II) and Zn(II) complexes are diamagnetic indicating square planar geometry for these complexes¹². The magnetic moments of Mn(II)complex is 5.98 corresponding to the presence of five unpaired electrons and characteristic of octahedral geometry.

CONCLUSION

From above discussion square planar geometry has been proposed for Cu(II),Zn(II), Co(II) and Ni(II) complexes and octahedral geometry for

Table 1.

S. No.	Molecular Formula of Complexes	Colour	m.p. (°C)	Elemental Analysis				
				%C	%H	%N	%S	%M
1.	(Zn(C ₂₆ H ₄₄ O ₆ N ₆ S ₂))Cl ₄ Mol. wt. = 711	White	310	43.62 (43.88)	6.12 (6.18)	11.76 (11.81)	8.96 (9.00)	9.00 (9.14)
2.	(Cu ₂ (C ₂₆ H ₄₄ O ₄ N ₆ S ₂))Cl ₄ Mol. wt. = 709	Bluish Yellow	312	43.96 (44.00)	6.12 (6.20)	11.80 (11.84)	8.93 (9.08)	8.69 (8.88)
3.	(Ni ₂ (C ₂₆ H ₄₄ O ₄ N ₆ S ₂))Cl ₄ Mol. wt. = 704	Greenish Yellow	308	44.23 (44.31)	6.20 (6.25)	11.91 (11.93)	9.00 (9.09)	8.20 (8.23)
4.	(Co ₂ (C ₂₆ H ₄₄ O ₄ N ₆ S ₂))Cl ₄ Mol. wt. = 705	Pinkish Yellow	306	44.21 (44.25)	6.23 (6.24)	11.90 (11.91)	9.00 (9.07)	8.32 (8.36)
5.	(Mn ₂ (C ₂₆ H ₄₄ O ₄ N ₆ S ₂))Cl ₄ Mol. wt. = 701	Brown	302	44.96 (44.50)	6.21 (6.27)	11.92 (11.98)	9.10 (9.12)	7.82 (7.84)

The Calcd. values are given in bracket.

Mn(II) complex. The ligand and complexes show antifungal activity and the antifungal activity of the ligand increased on complexation.

Fungicidal Activity

The ligand and its corresponding metal

complex were screened for fungicidal activity by mycelial dry weight method (MDW) against *Aspergillus niger* in glucose nitrate media (GN). The ligand showed toxicity in inhibition, which has increased in the complexes. The order of inhibition is ligand <Zn<Cu <Ni <Co<Mn.

Table 2. Fungicidal activity

Concentration (ppm)	MDW (mg) Ligand	MDW (mg)	MDW (mg of Complexes)				
			Zn	Cu	Ni	Co	Mn
200	65	88	58	52	48	42	25
400	30	88	28	26	24	22	17

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