

Synthesis and Characterisation of Co (II), Cu(II) and Fe (III) Macrocyclic Complex of 2, 3, 4 -Pyridine- 1, 3, 5, 8, 11, 14- Hexaazacyclohexadeca-2-ene bonded With Cyano and Thiocyanato Ligands

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Abstract

Macrocyclic complexes axially bonded with cyano and thiocyanato ligands, synthesized and characterized using FR, UV-Visible Spectra. Macrocyclic ligand finds their importance uses as model for protein-metal binding sites in biological system and selective metal extrants in hydrometallurgy and study host-guest interactions (8). The Macrocyclic molecules are also widely used as catalyst for industrial application (9). Macrocyclic complex show greater biocidal effect as they are potentially active against few bacteria and fungi. Recently a large number of macrocyclic ligands have been synthesized using Mass spectroscopy (15-20). Curtius (23) demonstrated the case of inter conversion of a series of complex containing different degree of unsaturation. A number of membranes were prepared with ionophore, PVC, anion excluder (STB) and solvent mediators (DBP and DOP) and were equilibrated with various metal ions. The sensor assembly was used as an indicator electrode in the potentiometric titration of Co (II) with EDTA. The practical utility of the proposed sensor was investigated in partially non-Aqueous media 30% water-methanol and water ethanol mixtures. 2,6- dichloropyridine (0.01 mol, 1.42g) was dissolved in minimum amount (20 ml) of methanol and tetraethylenepentamine (1.26 ml, 0.01 mol) was added to it. To this mixture a methanol solution of metal salt (chloride /nitrate) (0.01 mol) was added with constant stirring and heating. The mixture was refluxed for 8 h and coloured precipitate thus formed, was filtered in sintered crucible, washed with methanol and dried vacuum. The magnetic and electronic spectral values given in Table are entirely consistent with the octahedral geometry for the complexes of these metals. All the complexes are paramagnetic. ^1H NMR spectrum of Fe (III) complex shows a multiplet in the region 6.28-7.89 ppm due to pyridine ring protons (3H) multiplet in the region 8.22-8.42 ppm corresponds to secondary amine protons (5H) and a broad multiplet in the region 2.64-4.32 ppm due to methylene protons (16H).

Keywords: Analytical spectra, macrocyclic complex IR, UV-Visible, CHN, Mass spectroscopy, NMR.

Introduction

In recent years macrocyclic compounds and their diverse aspects have been paid considerable attention for research all over the world. A macrocycle is defined as a cyclic compound having nine or more members including all heteroatoms and with three or more donor atoms (1). The synthetic macrocyclic complexes are most important from the biological point of view as they are structurally similar to some of the naturally occurring macrocyclic complexes. Considering the roles of natural systems such as iron-porphyrin core in haemoglobin, cobalt-corrin of vitamin B₁₂ and magnesium-hydroporphyrin in chlorophyll (2), it would not be a total over statement to say that macrocyclic complexes lie at the centre of the life. The vital functions performed by the natural systems can be largely determined by the nature of the metal ions enclosed in it. The metal ions are trapped in such a

complicated structure that the fundamental properties of metal ions are still not well understood, which is a real limitation on the pace of advancement of knowledge in the macrocyclic field. It is therefore reasonable to synthesize simple macrocyclic complexes that can be considered as model compounds.

Ion selective electrodes based on macrocyclic ligands (ionophore) are well established for many inorganic cations and anions (3). During last two decades a large number of ionophores, especially a wide variety of neutral macrocyclic ligands, have been developed, and which find wide spread applications in potentiometric and optical sensors for the determination of respective ions in real samples (4-6). The design and function of synthetic ionophores for ion selective electrodes are based on diverse parameters such as the structure and cavity size of the ligands, the stability and selectivity of its metal ion complex, its solubility and the ability to extract the metal

ion into the membrane phase. In this area macrocycles get much importance among the compounds used as ionophore because their complexes have high stability constant and sufficient conformation flexibility for rapid ion-exchange (7).

Macrocylic ligands find their important uses as models for protein-metal binding sites in biological systems, as selective extractants of metallic ions, as therapeutic reagent for the treatment of metal toxicity, functional groups for chelating ion-exchange materials and selective metal extractants in hydrometallurgy and to study host-guest interactions (8).

Polyaza macrocylic ligands represent a class of macrocycles known for their ability to form the complexes with transition and non transition metal ions. The macrocylic molecules are also widely used as catalysts for industrial applications as they have the advantage of being readily separable or allowing flow-through processing (9). Moreover, macrocylic complexes show greater biocidal effect as they are potentially active against few bacteria and fungi.

Macrocylic ligands have remarkable selectivity towards metal ions. This property of macrocylic ligands makes them suitable for separating the metal ions which are otherwise difficult to separate (10, 11). Macrocylics have also been used for separating the metal ions by solvent extraction method or by the membrane transport of metal ions from an aqueous source phase through an organic membrane phase containing the ligand with an aqueous receiving phase.

The continued interest in new macrocycles stems mainly from their use in various aspects. Selective substrate recognition, stable complex formation, transport capabilities, and catalysis are the examples of the wide-ranging properties of these molecules. Recognition of the importance of complexes containing macrocylic ligands has led to considerable effort being invested in developing reliable and less expensive synthetic routes for these compounds (1, 12-14).

The volatility; diamagnetism and solubility of the ligand in less polar solvents make spectroscopic techniques such as mass spectrometry and NMR commonly used for characterization more effective to the organic ligand than to the complex.

Recently a large number of macrocylic ligands have been synthesized using the above method (15-20). The disadvantage of this technique is that the synthesis of the macrocylic complex often in low yield. In order to increase the yield and reduce the side reactions such as polymerizations, the final ring closure reaction in a stepwise synthesis is often carried out under conditions of high dilution.

The metal ion plays an important role in directing the steric course of the reaction and this effect is termed as "metal template effect" (21)

During the sixties, Pungor and Hollo's Rokosinyi prepared an electrode membrane by embedding silver

iodide in paraffin and demonstrated the selectivity to this electrode to iodide ions in the presence of chloride ions. This electrode was an ISE (non-glass) in true sense and gave a response, which is thermodynamically reversible with respect to the primary ion. (24)

Macrocylics have great potential to be used in ISEs, however all macrocylics are not useful for preparing electrodes. Macrocylics are likely to be used in ISEs provided they show (1) high complexation or extraction selectivity for a particular metal ion and (2) enough conformational flexibility for rapid ion exchange (3) high lipophilicity to remain in membrane and (4) moderate molecular weight to allow high mobility.

Ion-selective electrodes have been known since the work of Kolthoff and Sanders (25) in 1937, but had received little attention until the publication of Pungor (26) in 1961. Pungor and Hollos-Rokosinyi produced an electrode membrane by embedding silver iodide in paraffin, and demonstrated the selectivity of the electrode to iodide in the presence of chloride ions.

Koryta (27-28), the number of publications in this area over the past two decades is so large that it is rather difficult to report the total bibliography on the subject. Hence, literature on those metal ions of which ion-selective electrodes have been studied in the present work is being reviewed.

Literature survey reveals that very little work has been done on the development of ISEs for Ba(II) ion. In 1977 Guggi et al. (29) prepared a barium ion-selective electrode based on the neutral carrier N, N, N', N'-tetraphenyl 1-1, 3, 6, 9-trioxaundecanediamide.

Very recently Mashhadizadeh et al. (30) have reported a new PVC membrane electrode for Co(II) based on (2-mercapto-4-methylphenyl)-2-benzamido-3-phenyl-thiopropenoate (I) as an excellent neutral carrier.

Chemicals and Reagents

All the chemicals and solvents used were of analytical reagent grade. 2,6- Dichloropyridine (Merck, Germany), 1,3-diaminopropane (Fluka, Switzerland), N, N'-bis (3-aminopropyl) ethylenediamine (Lancaster, England), tetraethylenepentamine (Fluka, Switzerland), pyridine-2,6-dicarboxylic acid (Merek-Schuchardt, Germany), sodium tetraphenyl borate (BDH, United Kingdom), triethylenetetramine (Fluka, Switzerland), formaldehyde (BDH, United Kingdom), DOP (Aldrich, USA), DBP (Merck, Germany), TEP (Merck, Germany), TBP (Aldrich, USA), DBBP (Merck, Germany), polystyrene (BDH, England) and (pol vinyl chloride) (G.S.C., India) were obtained and used without further purification. Solutions for membrane studies were prepared in double distilled water and all metal ion solutions were standardized before use. 1-Phenyl-1, 3-butanedione was synthesized according to literature method. (31)

Physical Measurements

The UV-Vis spectra of the ligands and their metal complexes were recorded on a Shimadzu UV 2100 Double

Beam Spectrophotometer using 10 mm path length silica cell Infrared spectra of the complexes were recorded as KBr discs on a Perkin-Elmer 1600 series FTIR in the range $4000\text{--}650\text{ cm}^{-1}$ and in Nujol mulls over $650\text{--}200\text{ cm}^{-1}$ range on a Beckraan IR-12 spectrophotometer. The ^1H NMR spectra were recorded on a Bruker DRX 300 NMR spectrometer and conductance measurements of $1.00 \times 10^{-3}\text{ M}$ aqueous solutions of the complexes were carried out on a Systronics Conductivity meter type 302 at $25 \pm 1^\circ\text{C}$ using a dip type conductivity cell. Magnetic moments at room temperature were recorded on a Vibrating Sample Magnetometer (VSM model 155 Princeton Applied Research) incorporating a digital read-out, cross-checked against $\text{Hg}(\text{Co}(\text{SCN})_4)$ as calibrant. The VSM was calibrated with a high purity nickel standard showing a saturation moment of 55 emu g^{-1} with a saturation flux 5 Kg. C, H, N determinations were carried out microanalytically at the Bhabha Atomic Research Centre, Mumbai and CDRI, Lucknow. The potential measurements were carried out at $25 \pm 0.1^\circ\text{C}$ using pH 5652 digital pH meter/millivoltmeter (ECIL, India) and Century Digital Microvoltmeter-CVM 301 (Century Instruments Pvt. Ltd., India).

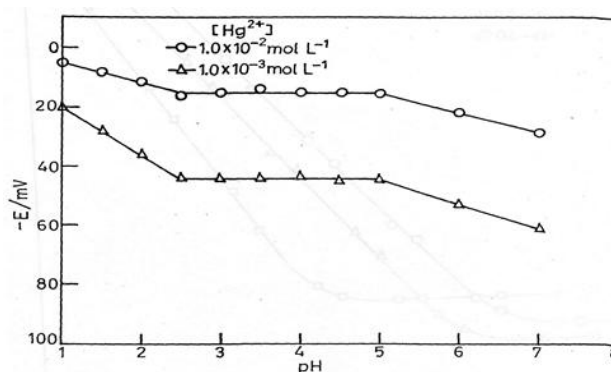
Results and Discussion

The values of molar conductance indicate that Co (II), Cu(II), Ni(II) complexes are 1:2 electrolyte in nature while Fe(II) complex 1:3 electrolyte. The magnetic and electronic spectral values given in table are entirely consistent with the octahedral geometry for the complexes of those metals. All the complexes of these metals. All the complexes are paramagnetic. IR Spectra of these complex are given in table. These complexes exhibit a C-N absorption in region $1371\text{--}1400\text{ cm}^{-1}$. The appearance of this band coupled with the absence of the C-Cl band around $800\text{--}710\text{ cm}^{-1}$ is conclusive evidence of condensation of 2-6 dichlorophyridine and tetra ethylene pentaamine. The band present at $3210\text{--}3235\text{ cm}^{-1}$ originates due to N-H stretching. The band at $2912\text{--}2965\text{ cm}^{-1}$ and $1370\text{--}1391\text{ cm}^{-1}$ are due to C-H stretching and bending libration of methylene proton respectively the M-N libration $412\text{--}465\text{ cm}^{-1}$ correspond to M-N libration (32) and substantiate the co-ordination.

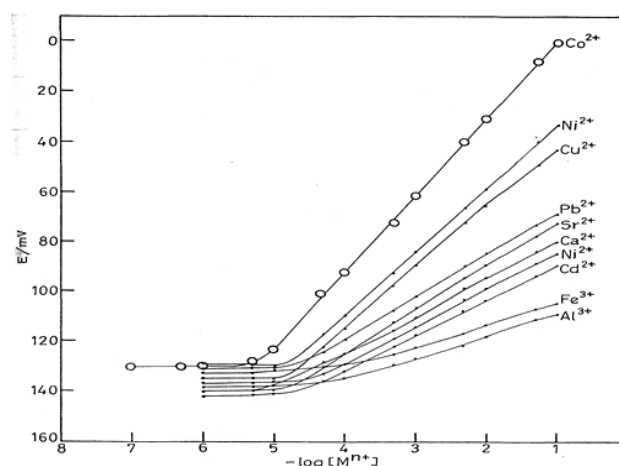
^1H NMR spectrum of Fe (III) complex shows a multiplet in the region $6.28\text{--}7.89\text{ ppm}$ due to pyridine ring proton (3H). A multiplet in the region $8.22\text{--}8.42\text{ ppm}$ corresponds to secondary amine protons (5H) and a broad multiple in the region $2.64\text{--}4.32\text{ ppm}$ due to methylene protons (16H).

A number of membranes were prepared with ionophore, PVC, anion excluder (STB) and solvent mediators (DBP and DOP) and were equilibrated with various metal ions. A perusal of working concentration range of these cations presented in Fig indicates that the electrode is best suited for Co^{2+} , while for other cations the response is either sub-Nernstian or non-Nernstian,

with poor working concentration range. Hence the ionophore was further studied as ionophore in Co^{2+} -ISE. Heterogeneous, membranes were prepared by dissolving (2, 3, 4-pyridine-1, 3, 5, 8, 11, 14-hexaazacyclohexadeca-2-ene) ionophore and PVC in diluent THF as detailed. Ratios of the ionophore and PVC were varied in order to get the composition of the membrane showing the best performance with regard to working concentration range, slope and response time. Anion excluder (STB) was added to inhibit the interference of anions, whereas plasticizers (DBP and DOP) were tried to enhance electrochemical performance of the membranes. The membranes having PVC-plasticizer-ionophore-anion excluder in different ratios have been prepared. The composition of the membranes and their performance with regard to their working concentration range, slope and response time are presented.



Plots showing the variation of the membrane potentials with pH at $1.00 \times 10^{-2}\text{ mol L}^{-1}$ and $1.00 \times 10^{-3}\text{ mol L}^{-1}\text{ Hg}^{2+}$ solutions



Potential response of various ion-selective membranes with (2, 3, 4-pyridine-1, 3, 5, 8, 11, 14-hexaazacyclohexadeca-2-ene).

The, experimental results show that the lifetime of the present electrode was about 100 days. During this time, the detection limit and the slope of the electrode remained almost constant. The electrochemical behavior

Table No. 1 Analytical, physical and spectral data of the complex derived from 2, 3, 4 /-pyridine-1, 3, 5, 8, 11, 14-hexaazacyclohexadeca-2-ene

Compl. No.	Complex Mol. Wt. (Cal.)	Color MP (°C) Yield (%)	μ_{eff} (BM)	Observed (Cal.) %				UV-Vis Spectra λ_{max} (nm)	Molar Conductance ($\text{cm}^2 \text{ohm}^{-1} \text{mol}^{-1}$)
				C	H	N	M		
1	(Co(C ₁₃ H ₂₄ N ₆)Cl ₂) (394)	Light brown >360, 69	3.78	40.14 (39.62)	6.00 (6.12)	21.54 (21.32)	14.24 (14.92)	29680, 38695	21.2
2	(Ni(C ₁₃ (C ₁₃ H ₂₄ N ₆)Cl ₂) (394)	Light green >360, 65	2.82	40.00 (39.62)	6.22 (6.12)	21.50 (21.32)	14.25 (14.90)	29563, 38750	22.3
3	(Cu (C ₁₃ H ₂₄ N ₆) (NO ₃) ₂) (452)	Blue 180, 69	1.72	35.12 (34.51)	5.52 (5.33)	24.18 (24.81)	14.00 (14.12)	28653, 38685	22.8
4	(Fe (C ₁₃ H ₂₄ N ₆) (NO ₃) ₃) (506)	Dark Brown 175, 78	1.8	31.12 (30.84)	4.54 (4.71)	25.22 (24.52)	10.88 (11.12)	38685, 34188, 29630	23

Table No. 2 Infrared spectral data of the complexes derived from 2, 3, 4-pyridine- 1, 3, 5, 8, 11, 14-hexaazacyclohexadeca- 2-ene

Compl. No.	Complex	C-N (cm ⁻¹)	N-H (cm ⁻¹)	-CH ₂ - (cm ⁻¹) (Str.) & (bend)	M-N (cm ⁻¹)
1	(Co(C ₁₃ H ₂₄ N ₆) Cl ₂)	1400	3212	2935, 1388	412
2	(Ni (C ₁₃ (C ₁₃ H ₂₄ N ₆) Cl ₂)	1385	3210	2912, 1380	450
3	(Cu (C ₁₃ H ₂₄ N ₆) (NO ₃) ₂)	1367	3242	2963, 1370	422
4	(Fe (C ₁₃ H ₂₄ N ₆) (NO ₃) ₃)	1371	3235	2902, 1391	465

Table No. 3 Composition of PVC-based membranes of (2, 3, 4-pyridine- 1, 3, 5, 8, 11, 14-hexaazacyclohexadeca-2-ene) and their performance as Co(II)-selective electrodes

Membrane No.	Composition of Membrane (w/w)					Working Concentration Range (mol L ⁻¹)	Slope (mV/decade of concentration)	Response Time (s)
	Ionophore	PVC	STB	DOP	DBP			
1	1	6	1	-	-	1.12 x 10 ⁻⁵ - 1.00 x 10 ¹	35	28
2	1	4	1	-	1	1.00 x 10 ⁻⁵ - 1.00 x 10 ¹	30.5	20
3	1	8	1	-	1	6.31 x 10 ⁻⁶ - 1.00 x 10 ¹	30	15
4	1	10	1	1	-	8.91 x 10 ⁻⁶ - 1.00 x 10 ¹	28.5	21

Table No. 4 Effect of concentration of internal solution on the working concentration range and slope of Co²⁺- selective (2, 3, 4-pyridine -1, 3, 5, 8, 11, 14- hexacyclohexadeca -2-ene) cobalt (II) complex based membrane electrode

Internal Solution Concentration (mol L ⁻¹)	Working Concentration Range (mol L ⁻¹)	Slope (mV/decade of concentration)
1	1.77 x 10 ⁻⁵ - 1.00 x 10 ⁻¹	35
1.00 x 10 ⁻¹	6.31 x 10 ⁻⁶ - 1.00 x 10 ⁻¹	30
1.00 x 10 ⁻²	3.55 x 10 ⁻⁵ - 1.00 x 10 ⁻¹	38

of the electrode gradually deteriorated after 100 days, which can be attributed to aging of the polymer (PVC), plasticizer and ionophore (macrocyclic ligand) resulting in their migration from the PVC membrane into a PVC foil. The pH dependence of electrode potential was tested over the pH range 1.0-7.0 for 1.00 x 10⁻² mol L⁻¹ and 1.00 x 10⁻³ mol L⁻¹ of Co(II) ions. The pH was adjusted with nitric acid or ammonia solution.

The practical utility of the proposed sensor was investigated in partially non-aqueous media using 20%,

30%, and 40% water-methanol and water-ethanol mixtures.

The addition of EDTA causes a decrease in potential as a result of a decrease in free Co(II) ion concentration due to its complexation with EDTA.

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