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SONICATED SYNTHESIS AND CHARACTERISATION OF MACROCYCLIC COMPLEXES WITH TRANSITION METALS

[1]***P. R. Shirode** and [2]**A. B. Jain**

[1]Department of Chemistry, Pratap College, Amalner (India).
[2]Department of Electronics, Pratap College, Amalner (India).
Affiliated to North Maharashtra University, Jalgaon.

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***Corresponding Author**
P. R. Shirode
Department of Chemistry,
Pratap College, Amalner
(India)., Affiliated to North
Maharashtra University,
Jalgaon.

ABSTRACT

A new series of complexes of the type [M $(C_{12}N_4H_{20}O_2)X_2$], where M=Co, Ni, Cu, X=Cl^- or NO_3 corresponds to the tetra dentate macro cyclic ligand. The complexes are characterized by elemental analysis, conductance and magnetic measurements, UV/Vis and IR spectroscopy. Based on these studies a octahedral geometry is suggested. All the synthesized macrocylic complexes were subjected for antimicrobial screening.

KEYWORDS: Antimicrobial activity ethylacetoacetate, ethylene diamine, template synthesis, macro cyclic Schiff's -base complexes.

INTRODUCTION

Macrocyclic species based on transition metal compounds and multi dentate ligands is an interesting field in chemistry and has been the subject of extensive research due to their potential applications in building block macrocyclic-based chemistry[1,2] and environmental chemistry[3] and biomedical.[4] The chemistry of Schiff-base is an important field in coordination chemistry.[5] This is due to their ability to react with a range of metal ions forming stable complexes which have applications in different fields.[6,7] The importance of macrocyclic systems in chemistry is also due to their many industrial applications and in a number of biological processes such as photosynthesis, catalytic properties, di oxygen transport and their potential application to extract specific metals.[9,10] The selectivity of the macrocyclic ligands that contain combination of Oxo (O), Aza (N), Phospha (P) and Sulpha (S) for the extraction of metal ions depends on the ligand flexibility, nature of the ligand backbone, the cavity size of the macrocyclic core, nature and number of donor atoms in addition to their relative position in the macrocyclic ligands and the pendant coordinating arms attached to the ligand.[8,10] Complexes with poly -azamacrocyclic ligands have attracted a focus of scientific attention.[7,13] Recently, much attention has been paid to macrocyclic compounds containing amide groups.[14,15] Macrocyclic amides have applications in elector fluorescence devices (EL) and homogeneous catalysis.[16] The template condensation for the preparation of the macrocyclic ligands often offers selective routes towards products that are not formed in the absence of metal ions.[17] The template condensation methods lie at the heart of macrocyclic chemistry.[18] Therefore, if the ligand yield is low, macrocyclic complexes have been widely isolated using the template reactions.[19] The transition metal ions are used as the templating agent.[20] The metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products.[21] Recently, poly-azamacrocycles and its transition metal complexes have been synthesized and characterized. The *in vitro* antitumor activity against human breast cancer cell line and human hepatocarcinoma cell line has been studied.[14,15,22] Taking into consideration the above facts, we have reported the preparation, spectral and thermal studies of novel Fe(II), Co(II), Ni(II), Cu(II), Pd(II) complexes. The *in vitro* antitumor activity of the compounds against human breast (MCF-7) and human hepatocarcinoma cancer cell lines (HepG2).

In the present paper first macro cyclic ligand is synthesized using ethyl acetoacetate and ethylene diamine by sonication method. Sonication uses sound waves to agitate particles in a solution. It converts an electrical signal into a physical vibration to break substances apart. Sound is a wave of alternating high and low pressure. The frequency of a sound wave is how often the particles of a substance vibrate when the sound wave passes through it. Sonication typically uses ultrasound waves with frequencies of 20 kHz-40 kHz or higher, the alcoholic solutions of the reaction mixture is placed in a sonicator bath at 70^0C at 40KHz frequence for one hour. Therefore sonicator bath is used for the synthesis of macrocylic ligands. In this process 5 minutes to one hour.

The macro cyclic ligand complexes are synthesized by using macro cyclic ligand in presence of transition metal ions such as Co(II), Ni(II), and Cu(II). The synthesized complexes are characterized using elemental analysis, molar conductance, magnetic susceptibility measurements, IR, electronic and 1H-NMR spectra. On the basis of studies made an octahedral geometry is proposed for all the complexes.

MATERIALS AND METHODS

All the chemicals used in present study were of AR grade. Ethyl acetoacetate and ethylene diamine and metal salts were purchased from S. D. fine chemicals. The Molar conductance of complexes was measured by preparing 10^{-3} M solutions in DMF solvent using Equiptronics conductivity meter with inbuilt magnetic stirrer model (Eq-664) at room temperature. Magnetic susceptibilities were determined on the Sherwood Scintific Magnetic Susceptibility Balance (model MSB Mk1) at room temperature using copper (II) sulphate as a standard. These magnetic susceptibility values were utilized to calculate magnetic moments using spin only formula $\mu eff = (n(n+2))^{1/2}$ for all the synthesized complexes. IR spectra were recorded in the region of 4000-400 cm^{-1} on JASCO 6700 FTIR Spectrophotometer. Electronic spectra were recorded on a JASCO 670-UV spectrophotometer. Elemental analysis was carried out on a Perkin CHNS elemental analyzer.

Synthesis of macrocyclic ligand

Equimolar quantities of ethyl acetoacetate and ethylene diamine are dissolved in ethyl alcohol and then this reaction mixture was placed in a sonicator for 45 minutes at 70^0C at frequency of 40KHz. Solid crystals separates out from the solution when this reaction mixture is added on crushed ice, filter this white product on ordinary filter paper wash the product with distilled water and then 1-2 ml of ether Dry and record the weight of product obtained.

Dry under IR lamp. Record the yield of the product obtained. Recrystallize the product from ethyl alcohol and record the melting point of the product obtained.

Reaction

Synthesis of Ligand

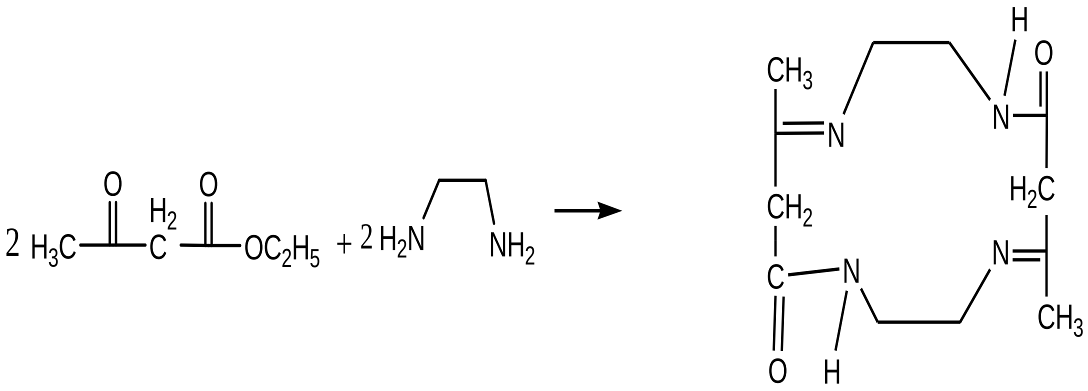


Table 1: Physical Properties of Ligands.

Name of the ligand	Mol. Formula	Mol. Wt	Melting point	Method of purification
	$C_{12}N_4H_{20}O_2$	323	128	Ethyl alcohol

Synthesis of Complexes

To synthesize the complex analytical reagent grade transition metal chlorides are used. There fore equimolar quantities of ligand and cobalt chloride were dissolved in about 20 ml of methyl alcohol separately. Then solutions were added in 100 ml round bottom flask and after attaching the water condenser the reaction mixture was heated on heating mental for 4-5 hours. The green colored solid product seperates out from solution on cooling. Filter the product on buchner funnel on a whatmann filter paper no 41, wash with ethyl alcohol and then with ether. Dry under IR lamp and record the yield of the product obtained.

By using the same procedure the complex were prepared by mixing equimolar quantities of ligand with nickel chloride and copper chloride.

Synthesis of Complexes

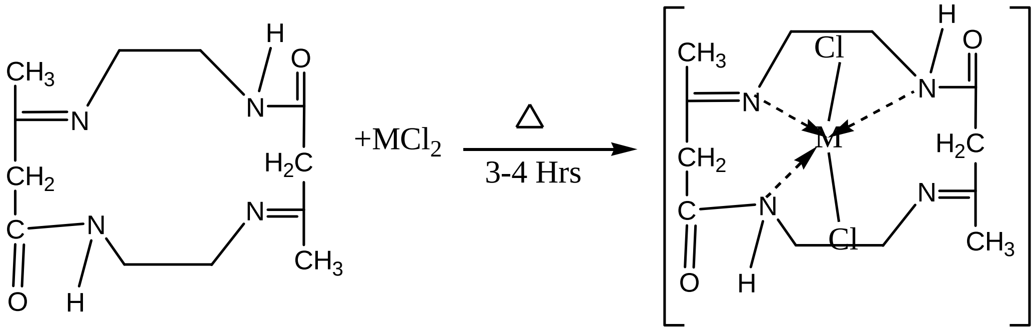


Table 2: Physlcal and analytical properties of complexes.

Empiricalformula of the complex	Colour	Mol.Wt	% Yield	% of metal (Calculated)	% of C	% of H	% of N
$C_{12}N_4H_{20}O_2$	White	323	74.29%	-	44.58	6.19	17.33
$CoC_{12}N_4H_{20}O_2Cl_2$	Green	381.93	84.72%	15.42	37.70	5.23	15.42
$NiC_{12}N_4H_{20}O_2Cl_2$	Faint green	381.69	83.10%	15.37	37.72	5.29	14.67
$CuC_{12}N_4H_{20}O_2Cl_2$	Ash colour	386.54	98.37%	16.43	37.25	5.17	14.48

SPECTRAL PROPERTIES

Electronic Spectra

Electronic absorption spectra are generally supporting the results obtained for the structural investigation by other methods. The electronic spectral measurement was used for determining the stereochemistry of metal ions in the complex based on the positions and number of d-d transitions peaks. The electron absorption spectra of the macro cyclic ligand and macro cyclic ligand complexes of Co (II), Ni (II) and Cu(II) were recorded at room temperature are shown in table 3.

Table 3: The electronic spectra of macro cyclic ligand and macro cyclic ligand complexes in cm^{-1}

Name of the complex	ν_1	ν_2	ν_3	ν_2/ν_1	LFSE Kcal/mol
$C_{12}N_4H_{20}O_2$	8688	9372	41152	1.0787	---
$[Co(C_{12}N_4H_{20}O_{2]}Cl_{2]}$	8410	9017	34602	1.0721	5046
$[Ni(C_{12}N_4H_{20}O_2)Cl_2]$	8643	9057	42016	1.0479	10371
$[Cu(C_{12}N_4H_{20}O_2)Cl_2]$	8733	11534	44444	1.3207	---

The electronic spectra of Co(II) complexes exhibits bands in the range 8410,9017 and 34602 cm^{-1} with ν_2/ν_1 ratio 1.0787 corresponding to $^6A_1g \rightarrow {}^4T_1g(^4G)$, $^4A_2g \rightarrow {}^4T_2g$ and $^4A_2g \rightarrow {}^4T_1g$ transitions, respectively suggesting octahedral environment around Co(II) ion. The electronic spectra of Ni(II) shows three bands at 8643,9057 and 42016 cm^{-1} for the transitions $^6A_1g \rightarrow {}^4T_1g$ (G), $^6A_1g \rightarrow {}^4T_2g$ (G) and $^6A_1g \rightarrow {}^4A_1g$ (G) with ν_2/ν_1 ratio of 1.0479 indicating octahedral geometry around Ni (II) ion in the complex.

The spectrum of Cu(II) consists of three bands 8733, 11534 and 44444 cm^{-1} with ν_2/ν_1 ratio 1.3207. The first transition corresponds to $^6A1g \rightarrow {}^4T_1g\ (t_2g)^4$ (eg), $^6A_1g \rightarrow {}^4T_2\ (F)(t_2g)^4$ (eg) and $^6A_1g \rightarrow {}^4Eg'^4A_1g\ (t_2g)^3\ (eg)^2$ respectively, indicating octahedral symmetry around Cu(II) ion.

Table 4: Electronic spectral transitions.

Complex	Electronic Spectra		Geometry
	ν_{max} (cm^{-1})	Assignment	
$[CoC_{12}N_4H_{20}O_2Cl_2]$	8410	$^6A_1g \rightarrow {}^4T_1g(^4G)$,	Octahedral (Oh)
	9017	$^4A_2g \rightarrow {}^4T_2g$	
	34602	$^4A_2g \rightarrow {}^4T_1g$	
$[Ni(C_{12}N_4H_{20}O_2)Cl_2]$	8643	$^6A_1g \rightarrow {}^4T_1g$ (G),	Octahedral (Oh)
	9057	$^6A_1g \rightarrow {}^4T_2g$ (G)	
	42016	$^6A_1g \rightarrow {}^4A_1g$ (G)	
$[Cu(C_{12}N_4H_{20}O_2)Cl_2]$	8733	$^6A1g \rightarrow {}^4T_1g\ (t_2g)^4$ (eg)	Octahedral (Oh)
	11534	$^6A_1g \rightarrow {}^4T_2(F)(t_2g)^4$ (eg)	
	44444	$^6A_1g \rightarrow {}^4Eg'^4A_1g\ (t_2g)^3\ (eg)^2$	

IR spectra

IR spectra of the macro cyclic ligand complexes shows bands at 1361-1367 cm^{-1} observed due to presence of C_6H_5 group in the structure. The bands at 1643-1631cm^{-1}may be assigned to the symmetric and asymmetric ν(C=N) vibrations, the bands at 1257-1220 cm^{-1} shown are due to symmetric and asymmetric ν(C-N) vibrations, the bands present in the range 1727-1723 cm^{-1} indicating presence of ν(C=O) vibrations. On complex formation, the position of these bands is shifted toward lower side as compared to the metal free ligand. This indicates that the coordination takes place through the nitrogen of the(C=N) groups. The band at 451-451 cm^{-1} indicates presence of metal nitrogen bonding.

Table 5: IR spectra of complexes.

Name of complex/Ligand	$\nu_{C=N}$	ν_{C-N}	$\nu_{C=O}$	ν_{M-N}
$C_{12}N_4H_{18}O_2$	1643	1218	1727	
$[Co(C_{12}N_4H_{18}O_2)Cl_2]$	1639	1218	1725	448
$[Ni(C_{12}N_4H_{18}O_2)Cl_2]$	1631	1257	1724	448
$[Cu(C_{12}N_4H_{18}O_2)Cl_2]$	1634	1220	1723	451

Electrical conductivity, Magnetic Properties

Molar conductivity of the cobalt (II), nickel(II) and copper(II) complexes is ranging from 1.68 to 3.23 ohm^{1}cm^{2}mol^{-1}, indicating non-electrolytic nature of the complexes. Magnetic susceptibility values of the complexes shows octahedral geometry of the complexes.

Table 7: Molar conductivity and Magnetic moment of complexes.

Complex	Molar Conductance(ohm^{1}cm^{2}mol^{-1})	μeff (B.M.)
$[Co(C_{12}N_4H_{18}O_2)Cl_2]$	3.23	3.53361363
$[Ni(C_{12}N_4H_{18}O_2)Cl_2]$	1.68	4.90922218
$[Cu(C_{12}N_4H_{18}O_2)Cl_2]$	2.47	1.977732851

Microbiological Activities

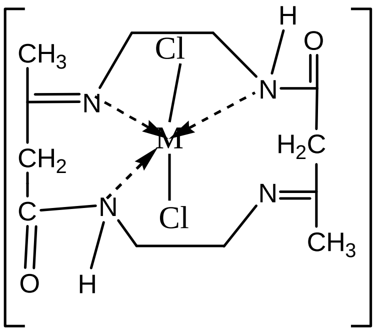
The macro cyclic ligand and macro cyclic ligand complexes synthesized in the present investigation has been subjected to antimicrobial screening programs based on their structural features so as to ascertain their activity against four different microorganisms *E.coli., Baciullus Sp Staphylococcus sp., and Proteus Sp.*

The solvent used was DMSO, and the sample concentrations were, 100ppm. The results of preliminary study on antimicrobial activity indicated that most of the complexes show activity as shown against these organisms.

Table 8: Microbiological activities (zone inhibition in mm).

Sr.no	Name of the ligand/complex	E-coli	Bacillius	Staphy	Proteus
1	$C_{12}N_4H_{18}O_2$	11	14	11	10
2	$[Co(C_{12}N_4H_{18}O_2)Cl_2]$		12	12	13
3	$[Ni(C_{12}N_4H_{18}O_2)Cl_2]$	10	-Ve	10	10
4	$[Cu(C_{12}N_4H_{18}O_2)Cl_2]$	10	11	11	-Ve

By considering all the above properties of the macro cyclic complexes the structure of the macro cyclic complexes with transition metals should be as given below



Where M=Co(II),Ni(II) or Cu(II)

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