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Synthesis of Dodecaaza-tetrachlorotricyclodotriacontane (DACD) Macro Cyclic Complexes of Transitional Metal Ions (Cu^{++}) Present in Pulp and Paper Mill Effluents

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ABSTRACT

Transition metal ion has been receiving a great attention in the recent years, as the high concentration of toxic metal ions. This paper deals with short review and to study the various types of transition metals present in waste water released from Pulp and Paper effluents. These are being constantly poured into the environment, which result in the long lasting bio-hazards in the aquatic eco-systems. So it is new technique of estimating Cu metals present in Pulp and Paper effluents .The investigation incorporates in the physio chemical properties of new divalent Cu (II) metal ion macro cyclic complexes. The investigation includes their synthesis and spectral magnetic properties.

Key words: Transition metals, diethylenetriamine, hexachloroethane, macro cyclic ligands.

INTRODUCTION

Hazardous metal ions, such as Cu, Ni, Co etc.have become prominent pollutants. Transition metals are a meal of high specific gravity characterized by strong attraction to biological tissues with slow elimination. Many transition metals are essential to life, if present in small quantity. They can be regarded as toxic if they present in high concentration because they injure the growth or metabolism to the body.Some of the metals such as Ni, Co, Cu, As, Hg, Pb, Zn, Cr etc. are highly toxic to human beings and when absorb in small quantity. In this paper an attempt is made to discuss studies in relation with transitional metal like Cu, its source, effect on health and its physio-chemical property.

The concentration of these metal ions is increased in water by different types of human activities like industrial effluents, mine drainages etc. Their removal from water is hence, significant and to meet these large number of methods have been suggested.

The body needs trace amounts of copper in order to function properly. But too much exposure to copper can cause a number of health problems. For instance, simply breathing in copper can cause irritation to your nose and throat. If you ingest copper orally, it may cause: Nausea, Vomiting, Diarrhea, Liver Damage Kidney, Damage, Death

In view of the importance of the macrocyclic chemistry, the copper (II) complexes of several new

catagories of azamacrocycles were synthesized. Template condensation of chlorocarbons such as hexachloroethane with tri-amine such as diethylenetriamine in presence of Cu (II) to yield a new macrocycle in which additional metal ions are incorporated in separate rings. The macrocyclic ligands and their complexes have been characterized by elemental analysis, molecular weight determination, conductance, IR and NMR spectral studies. The spectral data suggested tetra coordinated state for copper; its geometry is square planner .Conductivity data suggests that they behave as electrolytes. The formulation of the complexes has been established on the basis of chemical composition. The ligands and their complexes have been used as catalyst in many industries.

The isolation of Cu is possible if they are having a size of 10^6 parts per million in the Pulp and Paper effluents. The transition metal ions such as Cu (II) have isolated as $Cu(OH)_2$.

Methodology

In the present investigation di-polymetallic complexes of Cu (II) have been derived from polyamines. Template condensation of chloro carbon such as hexachloroethane with tri-amine such as diethylenetriamine in presence of Cu (II) which was formed by the Pulp and Paper mill effluent yield the corresponding metal complex of the following macro cyclic legend – 3,6,9,12,15,18,19,22,25,26,29,32-dodecaaza-1,2,10,11-tetrachlorotricyclo[9.7.7.7] dotriacontane (DACD) (Fig 1).

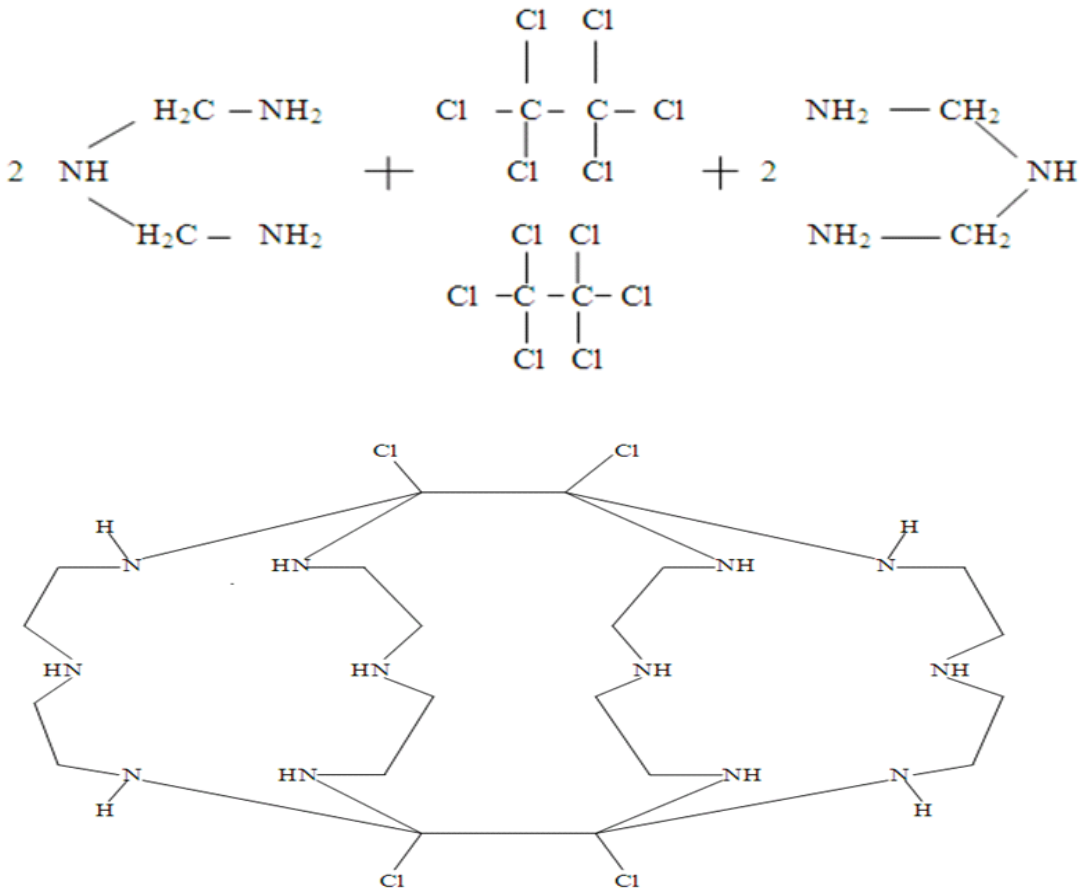


Fig.1 : Macro cyclic legend – 3,6,9,12,15,18,19,22,25,26,29,32-dodecaaza-1,2,10,11-tetrachlorotricyclo[9.7.7.7] dotriacontane (DACD)

A 6.34 g (61.45 mmole) diethylenetriamine was allowed to condense with 14.56 g (61.50 mmoles) of hexachloroethane in presence of 6.00 g (61.50 mmole) copper hydroxide. The blue reaction mixture was refluxed for 1 h.30 min in 180 ml butanol. The colour of the reaction mixture immediately changed from blue to green, followed by reddish-yellow and brownish- red within 5, 10 and 20 min respectively. After 1 hr, 30 min continuous heating the resulting solution (brownish-red) was cooled, stirred with 100 ml of water and filtered. A large amount of brown residue was rejected and the greenish-grey aqueous layer of the filtrate was separated from the non-aqueous brownish-red layer. Concentrated of the aqueous solution caused greenish-grey semi-solid crude product within was further treated with benzene-ether (1:1) mixture on filter paper. The resulting sticky product was further dissolved in 50 ml methanol/ water mixture (1:1) and evaporated at room temperature to yield the deep blue crystalline product $[Cu_4(DACD)(H_2O)_4]Cl_8$. The deep blue crystals were finally washed with methanol, followed by ether and dried under reduced pressure, yield 2.00 g. Isolated complex have the following molecular formulae confirmed by IR, NMR and Mass spectroscopy. $[Cu_4(DACD)\ (H_2O)_4]Cl_8$ or $Cu_4C_{20}H_{52}N_{12}O_4Cl_{12}$ (Fig. 2).

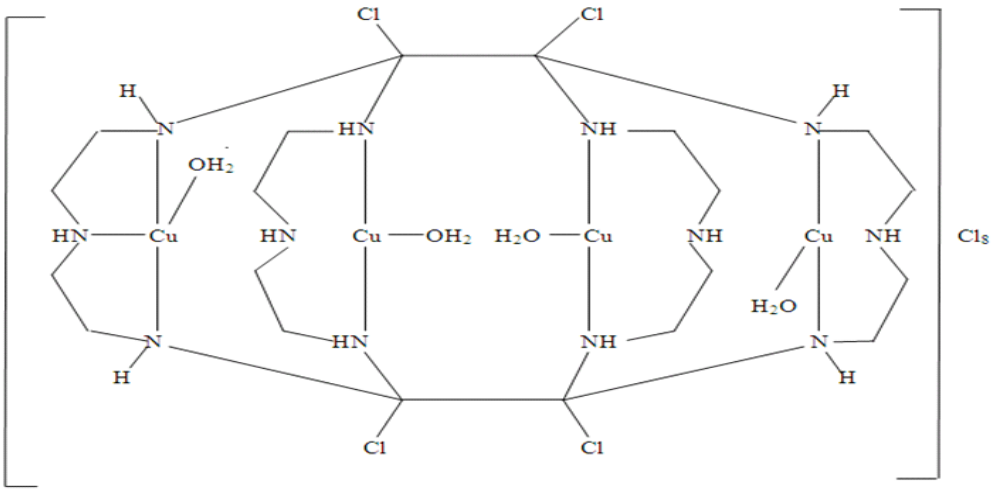


Fig. 2 : Cu (II) complex of 3,6,9,12,15,18,19,22,25,26,29,32-dodecaaza-1,2,10,11-tetrachlorotricyclo[9.7.7.7] dotriacontane (DACD)

RESULTS AND DISCUSSION

In the condensation of diethylenetriamine with hexachloroethane in presence of copper hydroxide under similar reactant molar ratio dodecaaza macrocyclic ligand 3,6,9,12,15,18,19,22,25,26,32-dodecaaza-1,2,10,11-tetrachlorotricyclo[9.7.7.7] dotriacontane (DACD) is generated. The metal complex $[Cu_4(DACD)(H_2O_4]Cl_8$ is tetranuclear. Cyclization proceeds by condensation of hexachloroethane with copper coordinated diethylenetriamine. Each copper (II) is a square planer structure is surrounded by three aza groups of the macrocyclic and one water molecule.

$$4\ Cu\ (H_2N.CH_2.CH_2.NH.CH_2.CH_2NH_2)(OH)_2 \;\Big|\; 2\ C_2Cl_6 \rightarrow [\ Cu_2(DACD)\ (H_2O)_4]Cl_8\ +\ 8\ H_2O$$

Cl atoms of DACD are responsible for an increase in the ring number of the macrocyclic.The template condensation of the triethylenetetramine with the copper (II)-DACD complex in the presence of the metal hydroxide in 1:2:2 molar ratio yields new metal complexes.

The complex was characterized on the basis of elemental analysis, conductivity measurements, mass spectra, infrared and proton nuclear magnetic resonance spectral studies. The results of elemental analysis reported in Table-1 indicate the stoichiometry which is in agreement with the formulation given. Evidence for cyclization is demonstrated by the absence of infrared absorption bands that may be attributed to either free or coordinated NH_2 groups.

The structure of macro cyclic complex can be stabilizing by the following method - Microanalysis for carbon, hydrogen and nitrogen were carried out at the Regional Sophisticated Instrumentation Centre, Central Drug Research Institute (CDRI) Lucknow.The metal (Cu^{++}) content in complex can be determined by EDTA titration. Ionizable Cl^- ion in compound was determined by conductometric titration using 0.01 m legend compound and 1 m $AgNO_3$ solution.

Conductivity data of the complex was recorded using their 0.01 M aqueous solution, with the help of a DDR Conductivity meter type 304. Mass spectra were recorded at the RSIC, CDRI Lucknow. A Jeol D-300 (EI/CI) spectrometer was used for obtaining the mass spectra of the ligand hydrochlorides of low molecular weight. Infrared spectra in the range 4000-250cm^{-1} were recorded by Perkin Elmer infrared spectrometer in KBr pellets at Regional Sophisticated Instrumentation Centre, C.D.R.I. Lucknow. The pmr spectra were taken in D_2O solution and recorded on Bruker DRX300 (300 MHz. PT NMR) using tetra methyl silane as an internal standard (Table 1).

Table 1: Analytical and physical data of the Macrocyclic Compounds derived from Diethylenetriamine:

Compound	Colour (colour at D.P.)	Yield (%), (D.P.v M.P. (^{0}C)	Conductivity (ohm^{-1}cm^2 mol^{-1})	% Found (Calculated) C	H	N	Cu	Cl	Mol.wt Found Calculated
$[Cu_4(DACD)(H_2O)_4]Cl_{12}$ $Cu_4C_{20}H_{52}N_{12}O_4Cl_{12}$	Deep blue (brown)	10.80 (225)	968	20.02 (19.94)	4.35 (4.36)	14.01 (13.96)	21.08 (21.10)	23.63 (23.55)	(1204.4)

In the infrared spectrum of the copper-DACD complex the medium but sharp N-H stretching modes of only secondary amine groups appear at 3125cm^{-1}.The compound exhibits a δ (N-H) vibrations at 1582 cm^{-1}.Very sharp bands at 1070 (strong) and 440 cm^{-1}(medium) frequencies may be assigned to ν(C-N) and ν(Cu-N), respectively. Vibrations for C-H asymmetric (medium, sharp), symmetric (weak, sharp) and scissoring (medium) are seen at 2920, 2870 and 1442 cm^{-1}respectively. The presence of coordinated water is indicated by appearance of a strong and sharp band at 3220 cm^{-1} followed by other peaks at 830,620 and 518 cm^{-1} attributed to O-H stretching, rocking, wagging and ν (Cu-O) ,respectively.

The metal-free macrocyclic molecules DACD.12HCl exhibits a very strong but very broad band in the region 3200-2800 cm^{-1}assigned to ν (C-N). A C-H scissoring peak appears at 1489 cm^{-1}. The í (N-H) vibration for secondary amine is not seen, probably due to its coupling with the strong and broad ν (C-H) vibrations. A peak at 1605 cm^{-1} may be attributed to N-H bending vibration. The number of weak bands associated with the amine hydrochloride in the region 2800-2000 cm^{-1} is low. A weak but broad band for ν (C-N) appears at 1110 cm^{-1}.

The pmr spectrum of DACD hydrochloride can be resolved into three distinct regions due to

Compound	IR Bands (cm^{-1}) Table1.2: for Important IR Bands of the Macrocyclic Compounds Derived from Diethylenetriamine
[$Cu_4(DACD)(H_2O)Cl_8$	3220(s,sp), 3125(m,sp), 2920(m,sp), 2870(w,sp), 1582(m,sp), 1442(m), 1380(w,vsp), 1360(vw,sp), 1290(v,csp), 1240(m,sp), 1140(m,vsp), 1070(s,vsp), 1020(s,vsp), 986(m,vsp), 940(m,sp), 892(w,vsp), 860(vw,vsp), 830(vw), 620(m,vsp), 518(m,vsp), 440(m,vsp), 383(w,vsp), 342(w,vsp), 315(vw,sp), 250(vw).

*Abbreviations Used: b = broad, d = doublet, m = medium, s = strong, sh = shoulder, sp = sharp, vb = very broad, vs = very strong, vsp = very sharp, vw = very weak, w = weak

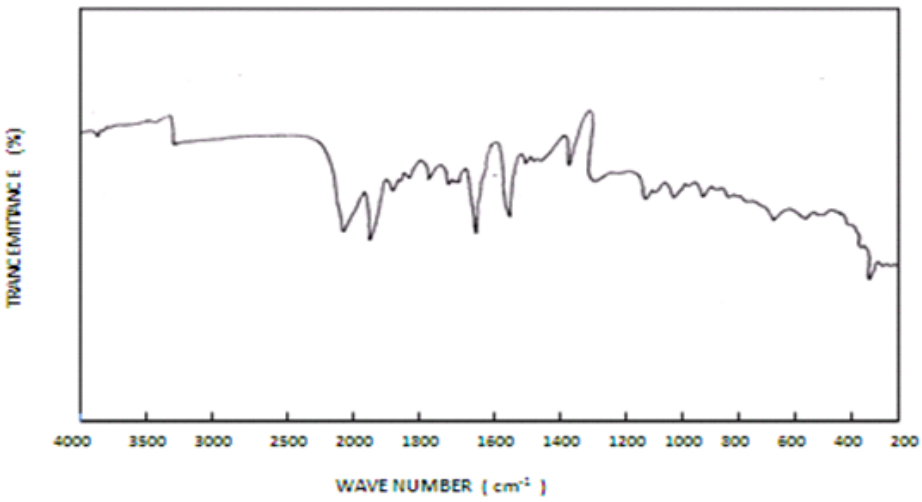
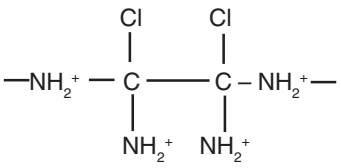


Fig.3 : IR Spectra of $[Cu_4(DACD)(H_2O)_4]Cl_8$ or $Cu_4C_{20}H_{52}N_{12}O_4Cl_{12}$

NH_2^+ and two monequivalent CH_2 protons. It shows a broad singlet at 4.99 ppm assigned to NH_2^+ resonances. The remaining two signals for nonequivalent CH_2 protons are broad triplets centred at 3.47 and 3.55 ppm (J-6.00 Hz).The first triplet resonance is attributed to the CH_2 proton



bonded to

groups whereas the second resonance is assigned to the remaining CH_2 protons. The relative areas of the two triplets being identical correspond to the expected protons.

Determination of molecular weight by mass spectra of the compound DACD.12HCl by FABMS has been very useful in completing their characterization .The highest mass peaks found in the spectrum occur at m/z values close to their molecular ions (Table 1.1) and are very weak and are comparable to those observed in earlier reported aza macrocyclic complexes.

$[Cu_2(DACD)\ (H_2O)_4]Cl_8$ compounds are highly soluble in water and generally in polar solvents like ethanol, methanol, DMF etc.The molecular conductivity of the complexes and number of ionizable chloride ion in all macrocyclic molecules recorded in Table 1.1 are in support of their ionic structures. The complex Copper-DACD is 8:1 electrolytes. The molar conductance value

968 ohm^{-1} cm^2 mol^{-1} determined for Copper-DACD complex. The copper complex is blue or deep blue. The metal-free ligand hydrochloride DACD-12HCl is yellowish-white in colour. This compound is thermally stable and decomposes above 200^{0}C.

CONCLUSION

According to the result of this study, transition metal ions present in pulp and paper mill effluents can be isolated and treated with equimolar amount of diethylenetriamine and hexachloroethane, macrocyclic complexes are formed. The above procedures outlined for the preparation of the resultant macrocyclic complexes are facile and appear to proceed smoothly. This is used as electro catalyst in fuel cell, enhances the electrical conductivity. It should prove useful for investigation of metal containing-biological molecules such as metalloenzymes and their catalytic activity for industries.

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