

SYNTHESIS OF 1,4,6,9 TETRA AZA CYCLO DECANE (TACD) MACROCYCLIC COMPLEX OF Ni (II) TRANSITIONAL METAL ION PRESENT IN INDUSTRIAL WASTE WATER

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ABSTRACT

An attempt has been made to study the various types of transitional metal ion, present in waste water released from the Industries. Thus It Is a new technique of estimating Cu, Ni metals present in water. Ni metal ions are seriously toxic to human being and when absorbed in quite small amount, they have great affinity for sulphur and attack sulphur bond in enzymes, thus immobilizing it. The investigation incorporates in the physio chemical properties of some new divalent Ni (II) metal ion macro cyclic complexes. The investigation includes their synthesis and spectral magnetic properties.

INTRODUCTION

Transitional metal ion (viz: - Ni, Co, Cu etc.) are discharged from various industries and cause serious environmental pollution.

Heavy metals have high specific gravity (Pitts and Metcalf, 1974) characterized by strong attraction to biological tissues with slow elimination. Some of the metals like Ni, Co, Cu, As, Hg, Pb, Zn, Cr etc. are highly toxic to human beings and when absorbed in small quantity, such as

1. They have great affinity for sulphur and attract sulphur bond in enzyme, thus immobilizing it.
2. They bind to cells membrane, affecting transport processes through cell wall.
3. They also tend to precipitate phosphate bi compounds or catalyze their decomposition

Many metals are essential to life, if the 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 tissue.

In this paper an attempt is made to discuss studies in relation with heavy metals like Ni their source, effect on health and its physio-chemical property.

Source: The most obvious is the process of extraction, purification mining, smelting, refining the second is release of metal from fossil fuel. The third and most diverse sources are production and use of industrial products containing metals. These all metals enter in to the surface and ground water and are generally considered as a part of environmental pollution.

Effect : Today, much more is known about the health effects of heavy metals. Exposure to heavy metals has

been linked with developmental retardation, various cancers, kidney damage, even death in some instance of exposure to very high concentration.

Physio chemical properties : Physio chemical property of some new divalent Cu (II), Ni (II), Co (II) Metal ions macro cyclic complex and their synthesis as well as magnetic property. This complex will be prepared via template synthesis using di-amine, metal salt and chloro carbon. By using chemical analysis, spectral and magnetic studies. Geometry of the complex has been established.

Isolation: The isolation of Ni, Co, Cu etc. is possible if they are having a size of 10^6 parts per million in the industrial waste water. The transition metal ions such as Cu (II), Ni (II), Co (II) have isolated as NiCl_2 with HCl and then treated with aqueous NaOH, it changes in to $\text{Cu}(\text{OH})_2$, $\text{Ni}(\text{OH})_2$, $\text{Co}(\text{OH})_2$.

MATERIALS AND METHODS

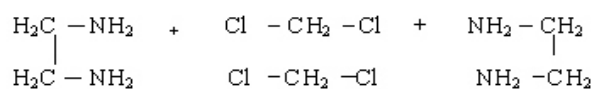
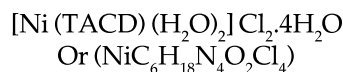
In view of the importance of macro cyclic chemistry (1-3), the Ni (II), Co (II), Cu (II) complexes of several new categories of aza macro cyclic were synthesized. Template condensation of chloro carbon such as dichloro methane with di-amine such as 1, 2 di-amino ethane in presence of Ni (II) which was formed by the industrial waste water yield the corresponding metal

complex of the following macro cyclic legend – 1,4,6,9 tetra aza cyclo decane

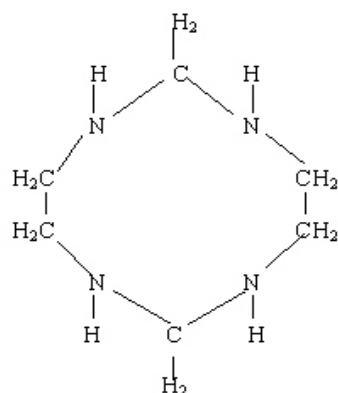
Experimental

Synthesis of the Ni (ii) complex of 1,4,6,9 tetra aza cyclo decane (Ni-TACD): A mixture of Nickel hydroxide (5.00 gm., 53.91 m mole), 1, 2 di-amino ethane (6.48 gm., 107.82 m mole) and di chloro methane (9.16 gm. 107.85 m mole) in 200 mL. butanol was reflux for 4 hrs. A mixture initially containing light green precipitate changes to yellowish – green turbid solution after 15 minute. The mixture then gradually changes to a mix. Of violetish – red and light green precipitate. The resulting content was treated with 150 mL. of water and filtered. The light green residue on filter paper was rejected, the filtrate contained colourless non aqueous layer and reddish pink aqueous layer containing the macro cyclic product. Concentration and refrigeration of aqueous layer yield violet crystals. The crystals are moderately soluble in water but their solubility is poor in methanol or acetone. Washing of the crystals with methanol followed by acetone gave analytically pure crystals, yield 1.8 gm.

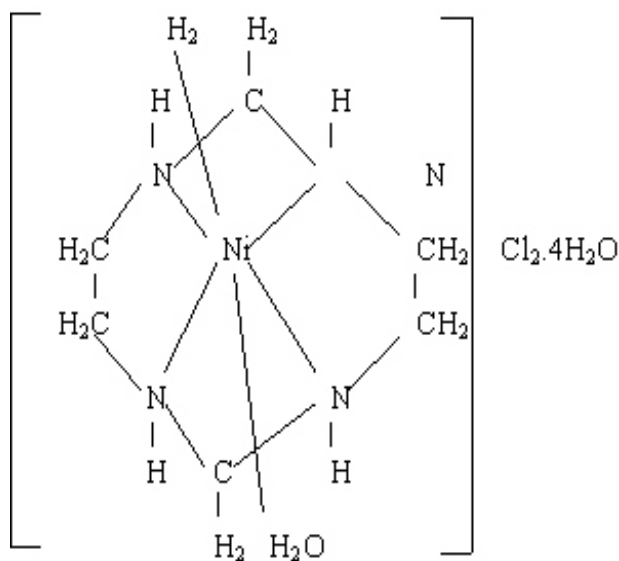
Isolated complex have the following molecular formulae confirmed by IR, NMR and Mass spectroscopy



— 4HCl



1,4,6,9 tetra aza cyclo decane



Ni (ii) complex of 1,4,6,9 tetra aza cyclo decane (Ni-TACD)

Table 1. Analytical and physical data of the Macrocyclic Compounds derived from 1, 2 diaminoethane

Compound	Colour (at D.P.)	Yield (%) (D.P.v M.P.) (°C)	Conduc- tivity (ohm ⁻¹ cm ² mol ⁻¹)	% Found (Calculated)					Mol. wt. Found (Calcu- lated)
				C	H	N	Ni	Cl	
Ni (TACD) (H ₂ O) ₂ Cl ₂ .H ₂ O NiC ₆ H ₁₈ N ₄ O ₂ Cl ₄	Violet (Black)	8.7 (250)	265	18.92 (18.86)	7.42 (7.40)	14.72 (14.67)	15.32 (15.37)	18.50 (18.56)	382.0

RESULTS AND DISCUSSION

Establization

The structure of macro cyclic complex can be stabilizing by the following method:

1. Chemical analysis

Microanalysis for carbon, hydrogen and nitrogen were carried out at the regional sophisticated instrumentation centre, central drug research institute (CDRI) Lucknow.

Ni content in complex can be determined by EDTA titration.

Ionizable Cl⁻ ion in compound was determined by conductometric titration using .01 m legend compound and 1 m AgNO₃ solution.

Physical measurements

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 D₂O solution and recorded on Bruker DRX300 (300 MHz's PT NMR) using tetra methyl silane as an internal standard.

i) Infrared spectra

TACD System: In the infrared spectrum of the nickel-TACD complex a shoulder of N-H stretching modes of only secondary amine groups appear at 3140 cm⁻¹. The compound exhibits a δ (N-H) vibration at 1580cm⁻¹.

1. Weak bands at 1080 and 465 cm⁻¹ frequencies may be assigned (4-6) to ν (C-N) and (Ni-N), respectively. Strong but very sharp vibrations for C-H symmetric, asymmetric stretching and scissoring are seen at 2852, 2920 and 1450 cm⁻¹ respectively. The presence of coordinated water is indicated by the appearance of a very strong and very broad band at 3250⁻¹ followed by other peaks at 1640, 630 and 520-1 attributed to δ(O-H), O-H wagging and ν(Ni-O), respectively. Many other strong/medium/weak bands at 1600, 1360, 1320, 1260, 1140, 1070, 1010, 965, 862, 810, 630, 465 and 392 cm⁻¹ are associated with the skeletal vibration of the whole complex molecule.

Table 2. IR Bands (cm⁻¹) for Important IR Bands of the Macrocyclic Compounds Derived from Diethylenetriamine

Compound	IR Bands (cm ⁻¹) for Important IR Bands of the Macrocyclic Compounds Derived from Diethylenetriamine
Ni(TACD) (H ₂ O) ₂ Cl ₂ .H ₂ O NiC ₆ H ₁₈ N ₄ O ₂ Cl ₄	3250(vs,vb), 3140(sh,sp), 2920(s,vsp), 2852(s,vsp), 2725(w,vsp), 2120(m,sp), 1640(m,vsp), 1600(s,d), 1580(s), 1450(s,vsp), 1360(w,sp), 1320(s,vsp), 1260(s,vsp), 1140(s,vsp), 1080(w), 1070(vw), 1010(vs,vb), 965(sh,vsp), 862(vw,sp), 810(vw,sp), 630(s,be), 520(s,vsp), 490(w,sp), 465(vw,sp), 390(w,sp).

*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

ii) Nuclear magnetic resonance spectra

Nickel Complexes of TACD: In the spectrum of Nickel-TACD complex a broad signal in the region

4.70-4.65 ppm is observed for NH and H₂O proton. On the basis of relative areas the two up field signal (doublets) in the region 4.14-4.04 and 3.73-3.30ppm are expected for resonances resulting from CH₂ and CH₂.CH₂ proton, respectively.

iii) Mass spectra

TACD System: Determination of molecular weight by mass spectra of the compound TACD.4HCl has been very useful in completing their characterization. The corresponding peaks in TACD.4HCl is very close to their molecular ions. The slightly low m/z values in these systems may be associated with the mass lost (H) due to fragmentation of the molecular ions.

iv) Solubility, conductivity and other data

[Ni (TACD) (H₂O)₂] Cl² .4H₂O are thermally stable and decompose near their melting point. In addition, attachment of chloride ion through and ionic bond in the nickel (II) – TACD complex gives indirect information on the metal – chloride ion coordinate linkage of the other chloride ion. This complex is highly soluble in water due to their ionic nature (7-10).

[Ni (TACD) (H₂O)₂] Cl₂ .4H₂O exhibit molar conductance values in the 210-265 ohm⁻¹ cm² mol⁻¹ range, and are 2:1 electrolytes.

CONCLUSIONS

According to the result of this study, Transitional metal ions present in industrial waste water can be isolated and treated with equimolar amount of diamine and chlorocarbon, macrocyclic complexes are

formed. This is used as electro catalyst in fuel cell, enhances the electrical conductivity, hydrogenation catalyst, Nahata catalyst which act as an efficient reusable heterogeneous catalyst. This catalyst use in drug discovery and drug development.

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