



## SYNTHESIS OF NICKEL (II) COMPLEX OF CTAAZATRICYCLOTETRACOSANE (OCTC) MACROCYCLIC COMPLEXES FROM THE CONTAMINATED SOIL

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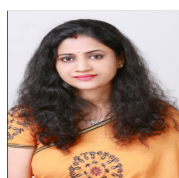
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### ABSTRACT

Consumer demand for better quality produce is now on an increasing surge. In particular, some metals are not desirable in agriculture as they may harm the environment or humans. Because of this, the concentrations of metals in soils and foods should be regularly monitored. This paper extensively addresses our concerns about these undesired metals in the farm soil and farm produce and how to manage the situation so that it does not become a menace. This paper deals with the synthesis and characterization of macro cyclic ligand and its complex compound. Template condensation of chlorocarbons such as 1,1,2,2-tetrachloroethane with 1,3-diaminopropane in presence of nickel (II) yielded the corresponding metal complexes such as 3,7,10,14,15,19,20,24- octaazatricyclotetracosane (OCTC). The macrocyclic ligands and their complexes have been characterized by elemental analysis, molecular weight determination, conductance, IR and NMR spectral studies. The magnetic moments, along with electronic spectral data suggested hexa coordinated state for Nickel, its geometry is outer orbit octahedral. Conductivity data suggests that they behave as electrolytes. The formulation of the complexes has been established on the basis of chemical composition. The significant ligand and their complexes have now widely being used as a catalyst in many industries.

**KEYWORDS:** Contaminated soil, Macro cyclic ligand, Macro cyclic complex, synthesis, spectroscopy, catalyst.



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## INTRODUCTION

Soils may become contaminated by the accumulation of heavy metals and metalloids through emissions from the rapidly expanding industrial areas, mine tailings, disposal of high metal wastes, leaded gasoline and paints, land application of fertilizers, animal manures, sewage sludge, pesticides, wastewater irrigation, coal combustion residues, spillage of petrochemicals, and atmospheric deposition.<sup>1,2</sup> Heavy metals constitute an ill-defined group of inorganic chemical hazards, and those most commonly found at contaminated sites are lead (Pb), chromium (Cr), arsenic (As), zinc (Zn), cadmium (Cd), copper (Cu), mercury (Hg), and nickel (Ni).<sup>3</sup> Soils are the major sinks for heavy metals released into the environment by aforementioned anthropogenic activities and unlike organic contaminants which are oxidized to carbon (IV) oxide by microbial action, most metals do not undergo microbial or chemical degradation<sup>4</sup> and their total concentration in soils persists for a long time after their introduction.<sup>5</sup> Changes in their chemical forms (speciation) and bioavailability are, however, possible. The presence of toxic metals in soil can severely inhibit the biodegradation of organic contaminants.<sup>6</sup> Heavy metal contamination of soil may pose risks and hazards to humans and the ecosystem through: direct ingestion or contact with contaminated soil, the food chain (soil-plant-human or soil-plant-animal-human), drinking of contaminated ground water, reduction in food quality (safety and marketability) via phytotoxicity, reduction in land usability for agricultural production causing food insecurity, and land tenure problems.<sup>7-9</sup> The adequate protection and restoration of soil ecosystems contaminated by heavy metals require their characterization and remediation. Contemporary legislation respecting environmental protection and public health, at both national and international levels, are based on data that characterize chemical properties of environmental phenomena, especially those that reside in our food chain.<sup>10</sup> In his paper, scattered literature is utilized to review the possible sources of contamination, basic chemistry, and the associated environmental and health risks of priority heavy metal (Ni) which can provide insight into heavy metal speciation, bioavailability, and hence selection of appropriate remedial options. The principles,

advantages, techniques as options for soil cleanup are also presented.

Curtis reported the first of a number of pioneering template reaction for macro cyclic systems which were published in the period 1960 to 1965.<sup>11</sup> In the Curtis synthesis, a yellow crystalline product was observed to result from the reaction of  $[\text{Ni}(1,2\text{-diaminoethane})_2]^2$  and dry acetone. The yellow product was shown to be a mixture of the isomeric macro cyclic complexes. 5, 5, 5, 7, 12, 12, 14 hexamethyl 1, 4, 8, 11 tetraazacyclotetradecane-1, 14 diene.<sup>13</sup> In this remarkable cyclization reaction, formation of bridges between the two 1, 2-diaminoethane moieties involves condensation of two acetone molecules per bridge.<sup>12</sup> Here, a hydrogen-bonding network may act as a template for the reaction and also serve to stabilize once it is formed. A revised synthesis of the metal-free ligands has been published.<sup>14</sup> In this paper an attempt is made to discuss studies in relation with heavy metal like Ni, its source, effect on health and its physio-chemical properties. Unfortunately, these soil additives can be contaminated with metals that can have negative effects on crops on quality and quantity. Today, much more is known about the health effects on human being of Nickel metals. In view of the importance of the macro cyclic chemistry, the Nickel (II) complexes of azamacrocycles were synthesized. Template condensation of chlorocarbons in presence of Ni (II) to yield a new macrocycle. In which additional metal ions are incorporated in separate rings. This paper describes synthesis and characterization of macrocyclic complexes of nickel (II) derived from 1, 3-diaminopropane. The 1, 3-diaminopropane has been condensed with 1, 1, 2, 2-tetrachloroethane in presence of a metal-ion in different molar ratios as mentioned in their synthesis.

## MATERIALS AND METHODS

In view of the importance of macrocyclic chemistry the Ni (II) complexes of new categories of aza macrocyclic were synthesized. Template condensation of chloro carbon such as 1,1,2,2-tetrachloroethane with 1,3-diaminopropane in presence of Ni (II) yield the corresponding metal complex of the following macro cyclic legend – 3,7,10,14,15,19,20,24-octaazatricuclo[7.5.5<sup>2,8</sup>] tetracosane (OCTC) (Figure 1).

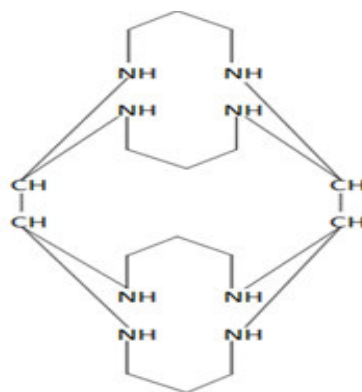


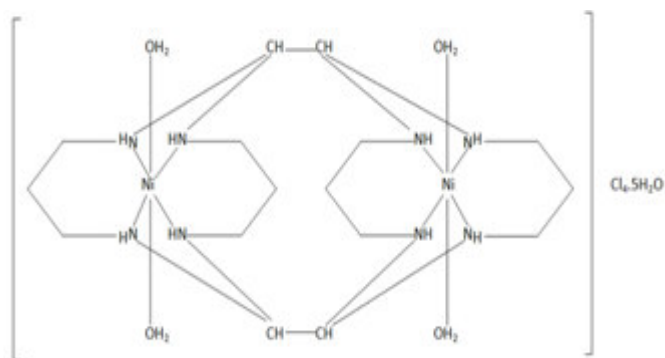
Figure 1  
Structure of OCTC

Solvents and reagents used in the synthesis of the nickel (II) complexes were reagent grade and were used without further purification.

**Synthesis of the nickel (II) complex of 3, 7, 10, 14, 15, 19, 20, 24-octaazatricuclio [7.5.5.5<sup>2,8</sup>] tetracosane (OCTC)**

Nickel hydroxide 95.00g, 53.92 (m mole) was added to stir mixture of 1, 3-diaminopropane (7.99 g, 107.78 m mole) and 1, 1, 2, 2- tetrachloroethane (9.05 g, 53.92 m mole) in 200ml butanol. The mixture was then refluxed for 4 hrs. After being refluxed about 5 min. the mixture changed to blue turbid solution containing a small quantity of the green precipitate. The whole mixture turned into a blue turbid solution after being refluxed for 4 h. It was then cooled treated with 150 ml of water and

aqueous bluish-violet solution was separated and the green precipitate and colorless non-aqueous butanol layer were rejected. Condensation and refrigeration of the solution gave crude, sticky violet crystals of  $[\text{Ni}_2(\text{OCTC})(\text{H}_2\text{O})_4]\text{Cl}_4 \cdot 5\text{H}_2\text{O}$ . The sticky material was removed by treating the product with ether-benzene (1:1) mixture on filter paper. The product was recrystallized to remove traces of white residue. Pure product was crystallized from the resulting solution. Violet crystals were finally washed with ether and dried, yield 10.2 g (Figure 2).



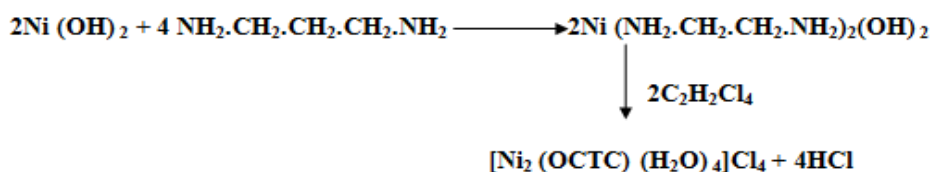
**Figure 2**  
**Structure of Ni-OCTC**

## RESULTS AND DISCUSSION

### Synthesis

The nickel (II) complex of 3, 7, 10, 14, 15, 19, 20, 24-octaazatricuclio [7.5.5.5<sup>2,8</sup>] tetracosane (OCTC) derived from 1:2:1 molar mixture of nickel hydroxide 1, 3-diaminopropane and 1, 1, 2, 2-tetrachloroethane

contain two nickel ions in the ligand cavities, where each metal is coordinated to four donors. The two molecules of 1:2 nickel-ammine complexes formed at the initial stage condensed with two molecules of 1, 1, 2, 2-tetrachloroethane yielding the corresponding dinuclear complex.



### Chemical analysis

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

The metal content was determined by EDTA titration. The ionizable chloride ions in the compounds were determined by conductometric titration using 0.01 M ligand /complex and 0.1 M  $\text{AgNO}_3$  solution. (Table 1)

**Table 1**  
**Analytical and physical data of the nickel (II) complex of 3, 7, 10, 14, 15, 19, 20, 24-octazatricyclo [7.5.5.5<sup>2,8</sup>] tetracosane (OCTC) Macro cyclic Compound derived from 1, 3-diaminopropane**

compound	Colour (colour at D.P.)	Yield (%), (D.P. v M.P.) (°C)	Conductivity (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	% Found ( Calculated)					Mol. wt. Found (Calculated)
				C	H	N	Ni	Cl	
[Ni <sub>2</sub> (OCTC)(H <sub>2</sub> O) <sub>4</sub> ]Cl <sub>4</sub> .5H <sub>2</sub> O Ni <sub>2</sub> C <sub>16</sub> H <sub>34</sub> N <sub>8</sub> O <sub>9</sub> Cl <sub>4</sub>	Violet (bluish-violet)	49.7 (122)	498	25.29 (25.22)	7.14 (7.16)	14.75 (14.71)	15.46 (15.41)	18.56 (18.61)	(762.0)

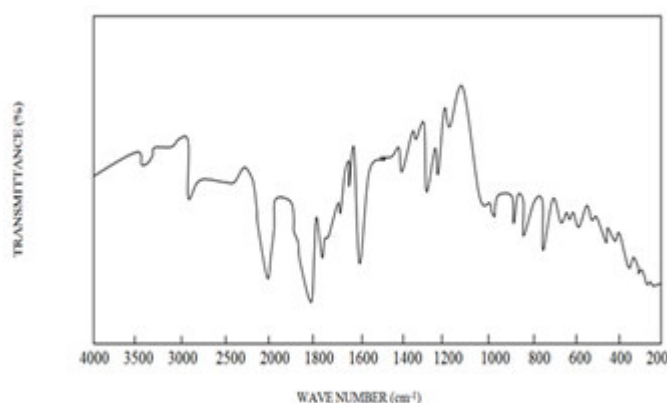
### Physical measurements

Conductivity data of the complex was recorded using their 0.01 M aqueous solution, with the help of DDR Conductivity meter type 304. A Joel D-300 (EI/CI) spectrometer was used for obtaining the mass spectra of the ligands hydrochlorides of low molecular weight. Infrared spectra in the range 4000-250 cm<sup>-1</sup> were recorded by Perkin Elmer infrared spectrometer in KBr pellets. FTIR spectra of a number of compound were recorded by Shimadzu 8201 PC (4000-350 cm<sup>-1</sup>) infrared spectrophotometer. The pmr spectra were taken in D<sub>2</sub>O solution and recorded on Bruker DRX300 (300 MHz PT NMR) using tetra methylsilane as an internal standard.<sup>15</sup>

### Infrared spectra

The infrared spectrum of [Ni<sub>2</sub> (OCTC) (H<sub>2</sub>O)<sub>4</sub>] Cl<sub>4</sub>.5H<sub>2</sub> O includes the absence of bands due to the NH<sub>2</sub> group. A very weak but very sharp band attributed to only a secondary amine appears at 3150 cm<sup>-1</sup>. This suggests the presence of a strong but sharp band at 1594 cm<sup>-1</sup>. A medium but very band at 1065 cm<sup>-1</sup> may be assigned in

the v(C-H) vibration. Medium but sharp scissoring band are seen at 2920, 2870 and 1438 cm<sup>-1</sup> respectively. The bands at 1470, 1380, 1328, 1278, 1160, 1100, 1008, 900, 878, 364 and 319 cm<sup>-1</sup> are associated with the skeletal vibration of the whole complex. A medium but sharp band at 478 cm<sup>-1</sup> is attributed to the nickel nitrogen bond. Coordination of water is supported by the presence of a very strong but very broad band at 3250 cm<sup>-1</sup> followed by a very weak band at 800 cm<sup>-1</sup> assigned to stretching and rocking vibrations of the water molecule, respectively. A band at 638 cm<sup>-1</sup> is attributed to the (Ni-O) vibration of coordinated water. In the complex the N-H stretching mode of the secondary amine is seen at 3110 cm<sup>-1</sup> while the position of the N-H bending vibration is at 1580 cm<sup>-1</sup>. A very weak very sharp band at 1050 cm<sup>-1</sup> is associated with (C-H). Coordination of the ligand through the nitrogen is evident by a medium but very band at 488 cm<sup>-1</sup>. The bands for coordinated water are seen at 3225, 812, 670 and 606 cm<sup>-1</sup> and are attributed to (O-H), rocking and wagging vibration of H<sub>2</sub>O molecule<sup>16</sup>. (Figure:3)



**Figure 3**  
**3,7,10,14,15,19,20,24-Octazatricyclo[7,5,5,5]**  
**Tetracosane (OCTC) (C<sub>16</sub>H<sub>36</sub>N<sub>8</sub>)**

The OCTC hydrochloride spectrum is different in several respects from the spectrum of its nickel. The major

difference occurs in the 1400-400 cm<sup>-1</sup> region where bands due to water molecules or metal coordinate bond



with nitrogen and oxygen are absent. The ligand hydrochloride exhibit a series of weak or very weak but generally sharp bands at 2775,2644,2495,2407,2366 and 2302  $\text{cm}^{-1}$ , and a prominent band at 2019  $\text{cm}^{-1}$  (medium, sharp) associated with  $>\text{NH}_2\text{Cl}$  groups. Such bands are absent in the OCTC complexes. The cyclic nature of the metal-free ligand is demonstrated by the

similarly of its amine bands with those of the nickel complex molecule.<sup>17</sup> A corresponding (N-H) vibration is seen at 1600  $\text{cm}^{-1}$  strong/medium/weak bands for C-H asymmetric and symmetric stretching and scissoring mode appear at 3008,2845 and 1402  $\text{cm}^{-1}$  are also characteristic of the whole ligand molecule.<sup>18</sup> (Table 2).

Compound	IR Bands ( $\text{cm}^{-1}$ )
$[\text{Ni}_2(\text{OCTC})(\text{H}_2\text{O}_4)\text{Cl}_4 \cdot 5\text{H}_2\text{O}]$	3250(vs,vb),3150(vw,vsp),2920(m,vsp),2870(m,sp),1595(s,sp),1470(m,vsp),1438(w,vsp),1380(s,vsp),1328(m,vsp),1160(s,vsp),1065(m,vsp),1008(s,vsp),900(s,vsp),878(vw,sp),800(vw,sp),638(s,sp),478(m,sp),478(vw,sp),319(m,sp)

**Table 2**  
**Important IR Band of the Macro cyclic compound from 1, 3-Diaminopropane**

### Nuclear Magnetic Resonance Spectra

Additional structural evidence for these ligands has been obtained from the pmr spectra of their hydrochlorides. The spectrum of OCTC hydrochloride<sup>19</sup> is slight shifting of the signals. The alpha and beta... methylenes resolved into broad triplets and pentlet, respectively, are centered at 3.16 and 2.01 ppm. Their positions of resonances are in agreement with the integrated of the signals (proton ratio 16:8). A sharp peak at 3.44 ppm expected for methylene protons is observed in the pmr spectrum of OCTC hydrochloride. Also, a broad singlet at 4.95 ppm may be assigned to (CH+NH<sub>2</sub>) proton resonance.<sup>19</sup>

### Nickel Complexes of OCTC

Very complex multiplets in the region 3.09-1.57 ppm in the spectrum of nickel complex with OCTC are uninterrupted. But, a broad peak observed in the region 5.12-4.38 ppm is expected for protons of coordinated water and the NH group.<sup>20</sup>

### Mass Spectra OCTC Systems

Determination of molecular weight by mass spectra of the compounds OCTC.8HCl has been very useful in completing their characterization. The corresponding peaks in OCTC.8HCl are 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. The mass loss corresponds to the sum of the masses of few H atoms and two and seven molecules of HCl attached with the macro cycles, respectively, through weak coordinate bonds.<sup>21</sup>

### Solubility, Conductivity and Other Data

The nickel complexes  $[\text{Ni}_2(\text{OCTC})(\text{H}_2\text{O})_4]\text{Cl}_4 \cdot 5\text{H}_2\text{O}$  have low decomposition points whereas others are thermally stable and decompose near their melting points. In addition, attachment of only one chloride ion through an ionic bond in the nickel (II)-OCTC complex gives indirect information on the metal-chloride ion coordinate linkage of the other chloride ion.<sup>22</sup> Also, the

colour of the nickel (II)-OCTC complex is Violet (bluish-violet). All the complexes are highly soluble in water due to their ionic nature.<sup>23</sup> Most of them are soluble in many other polar solvents, like methanol, ethanol, DMF, DMSO etc.<sup>24</sup> Similarly, the molar conductance ( $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ ) obtained for  $[\text{Ni}_2(\text{OCTC})(\text{H}_2\text{O})_4]\text{Cl}_4 \cdot 5\text{H}_2\text{O}$  (498) are consistent with formation of these complexes.<sup>25</sup>

## CONCLUSION

Background knowledge of the sources, chemistry, and potential risks of toxic heavy metals in contaminated soils is necessary for the selection of appropriate remedial options. Remediation of soil contaminated by heavy metals is necessary in order to reduce the associated risks, make the land resource available for agricultural production, enhance food security, and scale down land tenure problems and cleaning up heavy metal contaminated soils. The present investigation deals with the synthesis and characterization of macrocyclic ligands and its transition metal complexes. On the basis of elemental analysis, molecular weight determination, conductance, IR and NMR spectral studies, the nature as well as to some extent, structure and stereochemistry of macro cyclic ligands have been suggested. The above procedures outlined for the preparation of the resultant macro cyclic 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. This catalyst is use for major change in Pharmaceutical education. Nahata catalyst, which act as an efficient reusable heterogeneous catalyst. This catalyst is use in drug discovery and drug development.

## CONFLICT OF INTEREST

Conflict of interest declared none.

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