Synthesis and characterization of nickel(II) complexes with some tetraaza macrocyclic ligands

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The macrocyclic nickel(II) complexes of 1, 4, 7, 10-tetraaza-11,12-dichlorocyclocododecane ([NiC14H18N4Clz: 2H2O]2+ 2Cl-, TDC) and 1, 4, 7, 10, 12, 15, 18, 21-octaazabiscyclo (10, 10) docosane ([Ni2Cl4H34N8.Cl.3H2O]+3Cl-, ODC) have been prepared with some modifications in the usual template synthesis. In another approach, two macrocyclic complexes ([NiC14H18O4N4.2H2O].4H2O, DTO and ([NiC13H22O2N4.2H2O], DTH) derived from 1:1, nickel phthalate and adipate complexes respectively, have been isolated using triethylenetetramine as reagent for the cyclization [where C14H18O4N4 = 12, 13-benzo-11, 14-dihydrox-1, 4, 7, 10-tetraazacyclo
tradeca-10, 14-diene (dianion) and C13H22O2N4 = 11, 16-dihydrox-1, 4, 7, 10-tetraazacyclohexadeca-10, 16-diene (dianion)]. The complexes have been characterized by elemental analysis, conductivity measurements, melting points, spectroscopic and magnetic measurements.

A majority of synthetic macrocyclic ligand complexes have been obtained by the condensation of di- or polyamines with aldehydes or ketones1. The use of metal as template in such reactions has led to the synthesis of a large number of Co2+, Ni2+ and Cu2+ complexes of macrocyclic ligands1-7. The ring closing reactions involving cis-nitrogen functions of metal ammine complex and alkyl halide have also been reported8.

Further, a considerable interest has increased in the synthesis of dimetallic complexes which generally exhibit magnetic exchange between the two metal ions or tendency to undergo multi-electron redox reactions9. Related properties have been observed in several natural systems (e.g. enzymes) which are known to incorporate interacting metal centres. These complexes are also expected to be useful as homogeneous catalysts in a number of reactions10.

The purpose of the studies reported here is to further elucidate the scope of cyclization reactions, by some modifications in commonly used template synthesis, of 1, 1, 2, 2-tetrachloroethane (tce), triethylenetetramine (tren), adipic acid and phthalic acid to yield macrocyclic complexes of Ni2+ with one or two metal centres.

Experimental

All the chemicals used were of BDH/Glaxo or equivalent quality.

General synthetic procedure

Template synthesis of nickel(II) complexes were carried out in 500 ml round bottom flask using n-butanol as solvent. The macrocyclic products formed were extracted in water. The water content was removed by evaporating at 100°C. Finally, the complexes were washed with pet. ether and dried under reduced pressure.

Preparation of Ni(II) complex of 11, 12-dichloro-1, 4, 7, 10-tetraazacyclododecane (TDC)

The aforesaid general method of preparation was adopted to synthesise the macrocyclic complex species. The procedure involves. the addition of excess of nickel hydroxide (instead of equivalent amounts of nickel salt and sodium hydroxide required for cyclization to yield the product) to a 200 ml butanolic solution of triethylenetetramine (9.4642 g) and 1, 1, 2, 2-tetrachloroethane (10.7332 g) (in 1:1, molar ratio). The blue mixture was refluxed in a round bottom flask, which gradually changed to violet and finally turned into a thick violet precipitate after 7h continuous heating (Scheme 1). Finally, the mixture was cooled, treated with water and filtered to remove unreacted nickel hydroxide. The filtrate contains two layers, a violet aqueous layer and the other colourless non-aqueous layer. The resulting violet layer containing the macrocyclic complex, was separated and the solvent evaporated at 100°C on a water bath. The product (TDC) was washed several times with n-butanol. It was finally treated with pet. ether and dried under reduced pressure.

Preparation of dimetallic Ni(II) complex of 1, 4, 7, 10, 12, 15, 18, 21-octaazabiscyclo (10, 10) docosane (ODC)

The synthesis of the complex was followed by the preparation of a mixture containing excess of nickel(II) hydroxide, 1, 1, 2, 2-tetrachloroethane (8.0 g) and triethylenetetramine (14.1080 g) (in 1:2, molar ratio) in n-butanol. The mixture was
refluxed for ~9 h. The solution changed from blue to pinkish violet having thick precipitate of equivalent colour which proved to be indicative of complex formation. Water was added to the product and the unreacted metal hydroxide and the organic layer removed by filtration and separation, respectively. Violet crystals of ODC were obtained by evaporating water from the violet layer. Further, purification of the complex species was carried out as described above.

Preparation of nickel(II) complex of 12, 13-benzo-11, 14-dihydroxo-1, 4, 7, 10-tetraazacyclotetradeca-10, 14-diene (DTO)

An aqueous solution of nickel nitrate (5.0 g) was added dropwise to a stirred solution of sodium phthalate (a solution containing phthalic acid (2.7860 g) and sodium hydroxide (1.3428 g). The resulting solution was allowed to crystallize at room temperature under reduced pressure. Subsequently, the green crystals of nickel phthalate were filtered, washed several times with small quantity of water and dried. The analytical results show the complex composition as NiL₂·5H₂O (where L=phthalic acid dianion). For obtaining the macrocyclic complex, a mixture containing NiL₂·5H₂O and triethylenetetramine (in excess) was prepared in butanol. The contents when refluxed for ~5 h yielded a dark violet precipitate (Scheme 2). The precipitate was filtered and washed with n-butanol and water followed by pet. ether and dried in vacuo.

Preparation of nickel(II) complex of 11, 16-dihydroxo-1, 4, 7, 10-tetraazacyclohexadeca-10, 16-diene (DTH)

Nickel acetate (12.1034 g) mixed with adipic acid (10 g) in DMF was refluxed in a round-bottomed flask. The refluxing was continued until the evolution of acetic acid ceased. The parrot-green coloured precipitate insoluble in DMF was filtered and washed with the solvent. The complex was treated with benzene, in order to obtain DMF free compound. Further, this 1:1, Ni²⁺-adipate complex was dissolved in excess of butanolic solution of triethylenetetramine. The resulting solution was refluxed in a round-bottomed flask for ~6h. The appearance of a violet precipitate gives a clear view of the formation of macrocyclic species (Scheme 2). After the completion of the reaction, the precipitate was filtered and washed with n-butanol. Finally, the macrocyclic complex (DTH) was treated with pet. ether and dried.

The microanalysis was performed at the CDRI, Lucknow. Nickel was estimated by the known method. Conductivity measurements were made from resistance measurements on 10⁻² M solution using ODR conductivity meter, type 304. Ionizable chloride ion of the macrocyclic complexes (TDC and ODC) was determined by titrating their 50 ml solutions (10⁻² M) with 0.1 M AgNO₃ solution. The analytical data of the compounds are given in Table 1. The infrared spectra (4000-250 cm⁻¹) were recorded using Perkin-Elmer Model 337 spectrophotometer.

**Results and discussion**

On the basis of the analytical and physical data, the complexes have been characterized. The most convincing proof for formation of the macrocyclic complexes is obtained from the infrared spectra of the compounds. Evidence for cyclization is demonstrated by the absence of absorption bands that can be attributed to either free or coordinated -NH₂ group. In addition, >C=O band does not appear in DTO and DTH.
The infrared spectra of TDC complex is strongly suggestive of the cyclic nature of the complex there being an absence of band attributed to primary amine (–NH₂) group. The N – H stretching modes of the secondary amine groups is seen as a single band at 3100 cm⁻¹. The N – H bending band appears at 1584 cm⁻¹. The slightly broadened nature of the N – H stretching band in the spectrum of the complex may be an indication that a mixture of stereoisomers is formed. Strong and sharp bands for C – H stretching and scissoring appear at 2836 and 1440 cm⁻¹, respectively. The other important peaks appearing in the region 950-670 cm⁻¹ are attributed to coordinated water in the complex. The strong band at 1365 cm⁻¹ is associated with ligand framework. The νM-O, νM-N and νM-Cl stretches could not be identified due to poor resolution of the instrument in the far IR spectra.

In the infrared spectra of ODC, bands attributed to functional groups in the macrocyclic complex are observed at 2842 and 1443 (C – H sym. stretching and scissoring, respectively), 1050 (νC-N), 3130 (νN-H) and 1584 cm⁻¹ (N-H, bending). The nature of the amine band due to stretching vibrations is almost similar to that in IDC complex. A sharp band appears at 651 cm⁻¹ which shows the presence of coordinated water molecule in the complex. The νM-N and νM-Cl stretches could not be identified due to the reasons described in TDC complex. For νM-O (H₂O), a band is seen at 540 cm⁻¹. Many weak peaks including that appearing at 1365 cm⁻¹ may be associated with the skeletal vibrations of the whole complex molecule.

The presence of coordinated water molecules in DTO complex is indicated by the appearance of a weak band at 3220 cm⁻¹ followed by a sharp peak at 882 cm⁻¹ assigned to the stretching and rocking vibrations respectively. A broad and strong band at 592 cm⁻¹ is expected due to νM-O (H₂O). The characteristic strong bands at 2860 and 1443 cm⁻¹ are attributed to C – H, sym stretching and scissoring vibrations, respectively. A weak and sharp band of νC-N appears at 1137 cm⁻¹. The sharp band for N-H stretching modes splits into a doublet with the peak at 3148 cm⁻¹. The position of N-H bending vibration (1581 cm⁻¹) almost identical with that of TDC or ODC complex. The band related to >C=O group is absent. The other important bands at 1272, 483 and 400 cm⁻¹ may be assigned to the νC-O, νM-O (ligand) and νM-N, respectively. These vibrations indicate that metal is coordinated with ligand through two nitrogen and two oxygen donors. The absence of an absorption at 1650 cm⁻¹ for the dieno complex indicates that delocalisation of the imine π electrons has occurred due to anionic charge on coordinated oxygen and lone pair of electrons on uncoordinated nitrogen as observed by Cunningham et al. in case of some tetraaza ligand complexes as a result of

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<th>μeff (BM)</th>
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* Ionisable chloride ion
deprotonation of electrons for change of imine to secondary amine and subsequently involving nitrogen in coordination instead of oxygen (\(-\overset{\cdot}{N}C=\overset{\cdot}{N}\overset{\cdot}{C}\)) may reasonably be ignored on the basis of absence of \(\overset{\cdot}{C}=\overset{\cdot}{O}\) band and appearance of metal-oxygen frequency. Another peak at 1368 cm\(^{-1}\) may be associated with whole complex molecule.

The infrared spectra of DTH complex indicates absence of bands due to free or coordinated \(-NH_2\) and \(\overset{\cdot}{C}=\overset{\cdot}{O}\) groups suggesting the presence of a completely condensed macrocyclic organic ligand. The absorbance at 3168, 1542, 2842 and 1446 cm\(^{-1}\) are for \(N-H\) stretching, \(N-H\) bending, \(C-H\) stretching (sym.) and \(C-H\) scissoring vibrations, respectively. The presence of coordinated water is indicated by the appearance of a broad weak band at 3220 cm\(^{-1}\) followed by other peaks at 960 (broad), 760 (very weak) and 636 cm\(^{-1}\) (broad) assigned to the \(O-H\) stretching, rocking, wagging and \(M-O\) (\(H_2O\)) stretchings, respectively. A sharp and weak band attributed to \(M-O\) (ligand) stretching appears at 500 cm\(^{-1}\). The peak at 1374 cm\(^{-1}\) may be assigned to skeletal vibrations.

All the compounds are thermally stable and decompose near their melting points (Table 1). The high decomposition points also favour the cyclic nature of the compounds. Further, presence of ionisable chloride ions in TDC and ODC confirms their proposed structures. In addition, attachment of three chloride ions through ionic bonds in ODC gives indirect information on metal-chloride coordinate linkage involving one metal and one chloride ion. The molar conductivities of TDC, ODC, DTO and DTH recorded are in support of ionic (TDC, ODC) and neutral (DTO, DTH) nature of the complexes. All the complexes are highly soluble in polar solvents like methanol, ethanol, DMF, DMSO and water, etc. TDC and ODC are 2:1 and 3:1 electrolytes, respectively, exhibiting molar conductance values of 300 and 340 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\). The magnetic moment values of the violet complexes are in the range of 2.95-3.14 B.M. The violet colour is characteristic of six coordinate Ni\(^{2+}\).

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References