Metal Complexes of Copper(II), Nickel(II) & Cobalt(II) with Ligands Derived from the Reactions of Diamines with 3-Hydroxyiminobutane-2-one

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4,7-Diaza-2,9-dihydroxyimino-3, 8-dimethyldeca-3,7-diene, 4,8-diaza-2,10-dihydroxyimino-3,9-dimethylundeca-3,8-diene and bis (3-hydroxyimino-2-butylidine)-o-phenylenediamine when react with metal acetates yield inner complex salts of the type, ML[M = Co(II), Ni(II) or Cu(II)]. The preparation of the complexes has been achieved by isolating the ligand first and then complexing the metal ion or by adopting an in situ method involving the metal ion catalysed template syntheses of the ligand and simultaneous isolation of the complexes. Besides the inner complex salts, a series of nickel(II) complexes of the type, Ni(H$_2$L)$_2$X$_2$(X = Cl$^-$, Br$^-$, NO$_3^-$ or O$_2$C') have been synthesised where the organic ligands coordinate with the metal ion in their uncharged states. These complexes have been obtained by treating ethanolic solution of the ligands with ethanolic solutions of nickel(II) salts in the molar ratio 1 : 1. A series of binuclear copper(II) complexes of the type, Cu$_2$CuX$_2$(X = Cl$^-$ or Br$^-$) have been obtained as coloured crystalline products by treating an ethanolic solution of the corresponding copper(II) inner complex salts, CuL, with ethanolic solution of the respective copper(II) salts in equimolar quantities. Vibrational spectra of the ligands and metal complexes suggest that in the inner complex salts, the oxime ligand acts as an endo quadridentate ligand through its N-atoms and in the complexes of the type, M(H$_2$L)$_2$X$_2$ with the uncharged ligand, the metal ions are coordinated in a similar way and a hydrogen bonded cyclic ring structure is formed. Electronic spectra and magnetic properties of the complexes have been studied.

Metal complexes with hydroxyimines (oximes) as ligands have been widely studied. The significant outcome of research in this field provides substantial evidence that the oxime complexes possess the ability to form organometallic derivatives and bind reversibly molecular oxygen to the metal centre. A more recent investigation demonstrates that they can act as complexing ligands for other metallic elements. The oximes are unique in their ability to form encapsulation compounds many of which possess unusual properties. Sahoo and coworkers observed that dimethylglyoxime and acetylacetonedioxide act as tetra-functional ligands and diaethylazinedioxide as a hexadentate ligand. The bis-complexes such as M(dmg)$_2$ and M (aado)$_2$ and M (daado)$_2$ simulate as exo-bidentate and exo-quadridentate ligands respectively leading to the formation of binuclear, trigonular and tetracnuclear metal clusters. Inspite of highly stimulating works in this field, such investigations have been confined only to a few oximes which are, to some extent, structurally similar to glyoximes. This situation has prompted us to carry out researches using oximes with different structural characteristics, such as imine oximes of the type (I) obtained by the condensation of ethylenediamine, propylenediamine and o-phenylenediamine with 3-hydroxyiminobutane-2-one. These promising ligands act as endo-quadridentate ligands. The metal complexes isolated this way, may further act as exo-bidentate ligands to yield metal clusters.

Earlier works on the former two ligands are rather scarce and only one type of mononuclear nickel(II) complexes having the stoichiometry, NiLHX is known, though cobalt (II) complexes having similar stoichiometry as well as inner complex salts are known.

Bis (3-hydroxyimino-2-butylidine)-m-phenylene diamine and bis(3-hydroxyimino-2-butylidine)-p-phenylenediamine have been recently synthesised in this laboratory. These two ligands form binuclear and tetracnuclear complexes with a variety of metal ions and the results will be communicated later.

Materials and Methods

Ethylenediamine, propylenediamine and o-phenylenediamine were of BDH quality. All other chemicals were of reagent grade. NiL$_2$.6H$_2$O was prepared by the metathetical reaction of alcoholic solution of Ni(NO$_3$)$_2$.6H$_2$O and sodium iodide and filtering off the precipitated sodium nitrate.

The ligand 4,7-diaza-2,9-dihydroxyimino-3,8-dimethyldeca-3,7-diene was prepared by the literature method.
mixed with a warm ale. solution of the appropriate to prepare macrocyclic complexes with boric esters,
in sharp contrast to inner complex salts which are however failed.
The complexes of the type, ML, and the method of preparation of one such complex is given below.

(4, 7-Diaza-2, 9-dihydroxyniminato-3, 8-dimethyldeca-3,7-diene)copper (II) — The ligand (2.26 g, 0.01 mol) was dissolved in a minimum amount of absolute ethyl alcohol by warming. To the ligand solution, an alcoholic or aqueous solution of cupric acetate monohydrate (2.0 g, 0.01 mol) was added. A green crystalline compound was formed in a few minutes and its quantity increased on standing. It was filtered, washed with small quantities of ethyl alcohol and finally washed with ether and analysed after drying. In the preparation of other complexes solid compounds were not always formed immediately, but appeared on standing for some time.

Preparation of complexes of the type, Cu(L)-CuX₂ (X=Cl-, Br- or NO₃⁻) — The following general procedure was adopted for the preparation of all these complexes.

Dichloro[4,7-diaza-2,9-dihydroxyniminato-3,8-dimethyldeca-3,7-diene]copper (II)coppper (II) [Cu (L')] - CuCl₂ — (4, 7-Diaza-2, 9-dihydroxyniminato-3, 9-dimethyl deca-3,7-diene)copper (II) (1.44 g, 0.005 mol) was dissolved in ethanol and to it an ethanolic solution of cupric chloride dihydrate (0.85 g, 0.005 mol) was added with constant stirring. A green crystalline solid was obtained which was filtered, washed with small quantities of ethanol followed by ether and dried in vacuo.

Preparation of complexes of the type, Ni (H₂L)X₂ (X=Cl-, Br- or NO₃⁻) — The corresponding metal salt solution (0.01 mol) in absolute ethyl alcohol was mixed with a warm alc. solution of the appropriate ligand (0.01 mol) and the mixture vigorously shaken. The colour of the solution immediately changed to red or dark brown. The solution on being allowed to stand for a few minutes gave red or dark brown crystals which were filtered, washed with ethanol and finally washed with solvent ether and dried in vacuo.

Results and Discussion

The analytical data, colour and magnetic moment data of the compounds obtained are listed in Table I. The complexes Ni(H₂L)X₂ which are obtained in dry alcoholic medium are unstable in aqueous solution and in mild basic solutions such as in the presence of Na₂CO₃ or sodium acetate they transform into the inner complex species. The complexes of the type, Ni(H₂L)X₂ are paramagnetic and octahedral in sharp contrast to inner complex salts which are diamagnetic and square planar. Repeated attempts to prepare macrocyclic complexes with boric esters, however failed.

It is significant to note that the inner complex salts of Cu(II) have been found to further act as exo-bidentate chelating agents to give binuclear clusters of the type, CuLCuX₂ and a series of such complexes have been isolated.

Infrared spectra of the complexes of the type, ML [M = Cu (II), Ni (II), Co (II)], Ni(H₂L)X₂ and CuLCuX₂ have been recorded in the region 4000-400. The spectra of 3-dihydroxynimobutane-2-one and bis (3-dihydroxynimobutylidene) -o-phenylenediamine have been recorded which serve as useful guides for band assignments. The spectra of 4, 7-di diaza-2, 9-dihydroxynimino-3, 8-dimethyl deca-3,7-diene and 4, 7-diaza-2,10-dihydroxynimino-3, 9-dimethyl deca-3, 8-diene could not be obtained since they decomposed on exposure to atmosphere due to absorption of moisture. Although the IR spectra of all the complexes are quite complex, structurally important vibrational bands such as ν(O-H), N-OH scissoring, ν(C=C-N) and ν(N-O) are quite discernible and provide unequivocal evidence concerning the nature of bonding of the ligands to the metal ions.

The complexes of the type, Ni (H₂L)X₂ show a strong and broad band centred ~3380. The band can be assigned to ν=O-H of the N-OH group involved in hydrogen bonding, most probably intramolecular in nature and suggests that the ligand occurs in its neutral form. Intramolecular hydrogen bonding in oxime complexes where the protons of the N-OH groups have not been ionised or partially ionised such as Ni (Hdmg)₂ and related complexes are now well established10-12 and have been observed in the same region.

The IR spectrum of 3-dihydroxynimobutane-2-one shows a group of two bands located respectively at 3410 and 3350 which are fairly broad and strong implying hydrogen bonded structure involving the N-OH group. In the present series of complexes, the above assignment gains further support from the fact that in the inner complex salts of the type, ML, and binuclear copper (II) complexes of the type, CuLCuX₂, these bands fully disappear and the ligands occur as binegative charged ions.

The spectra of the ligand bis(3-dihydroxynimino-2-butyldiene)-o-phenylenediamine and the complexes of the type, Ni (H₂L)X₂ show an absorption band of medium intensity ~1680 while a common aspect of all the spectra of other types of complexes, i. e. ML and CuLCuX₂ is the disappearance of this band from this position. This characteristic behaviour leads us to believe that this band arises due to N-OH deformation vibration ~ 1700. This band disappears from the spectra of the inner complex salts.

The spectra of the ligand as well as of the metal complexes in the frequency region 1650-900 are most valuable for the elucidation of structure and bonding. In the spectra of all the metal complexes of the ligands, 4, 7-diaza-2,9-dihydroxynimino-3,8-dimethyl

\[ \text{IR } \nu_{\text{max}} \text{ in cm}^{-1} \]
Yellowish Green
Reddish green
Green
Reddish brown
Dark brown
Brown
Brownish green
Green
Red
Red
Red
Red
Red
Red
Red
Red

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\(L' = 4,7\)-diaza-2,9-dihydroxymino-3,8-dimethyldeca-3,7-diene
\(L^* = 4,8\)-diaza-2,10-dihydroxymino-3,9-dimethylundeca-3,8-diene

\(\Delta \nu \) is in cm⁻¹ and \(\Delta \nu_{30-40} \) cm⁻¹ is given for the above assignment.

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characteristic of phenyl ring vibrations. The four bands in the spectra of bis (3-hydroxyimino-2-butylidene)-o-phenylene diamine are located near 1580, 1570, 1500 and 1440 respectively. The first and last two bands are of medium intensity whereas the second band is very weak and appears in the form of a shoulder. These bands are much less affected in the metal complexes.

In the series of metal complexes of the type, ML, the high frequency C=N band shifts to a lower frequency region and the low frequency oxime C=N band undergoes a blue shift. These changes appear to be caused by change in electronic environment on account of co-ordination with the metal ions. It is believed that the oxime ligands are bonded by donating their nonbonding electron pairs with the simultaneous metal ligand electron interactions.

These spectral features lead us to conclude that the ligands and their inner complex salts of the type ML, have structures of the type (II). The shift in C=N and existence of hydrogen bonded O-H groups as evidenced by the IR spectra of the nickel (II) complexes of the type, Ni(H2L)X2, clearly manifest a hydrogen bonded macroyclic ring structure for these metal complexes as shown in structure (III). The band around 1370 which is present in the spectra of 3-hydroxyiminobutane-2-one and all the metal complexes are easily recognisable as due to CH3 deformation vibration.

The medium intensity bands located at 1300-1200 may be attributed to C-CH3 stretching or CH3 rocking modes. Besides these bands, in the spectra of bis (3-hydroxyimino-2-butylidene) - o-phenylenediamine and its metal complexes, an additional band at 1250 has been observed and assigned to C-H out-of-plane vibrations. Another band of considerable intensity which appears in the spectra of bis(3-hydroxyimino-2-butylidene)-o-phenylenediamine and its metal complexes located at 770 has been assigned to C-H out-of-plane vibration.

As to the spectra of the complexes, the most interesting band is due to νN-O, as this band would be most informative on the structure of the complexes as well as bonding between inner complexes of copper(II) with the copper (II) salts in their respective binuclear clusters. In the spectra of the complexes as well as the ligand, bis(3-hydroxyimino-2-butylidene)-o-phenylenediamine three distinct bands appear in the region 1100-900, the strongest one being the middle one and most susceptible to change on co-ordination. This band, in our opinion, arises due to νN-O. In the ligand, bis(3-hydroxyimino-2-butylidene)-o-phenylenediamine, this band appears at 1010 and in inner complex salts of nickel(II) of the type, Ni(HL)X2, this band moves to a higher frequency region appearing in the region 1120-1090. In 3-hydroxyiminobutane-2-one, this band appears at 1020. In the complexes, Ni(LH2)X2 and Ni(LH2)X4 this band appears in the region 1115-1095. It is most striking to observe that in all the complexes of the type, CuLCoX2, there is a decrease in the absorption frequency of this band and the band appears in the region 1040-1000 which undoubtedly occurs due to the formation of new links between the copper(II) inner complexes and copper(II) salts. This criterion when taken into account are reminiscent of the fact that the inner complex salts act as exobidentate ligands giving rise to binuclear clusters which are postulated to possess the structure of the type (IV). The binuclear complexes of copper(II) have magnetic moments in the region 1.7 to 1.9 B. M. per copper atom and the ground term is 2D. The electronic spectra of the complexes have been studied in the ligand field region 10,000-25,000. In all cases, the spectra consist of two broad ligand field bands, the first in the region 12000-12700 and the second in the region 17,000-17,800. These spectral features resemble those reported for the bi- and tri-nuclear Schiff base metal clusters and lead us to believe that the copper(II) ions are in similar ligand field environments respectively. Both these bands arise due to d-d transitions differing in their energies due to different ligand fields. It would be reasonable to say while the high frequency band arises for the chromophore CuN4 in D4h symmetry, the low frequency band originates due to the chromophore, CuO2X2 under a lower symmetry such as C2v.

A single broad band in the electronic spectra of inner complex salts of copper (II), centred near 14,000 has been attributed to the ligand field band due to the chromophore CuN4. The broad band which shows considerable structure represents two or three superposed absorptions. The band is comparable both in position and width with the earlier reported planar copper(II) complexes and lead us to believe that all the inner complex salts of copper(II) are essentially planar.

The nickel(II) complexes of the type, Ni (H2L)X2 with uncharged ligand show magnetic moments in the range 2.7-3.1 B. M. at room temperature, suggesting octahedral arrangement of the ligand atoms around the central nickel(II) ion. The electronic spectra consist of three bands, one in the region 13,000-14,100, the next one in the vicinity of 20,000 followed by a strong intense band near 24,000. The band in the lower frequency region can be assigned to the transition 3A2g→3B1g whereas the higher
quency band can be assigned to the transition $^3E_g \rightarrow ^3B_{1g}$ and $^2E_y$ which in some cases overlaps the strong charge transfer bands.

The nickel (II) inner complexes are diamagnetic and possess a singlet ground term $^1A_g$. The electronic spectra of these complexes have been measured in the range 10,000-25,000. The spectra consists of a broad band in the region 12,000-20,000 which under a square planar environment possessing the chromophore, Ni N₄²⁻. The third ionisation potential energy of cobalt (II) ion being low, the charge transfer band may be metal→ligand in nature.

References