



Synthetic Strategy and Characterization of IPMCO Complexes of Cu^{+2} , Ni^{+2} and Co^{+2}

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ABSTRACT

The complexes of Cu^{+2} , Ni^{+2} and Co^{+2} with terpenoids derivatives (L) have been prepared. The reaction of Cu^{+2} , Ni^{+2} and Co^{+2} with terpenoids derivatives were carried out in stoichiometry. For this purpose essential oils were obtained from plants. Essential oil which is called volatile oil, these were obtained from various plant materials just like flowers, seeds, buds, barks, twigs, herbs roots, fruits, and wood, are natural aromatic and complex oily liquid and composed maximum of terpenes, in comparison to some other nonterpene component. The complexes were studied on the basis of physico-chemical and spectral data and stability of these complexes was evaluated by techniques such as conductometry, potentiometry, spectral studies of complexes, elemental analysis, magnetic susceptibility measurements

Key words: Essential Oil, Conductometry, Potentiometry

INTRODUCTION

Essential oils with metal complexes were found effective as antiprotozoal, insecticidal and antifungal. Metal complexes of citral showed toxicological activities at very low concentration on bacteria and fungi of bread mould that is the compound was found to be very effective over *Rhizobium* fungi. Co-ordination compounds of many of the metals are involved in life process, chlorophyll, vital to photosynthesis in plant is a magnesium complex, haemoglobin an oxygen carrier for blood cells in animals, is an iron complex and vitamin B₁₂ is a cobalt complex, manganese in glycoprotein synthesis. Besides, Fe, Mg, and Mn there are many other metals such as Cu, Ni and Co, which are essential in human life process. The growth of interest in the role of metal ions in biological processes has stimulated work in the field of bioinorganic chemistry. Terpenoids are the important secondary plant metabolites. These also found in special glandular cells of the leaf surface [1]. These ligands are so much active against bacteria and fungi due to presence of N and S atom. So in future it can be used as bactericide and fungicide to destroy fungi and bacteria from crops. Terpenoids are derived from isoprene units ($\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}=\text{CH}_2$) joined together generally in head to tail fashion forming open chain or cyclic compounds. The mono and sesquiterpenoids are steam volatile constituents and are responsible for the characteristic odour of plants. The skeleton of diterpenoids are made up of four isoprene units and are less volatile, while non-volatile triterpenoids, steroids, carotenoids and natural rubber are the other member of terpene family. Only few chemical mixture of essential oils consist a high percentage of a single component. Terpenes and phenyl propenoids are two broad classes in which these chemical constituents are divided. We get essential oils from plants and they are natural product of plant. They were formed by voided and complex volatile mixtures of chemical compounds, with predominance of terrene associated to aldehyde, alcohols and ketene which were deposited in various structure of the plant¹. Lemongrass contains mainly citral [2] and 1 to 2% essential oil on a dry basis [3]. Essential oil and citral of lemongrass were detected to gather at parenchyma tissue cells, specifically in the ad axial surface of leaf mesophyll [4]. We gain citral from lemon-grass which is combination of geranial (i-citral) and neral (1-2 neral) [5] which are isomers others unusual active components are limonene, citronellal Mycenae and geranial². Lemongrass [6] is a tall, clumped perennial grass and it can grow with height of 1 m. It has linear leaf blade which are tapered at both ends and, its maximum growth would be near about 50 cm. and width would be of 1.5 cm [7]. This plant produces flowers at matured stages of

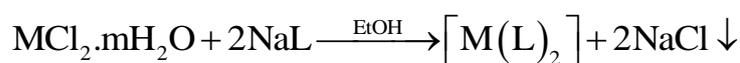
growth [8]. These aromatic plants are known for volatile growth inhibitors [9]. Germination and elongation of root are showed by accumulated data. These are showed by roots of *Brassica compestris* to inhibit cell proliferation. These are interfered by organeller and nuclear DNA synthesis with in the meristem cells [10]. For inhibition of maize root growth and introduction of oxidative stress [11] Some other monoterpones, 1,8 – cencole, geraniol, hrymol and camper were reported. In different species [12] Seed germination and early root elongation are inhibited reduction are showed in seed germination and seedling growth in three weeds. These are observed in the presence of *Artemisia Scorpi*a oil and its major constituent b-myrcine [13].

EXPERIMENTAL

All glass apparatus were cleaned and dried before use. The solvents and reagents were dried and purified according to the reported standard. All fractionations were carried out in columns of various lengths and packed with rashing rings and assembled with a total condensation variable take off stills head. Weighing tubes pipettes and transferring tubes, all fabricated with standard joints were used to weigh out reactants and products.

RESULT AND DISCUSSION

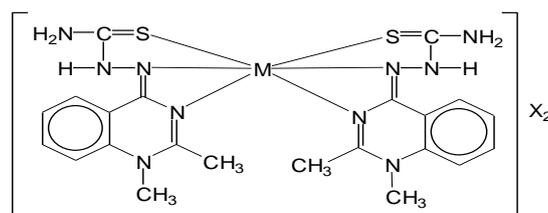
Reaction of Metal (II) chloride with Na salt of oxime (NaL) were carried out in 1:2 molar ratio in refluxing ethanol. The general reaction may be illustrated schematically as:



(Where NaL = sodium salt of IPMCO)

(Where M = Co(II), Ni(II), and Cu(II) [m = 2 for Cu(II) and 6 for Co(II) and Ni(II)]

The complexes of the type $[M(IPMCO)_2]$ were obtained after purification. These complexes were obtained as coloured solids. These solids are insoluble in water as well as in normal organic solvents but in DMF, DMSO, dichloromethane and THF these are soluble.



M = Co(II), Ni(II) and Cu(II)
X = Cl⁻, Br⁻ or I⁻

Structure-1.0

These complexes are non-hygroscopic in nature and decompose at high temperature (~280⁰ C). Molecular weights were determined by cryoscopic method. It reveals the monomeric nature of the complexes. The molar conductivity data show that these complexes are nature of non-electrolyte. The physical data are summarized in Table -1

Table 1: Physical Data

Compound	Empirical formula	Colour and Physical state	Yield (%)	B.M.	Analysis (Found / Calcd) (%)					M. wt. found (calcd.)	M. pt. (0°C)	Molar conda (Ω ⁻¹ cm ² mol ⁻¹)
					C	H	N	M	Cl			
[Co(IPMCO) ₂]	[Co(C ₁₀ H ₁₅ NO) ₂]	Brown (Solid)	78	4.51	61.02 (61.70)	7.12 (7.71)	7.01 (7.19)	14.98 (15.15)	-	378 (389)	253	0.88
[Ni(IPMCO) ₂]	[Ni(C ₁₀ H ₁₅ NO) ₂]	Yellowish (Solid)	72	2.84	61.31 (61.74)	7.58 (7.71)	7.05 (7.20)	14.90 (15.09)	-	3.81 (389)	268	1.25
[Cu(IPMCO) ₂]	[Cu(C ₁₀ H ₁₅ NO) ₂]	Green (Solid)	79	1.89	60.38 (60.98)	7.40 (7.62)	7.01 (7.11)	15.99 (16.14)	-	382 (3.94)	270	1.54

Metal Complexes

Reverse conductometric titrations by Job's molar ratio method were carried out by taking 40 ml of respective ligand - IPMCO, which is ten times diluted than metal ion solution) and titrating it against respective metal salt ($\text{Cu}(\text{NO}_3)_2$, $\text{Ni}(\text{NO}_3)_2$, and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ solution). By plotting a graph between conductance (in mho's) and volume of metal salt solution added, an inflection in the curve was obtained at the point of complexation. Molar conductance was calculated by measuring the conductance value at the complexation point.

Stability Complex

The stoichiometry and stability of complexes of Cu (II), Ni (II), Co (II) ions which are associated with terpenoids and their derivatives (L) as ligands (where, L= 5-isopropenyl-2-methyl-2-cyclohexenoxime, 5-isopropenyl-2-methyl-2-cyclohexeno semicarbazone, 2 cis 3,7-dimethyl-2,6-octadien Oxime and 3,7-dimethyl-2,6-octadiensemicarbazone) have been evaluated by following techniques :Conductometry, Potentiometry, Spectral studies of complexes, Elemental analysis, Magnetic susceptibility measurements

Conductometric Studies

These titrations are based on the principle that the equivalent conductivity depends upon the number and mobility of ions. Conductometric curves or atleast the portion of them that establish the end point, are straight lines or newly the straight lines and can be fixed by relatively few readings on each side of the equivalent point. This method has the advantage that it can be used with coloured solutions and will work where no indicator is found to be satisfactory. In order to get accurate results i.e. accurate end points reading, it is necessary to keep the temperature of the solution constant and to have one of the constituents fairly concentrated to avoid diluting of the solution.

Metal Complexes of Transition Metal Ions

Composition of the complexes which are formed by the direct interaction of 5-isopropenyl-2-methyl-2-cyclohexenoxime(IPMCO), with Copper (II), Nickel (II) and Cobalt (II) metal ions was determined by carrying out conductometric titrations. The reverse method (40 ml ligand - IPMCO in cell) was performed. The conductometric titration curves show sharp break at 1: 2 stoichiometry of the complex, indicating the formation of complex in the solution. The molar conductance was calculated through measuring the conductance at the complexation point. Stability order of metal ions follows Irving William's order which is reported earlier. The stoichiometry and stability of complexes determined from conductometric data are agree well with the corresponding data obtained from pH metric studies as described later.

Potentiometric studies

Potentiometric techniques have been used to establish the complex formation and confirmation of binary systems. The potentiometric titration of ligands (l) (where, l = 5-isopropenyl-2-methyl-2-cyclohexenoxime, 5-isopropenyl-2-methyl-2-cyclohexeno semicarbazone, 2 cis 3,7-dimethyl-2,6-octadien oxime and 3,7-dimethyl-2,6-octadiensemicarbazone) against 0.1 m koh solutions were carried out. An inflection at two moles of base was noticed in these curves. The ph data of impco have been observed at $35 \pm 0.5^\circ\text{c}$ when we use ionic strengths of 0.10 m potassium nitrate (kno3). The accuracy was of the order of ± 0.02 . The dissociation of protonated ligand can be given as:



The stoichiometries of the complexes along with the nature of the ligand species present in the different regions of ph have been determined. the cationic species in equilibrium with the neutral species are present in the range $\text{ph} \approx 3$ to 1.1. curve shows drop in the ph at complexation point and hence an inflection at "m" = 2 in the curve was seen in the present investigation, it has been observed that the ligand titration curves of the terpenoids and their derivatives did not show any basic buffer region. In acidic medium IMPCO, is protonated to give a cationic species H_2L^+ . Addition of base shows deprotonation of H_2L^+ groups in the first stage, when the pH is increased. Further deprotonation of HL took place.

pH metric studies of metal complexes with ligands IMPCO

Bjerrum's pH metric titrations⁴ were carried out by the same method as applied before and gave the same results. The variation in pH obtained from pH metric titrations. An appreciable shift in pH was observed in all cases indicating there by the possibility of complex formation in solution. The lowering in the value of pH was due to complex formation reaction in solution⁵⁻⁶. In these titrations ligand acts as a Lewis acid which can donate single pair of electrons which are shifted to metal ion acting as a Lewis base.

The interaction of ligand with the proton (H⁺) and metal ion (M²⁺) can be represented as shown below (eqn. 3-5).



The metal ligand titration curves found to be below the ligand titration curve and pH range of complexation was found to be well below the pH of hydrolysis of these metal ions. Hence the decrease in pH in the metal ligand titration curve could be attributed to the release of electron pairs or proton upon complexation. The titration curves containing equimolar quantities of metal ions and terpenoid solutions (at 0.1 M KNO₃) showed an inflection at 2 mole of base. The stability follow the trend Copper (II)>Nickel (II)>Cobalt (II), and it is a good agreement which are done with the *Irving* and *Williams's* order⁷⁻⁸. When we see stability order, It was found to be Cu(II)>Ni(II)>Co(II) for all these ligands viz., IPMCO complexes.

IR SPECTRUM

The IR spectra of oxime represent a strong broad band at 3365-3360 cm⁻¹ assigned to ν(OH) stretching vibration. At the frequency range 3030-2915 cm⁻¹ appears the typical bands of aliphatic CH. When we see the spectrum of IPMCO, the ν(C=C) and ν(C=N) assigned two band at 1605 cm⁻¹ and 1630 cm⁻¹ respectively.

¹H NMR SPECTRUM

In the ¹H NMR spectra of oxime the methyl proton of CH₃ on C-9 and C-10 carbon gives two singlet in the range 2.09-2.13 ppm. In the spectrum of IPMCO, the methylene CH₂ proton shows a multiplet at 3.18-3.27 ppm. The proton on =CH group of ligand shows a multiplet in the range 4.74-4.89 ppm. The CH proton appears as a multiplet at 2.36-2.40 ppm. The =CH₂ proton shows singlet at 4.74-4.95 ppm. The oximic proton (C=NOH) gives a broad singlet in the range 8.75-9.76 ppm.

¹³C NMR SPECTRUM

The [¹³C] NMR data of oxime are summarized in Table 3.12. The methyl and methylene carbon of ligand resonated in the upfield region in the range of 17.66-40.19 ppm. In the [¹³C] NMR spectrum of IPMCO, the C-2 and C-3 carbon appears at 147.7 and 128.3 ppm, respectively. The C-5 and C-7 carbon resonated in the range 110.0-116.2 and 130.0 ppm, respectively. The C-8 carbon resonated in the range 131.4-133.1 ppm. The azomethine carbon (C-1) resonated in the most downfield region in the range 156.93 ppm.

Spectral Studies of Metal Complexes of IPMCO

IR SPECTRA

Visibility of IR spectra of these complexes has been carried out by comparison with free ligands and other related complexes in table 1. Absence of hydroxyl group of oxime (3387-3360) cm⁻¹ in the Spectra of these complexes shown Deprotonation of ligand and concomitant Bondation of the M-O bond, the fact was then supported by the visibility of a new medium intensity band at 340-390 cm⁻¹ in complexes, assigned to ν(M-O) mode. In the IR spectra of these complexes, the ν(C=N) stretching type vibration are shifted to the lower wave number by (35-40 cm⁻¹) which are as compared to free oxime moieties, this event indicated that the azomethine nitrogen was coordinated to metal (II) ion which are then supported via the presence of a new intensity band medium in the region 430-470 cm⁻¹, due to ν(M-N) mode. In the complexes the ν(C=C) stretching frequency did not show significant shift than comparison to free ligand moiety.

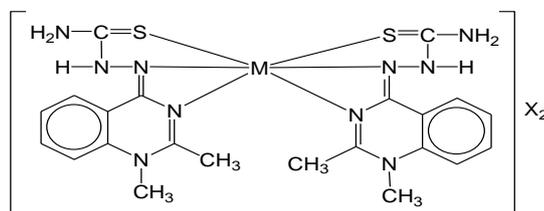
Magnetic Moments and Electronic Spectra

The Magnetic Moment Data and Electronic Spectral Data have been found useful for determining the geometry of Complexes. The Magnetic Moment Measurements of the Co (II) complex at room temperature shifted in the range 4.30-5.20 B.M. corresponding to 3 unpaired electrons. The electronic spectrum of the cobalt(II) complex exhibit absorption in the region 8693-18656 cm⁻¹ which are assigned to ⁴A₂(F) ⁴T₂(F), ⁴A₂(F) ⁴T₁(F) and ⁴A₂(F) ⁴T₁(P) transition respectively. These transition suggest tetrahedral environment around the cobalt ion. At room temperature, nickel (II) complex showed nature of magnetic moments in the range of 2.80-3.50 B.M. These values correspond to configuration of high spin and show the production of tetrahedral environment around the nickel (II) ion in the complex. The Electronic Spectrum of the Ni (II) complex display 3 absorption bands in the range 9997-16257 cm⁻¹ and 24867 cm⁻¹. These band may be assigned to the three spin allowed transition :[3] F₁(F) ³T₂(F), ³T₁(F) ³T₂(P) and ³F₁(F) ³A₂(F), respectively corresponding to an tetrahedral geometry. When we take Cu (II) complex at room temp and measured its magnetic movement that it shows in the range 1.70-2.20 B.M. which are going to one unpaired electron. The electronic (IR) spectrum of the copper(II) complex shows bands in the range 10219-14448 cm⁻¹ and

one Charge Transfer band at 20181 cm^{-1} . These bands may be associated to the following transition as ${}^2B_{1g} \rightarrow {}^2B_{2g}$ (ν_1), ${}^2B_{1g} \rightarrow {}^2E_g$ (ν_3).

CONCLUSION

The electronic (IR, NMR and ${}^{13}\text{C}$ NMR) spectroscopy data reveals dechlorination in metal complexes. On the basis of these studies tentative structure of the complexes is square planner geometry with the coordination of two N / O containing ligands has been proposed.



M = Co(II), Ni(II) and Cu(II)
X = Cl⁻, Br⁻ or I⁻

Structure-1.0

Proposed structure formula for the IPMCO complexes

Molecular weights were determined by cryoscopic method. It reveals the monomeric nature of the complexes. The stability order of Cu(II)>Ni(II)>Co(II) for the ligands IPMCO complexes was found by Bjerrum's pH metric titrations.

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