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## Synthesis, characterization and catalytic activity of mixed ligand transition metal complexes

Vitthal S. Shivankar<sup>a</sup>, Arvind S. Burungale<sup>b</sup>, Mohan M. Rajmane<sup>c</sup>  
and Laxman V. Gavali<sup>a\*</sup>

<sup>a</sup>Department of Chemistry, Karmaveer Bhaurao Patil College, Vashi, Navi Mumbai (Maharashtra) – 400 703, India.

<sup>b</sup>Yashvantrao Chavan Institute of Science, Satara, Maharashtra-415 001, India

<sup>c</sup>Sadguru Gadage Maharaj College, Karad, Dist. Satara, Maharashtra-415 124, India

### ABSTRACT

Chiral mixed ligand (CML) metal complexes are synthesized by using isonitrosopropiophenone (HINPP) as a primary ligand and saccharides such as (+)-glucose and/or (-)-fructose as a chiral secondary ligand. The metal complexes have been characterized by elemental analysis and various physico-chemical techniques such as molar conductance, magnetic susceptibility, electronic absorption, infrared spectral studies and thermal analysis. Room temperature magnetic susceptibility measurements of these complexes are indicative of a tetrahedral and/or octahedral geometry. The molar conductance studies of the complexes indicate their non-electrolytic nature. Electronic absorption/reflectance spectra of the complexes show intra-ligand, charge transfer, and the d-d transitions, consistent with their proposed geometry. Thermal studies show the presence of lattice water in the complexes. The specific rotation of the complexes is due to the corresponding chiral saccharide moiety. The CML Co(II)/Ni(II) complexes, synthesized and characterized in the present work, have been used as catalysts decomposition of hydrogen peroxide. The study on catalytic decomposition of hydrogen peroxide deals with the use of these complexes as two different types of catalysts i.e. heterogeneous and homogeneous catalysts heterogenized on alumina. It has been observed that complexes adsorbed on alumina (heterogenized) are better catalysts as compared to non-adsorbed complexes (heterogeneous catalysts).

**Key words:** Mixed ligand metal complexes, isonitrosopropiophenone

### INTRODUCTION

In recent years, there has been renewed interest in the synthesis and study of mixed ligand transition metal complexes. The utility aspects of these complexes have received their share of attention as these have found applications in diverse fields. Chiral metal complexes are well known for their use as catalysts, especially in asymmetric synthesis [1, 2], asymmetric epoxidations or Sharpless epoxidations [3] and resolution of racemic compounds [4]. Light catalyzed inversion and diastereoisomeric equilibration [5] in chiral metal complexes have been studied extensively.

Some metal ligand complexes are found to catalyze reactions such as oxidation, oxidative cleavage, hydroformylation, etc. and have shown *catalyses* like activity in decomposition of hydrogen peroxide. Phthalocyanines have found wide applications in diverse areas [6]. It is well established [7] that ternary complexes play a decisive role in the activation of enzymes and also in the storage and transport of active substances. The binary and ternary transition metal complexes have shown biological activity [8]. Mixed ligand complexes of transition metals are commonly found in biological systems. During recent years metal complexes of some N/O-donor ligands have attracted considerable attention because of their greater antifungal and antibacterial activities than those of the parent ligands [9]. Ternary complexes containing an amino acid as a secondary ligand are of significance as they are potential models for enzyme-metal ion substrate complexes.

The present work comprises of synthesis and characterization of chiral mixed ligand Co(II)/Ni(II) complexes prepared by using HINPP as a primary ligand (HL) and various chiral saccharides as secondary ligands (HL'). These complexes have also been employed as catalysts in reactions such as decomposition of hydrogen peroxide and hydrolysis of esters.

### MATERIALS AND METHODS

Analytical grade cobalt(II) chloride hexahydrate and nickel(II) chloride hexahydrate were used as received without further purification. Chiral saccharides were obtained from E. Merck. Saccharide was obtained from S. D. Fine Chemicals, Mumbai, India. Ethanol, methanol and chloroform used as solvents were purified and dried according to standard procedures [10]. N,N-Dimethyl formamide was obtained from E. Merck and used without further purification. The bacterial and fungal subcultures were obtained from the Haffkine Institute, Mumbai.

Isonitrosopropiophenone (HINPP) was prepared according to the reported procedure [11]. CML Co(II) and Ni(II) complexes were prepared from cobalt(II) chloride hexahydrate /nickel(II) chloride hexahydrate, Isonitrosopropiophenone (HINPP) and chiral secondary ligands (HL') such as (+)-glucose (Dextrose) and (-)-fructose.

To a blue-colored ethanol solution of cobalt(II) chloride hexahydrate (237 mg, 1 mmol), was added an ethanol solution of HINPP (163 mg, 1 mmol). The mixture was stirred and kept in a boiling water bath for 10 minutes. To this was added an aqueous solution of the saccharides (1 mmol). This mixture (1:1:1 molar proportion) was heated in a hot water bath till the temperature reached 50°C. The complexes precipitated by raising the pH of the reaction mixture. The mixture was cooled and the solid was filtered, washed with ice-cold water followed by 1:1 ethanol: water. The complexes thus prepared were dried under vacuum. The complexes with nickel (II) chloride hexahydrate were prepared by the same method reported above.

#### Instrumentation

The complexes were analyzed for the metal contents, C, H and N using standard procedures. For the determination of metal content determined by complexometric EDTA titration [12]. The nitrogen content of the complexes was determined by Kjeldahl's method [13]. Analyses for carbon and hydrogen were carried out at the Microanalytical Laboratory, University Department of Chemical Technology, Mumbai.

The molar conductance values were measured in methanol at the range of  $10^{-3}$  M concentration on a model CM-180 Elico digital conductivity meter with a dip-type conductivity cell fitted with a platinum electrode (cell constant =  $1.0 \text{ cm}^{-1}$ ). Room temperature magnetic susceptibilities were measured by a Guoy balance using  $\text{Hg}[\text{Co}(\text{SCN})_4]$  as the calibrant. Effective magnetic moments were calculated after applying diamagnetic corrections for the ligand components using Pascals constants [14].

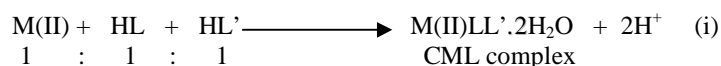
The specific optical rotation values for the complexes were determined in methanol solution (0.01%) on a Jasco DIP-140 polarimeter. Electronic absorption spectra in the ultraviolet range in methanol at  $10^{-4}$  M concentration were measured on a Shimadzu UV-160A spectrophotometer. Electronic spectra in the visible range in chloroform at  $10^{-3}$  M concentration were measured on a Spectronic-20 spectrophotometer. FTIR spectra were recorded as KBr discs on a model 160 Perkin-Elmer FTIR spectrophotometer.

TGA studies of the complexes were made on a Mettler TC 10A TA processor at Indian Institute of Technology, Mumbai by recording the change in weight of the complexes on increasing the temperature up to 700 °C at a heating rate of 10 °C/min.

## RESULTS AND DISCUSSION

### Characterization of metal complexes

The synthesis of CML complexes may be represented as shown in equation (i):



(where HL is HINPP and HL' is a chiral saccharide ligand).

All of the complexes are non-hygroscopic stable solids. They are colored and thermally stable, indicating a strong metal-ligand bond. The elemental analysis data of metal complexes (Table 1) is consistent with their general formulation as mixed ligand complexes  $\text{MLL}' \cdot 2\text{H}_2\text{O}$ . The molar conductance values of the complexes in methanol at  $10^{-3}$  M concentration are very low ( $<1$ ), indicating their non-electrolytic nature [15]. The specific rotation values for the complexes with (+)-glucose in methanol solution (0.01%) were found to be positive. The value for the complex with (-)-fructose was found to be negative. This indicates that the specific rotation of the complexes is due to the corresponding chiral saccharide moiety.

### Magnetic studies

The observed  $\mu_{\text{eff}}$  values are suggestive of the tetrahedral geometry for the Co(II) complexes and an octahedral geometry for the Ni(II) complexes (Table 2).

### Electronic absorption spectra

The electronic spectra of the metal complexes in methanol solution, recorded in the ultraviolet region, exhibit intra-ligand and charge transfer transitions in the range around 25,940-48,192  $\text{cm}^{-1}$  and near 26,000  $\text{cm}^{-1}$ , respectively. The electronic absorption spectra of Co(II) complexes in chloroform solution in the visible and near infrared region shows three transition bands in the region around 25,000  $\text{cm}^{-1}$ , 16,666  $\text{cm}^{-1}$  and 12,000  $\text{cm}^{-1}$  respectively, while that of the Ni(II) complexes show two transition bands in the region around 25,000  $\text{cm}^{-1}$  and 12,195  $\text{cm}^{-1}$ , respectively.

The diffuse reflectance spectra of Co(II) complexes show the d-d transition bands (Table 2) in the region around 12,900 and 17,500  $\text{cm}^{-1}$ , which are assigned to transitions  ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{F})$  ( $\nu_2$ ) and  ${}^4\text{A}_2(\text{F}) \rightarrow {}^4\text{T}_1(\text{P})$  ( $\nu_3$ ), respectively. The Ni(II) complexes show two transition bands (Table 2) in the region around 12,700 and 18,900  $\text{cm}^{-1}$ , which are ascribed to transitions  ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_1(\text{F})$  ( $\nu_2$ ) and  ${}^3\text{A}_2(\text{F}) \rightarrow {}^3\text{T}_1(\text{P})$  ( $\nu_3$ ), respectively. As the  $\nu_1$  band occurs at low energy, usually in the range not accessible due to instrumental limitations, it is not observed in the present cases.

The parameter B, which measures Racah inter electronic repulsion, is usually lower in a complex than in the free ion (and is usually referred to as B'), which is an indication of orbital overlap and delocalisation of d-orbitals.

The value of B for free Co(II) ion is 971  $\text{cm}^{-1}$ . The present  $\beta$  values are less than unity, suggesting an appreciable covalent character of the M-O bond. The observed spectral features of all the Co(II) complexes are, therefore, in conformity with the tetrahedral geometry proposed on the basis of their analytical data and observed magnetic moments.

For many octahedral Ni(II) complexes, the ratio  $\nu_2/\nu_1$  is found to be in the range 1.6-1.8. with the present Ni(II) complexes this ratio lies around 1.84. the value of Dq for the complexes are in the range 687-690  $\text{cm}^{-1}$ , which lies well within the range reported for octahedral Ni(II) complexes (640-1270  $\text{cm}^{-1}$ ). The B' values for octahedral complexes under investigation are in the range 726-729  $\text{cm}^{-1}$ , which is less than the value of 1041  $\text{cm}^{-1}$  found in the free ion [16], indicating that the free ion value is reduced considerably, suggesting appreciable orbital overlap.

**Infra-red spectra**

The FT-IR spectra of the CML metal complexes were recorded as KBr discs. Some of the important bands have been assigned (Table 3).

1. A broad band observed in the region between 3325-3318  $\text{cm}^{-1}$  due to asymmetric and symmetric O-H stretching modes and a strong peak in the range 1574-1572  $\text{cm}^{-1}$  due to H-O-H bending showing the presence of water of crystallization [17].
2. An important feature of the IR spectra of the complexes is the absence of band due to O-H stretching vibrations of =N-OH group of HINPP indicating the complex formation takes place by deprotonation of the oxime of HINPP. The  $\nu(\text{C}=\text{O})$  region of IR spectra of complexes shows a strong band in the region 1595-1600  $\text{cm}^{-1}$  due to C=O stretching vibrations of the coordinated carbonyl group of HINPP. The shift of  $\nu(\text{C}=\text{O})$  of HINPP towards lower wave number from its position at 1660  $\text{cm}^{-1}$  in free HINPP suggests the involvement of carbonyl group of the ligand in bonding to the metal ion. The C=N stretching frequency observed at 1593  $\text{cm}^{-1}$  in the spectrum of HINPP is found to be shifted to the range 1495-1515  $\text{cm}^{-1}$  in the spectra of the complexes, indicating coordination through the N donor atom of the HINPP[18] group. A new medium intensity band, attributed to  $\nu(\text{N}\rightarrow\text{O})$ , observed in the range 1180-1203  $\text{cm}^{-1}$  in the spectra of the complexes, further supports above observation.
3. The merging and broadening of bands was found to be a common feature of transition metal-saccharide complexes. The spectra of all the complexes with saccharides showed broad bands in the O-H and C-H regions, indicating a merging of individual bands. The spectral characteristics are similar to those observed with other 1<sup>st</sup> row transition metal complexes. The structural vibrations of the intermolecular hydrogen bonded O-H groups of the free saccharides were affected ionization and exhibited a broad but nearly symmetrical band at  $\sim 3400 \text{ cm}^{-1}$ . The strongly coupled ring vibrational frequencies for bending modes COH, CH<sub>2</sub> and CCH of the free saccharides (1460-1340  $\text{cm}^{-1}$ ) showed merging at 1400  $\text{cm}^{-1}$  upon complex formation. Similarly, the C-O and C-C stretching vibrations in the region 1140-990  $\text{cm}^{-1}$  were also merged at  $\sim 1050 \text{ cm}^{-1}$  upon complex formation, in contrast to the sharp bands observed for the free saccharides and other metal-saccharide adducts. The anomeric region (950-500  $\text{cm}^{-1}$ ) showed very weak marker bands of mostly  $\alpha$ -anomer. It was clear from the spectra that the saccharides were involved in coordination through some deprotonated -OH groups as observed from the broad bands in  $\nu(\text{O-H})$  region, 3500-3200  $\text{cm}^{-1}$ . On the basis of coordinating abilities of the various saccharides reported, a 3,4-trans-diol arrangement[19] has been proposed for CML complexes with glucose and fructose.
4. The C-O and C-C stretching vibrations in the region 1140-990  $\text{cm}^{-1}$  were also merged at  $\sim 1050 \text{ cm}^{-1}$  upon complex formation, in contrast to the sharp bands observed for the free saccharides and other metal-saccharide adducts. The new bands of weak intensity, observed in the regions about 648-595  $\text{cm}^{-1}$  and 465-420  $\text{cm}^{-1}$ , may be ascribed to M-N and M-O vibrations, respectively.

**Thermo gravimetric and X-ray analysis**

The thermograms (TG) of the complexes have been recorded in flowing nitrogen atmosphere at the heating rate of 10°C/min on approximately 10 mg samples. All the complexes investigated show similar behavior in their TG and Differential Thermal Analysis (DTA) studies. The DTA curve has been recorded in static air. The complexes display an endothermic peak at 99°C, which is attributed to the release of a water molecule.

X-ray and chemical analysis showed that the final product of the decomposition process was CoO, left as residue representing 21.6 % of the initial mass of the complex. This indicates that the metal powder produced in the decomposition process was too reactive and transforms to metal oxide spontaneously even in the presence of traces of oxygen present in the nitrogen gas used in the experiment or that produced due to disproportionation reaction during the decomposition.

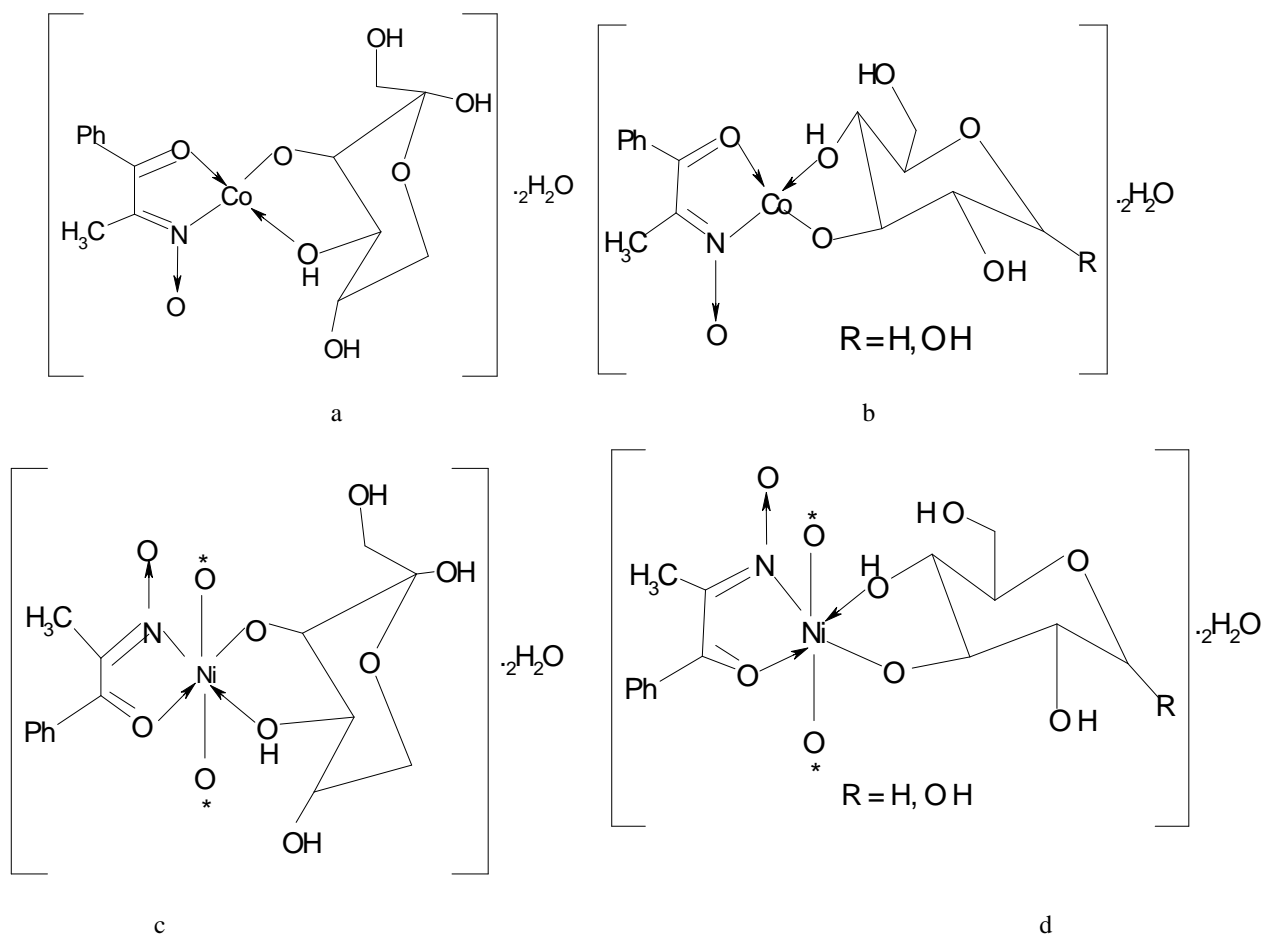


Fig.1 Probable structure for mixed ligand complexes (a)  $[\text{Co}(\text{INPP})(\text{Fru})].2\text{H}_2\text{O}$ , (b)  $[\text{Co}(\text{INPP})(\text{Dex})].2\text{H}_2\text{O}$ , (c)  $[\text{Ni}(\text{INPP})(\text{Fru})].2\text{H}_2\text{O}$  and (d)  $[\text{Ni}(\text{INPP})(\text{Dex})].2\text{H}_2\text{O}$

### Catalytic Activity of Complexes

The study on catalytic decomposition of hydrogen peroxide deals with the use of these complexes as two different types of catalysts i.e. heterogeneous catalysts and homogeneous catalysts heterogenised on alumina.

### Decomposition of Hydrogen Peroxide

The use of CML cobalt(II) complexes in the kinetic study of catalytic decomposition of  $\text{H}_2\text{O}_2$  is studied recently [20]. In the present studies CML Co(II)/Ni(II) complexes have been employed in the kinetic study of catalytic decomposition of  $\text{H}_2\text{O}_2$ .

The CML Co(II)/Ni(II) complexes were used in the form of heterogeneous catalysts and homogeneous catalysts heterogenised on alumina support in the catalytic decomposition of  $\text{H}_2\text{O}_2$ . The reactions were studied at two different volume strengths (3 and 5 V) and at three different temperatures (35, 55 and 60 °C). The method adopted for the purpose consisted essentially of following the kinetics of catalytic decomposition of  $\text{H}_2\text{O}_2$  using a gasometrical technique [21] involving the measurement of the volume of oxygen evolved.

#### A) CML Co(II) and Ni(II) Complexes as Heterogeneous Catalysts:

The kinetic studies of catalytic decomposition of  $\text{H}_2\text{O}_2$  in presence of CML Co(II)/Ni(II) complexes, used as heterogeneous catalysts, have been carried out at three different temperatures (35, 55 and 60 °C) and at two different volume strengths (3 and 5 V) of  $\text{H}_2\text{O}_2$ . The catalytic nature of the reaction was confirmed by recovering the complexes unchanged, both in amount and composition, at the end of the reaction. The FTIR spectra of some of the

complexes recorded before and after the reaction are almost identical indicating that the catalysts do not suffer any irreversible, compositional or structural change.

The cobalt(II) as homogeneous ion in the form of its chloride solution shows a very low catalytic activity [22] with respect to the decomposition of  $\text{H}_2\text{O}_2$ , the specific reaction rates at 35, 55 and 60°C being  $0.195 \times 10^{-2}$ ,  $0.702 \times 10^{-2}$  and  $0.832 \times 10^{-2} \text{ min}^{-1}$ , respectively. However, in presence of the present CML Co(II)/Ni(II) complexes in heterogeneous phase, the rate of catalytic disproportionation is enhanced considerably, as can be easily inferred from the observed specific reaction rates. It follows, therefore, that complexation and heterogenization of Co(II)/Ni(II) have an enhanced effect on the catalytic decomposition of  $\text{H}_2\text{O}_2$ , especially at higher temperatures.

All the CML Co(II) complexes with tetrahedral geometry show almost similar catalytic activities. This would be expected on the basis of the similar structures proposed for the complexes. Normally, more stable complexes should show higher E and lower k values. However, the values of activation energy, E, and various thermodynamic parameters depicted, indicate that lower k values are found to be associated with relatively lower E values.

It has also been reported that when a system passes into a transition state, accompanied by an increase in entropy, then notwithstanding the high activation energy, the reaction will proceed at faster rates. Conversely, therefore, a reaction accompanied by decrease in entropy will be expected to proceed slowly, notwithstanding the low activation energy.

The effect of change of metal ion during complexation interestingly affects the rate of the reaction when it has been observed that octahedral Ni(II) complexes with dextrose and fructose show lower k values as compared to the tetrahedral and octahedral Co(II) complexes. Obviously, the Co(II) complexes are catalytically more active than the Ni(II) complexes. It is observed that  $\Delta H^\ddagger$  values are closer to E values in accordance with absolute reaction rate theory for solution (Table 4). The value of  $\Delta G^\ddagger$  has been found to be higher in all the cases and not much difference has been found in both the systems. The values of  $\Delta S^\ddagger$  were found to be negative in all the cases indicating that molecules in transition state are more ordered than the reactants in ground state.

The plot of  $\log(a-x)$  against t for the complexes is linear indicating that the decomposition of  $\text{H}_2\text{O}_2$  in the presence of catalyst follows first order kinetics. Keeping the quantity of the catalyst and  $\text{H}_2\text{O}_2$  constant, when the temperature was varied in the range 35-60°C, the value of k increased with increase in temperature.

By comparing the k values with those obtained with 5 V  $\text{H}_2\text{O}_2$  (Table 5), it can be inferred in general, that the rate of the reaction decreases with increase in the concentration of  $\text{H}_2\text{O}_2$ , though discrepancies are observed in a few cases.

Keeping the quantity of  $\text{H}_2\text{O}_2$  and the temperature constant, when the quantity of catalyst was varied in the range 0.01-0.05 g, the value of k increased with increase in the quantity of the catalyst. The plot of  $\log k$  against  $\log [\text{Co}(\text{INPP})(\text{Dex})\cdot 2\text{H}_2\text{O}]$  is linear with a slope of 0.8, indicating that the order of the disproportionation reaction is almost unity (Fig. 2).

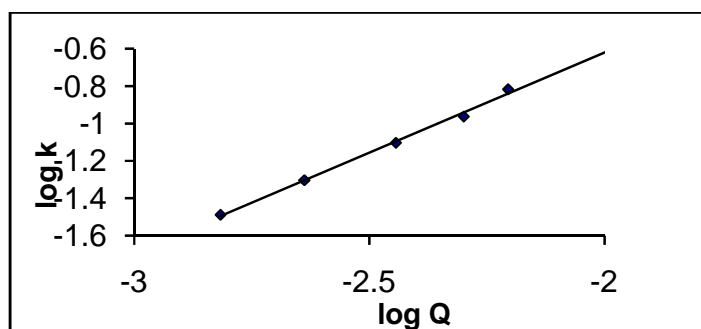


Fig. 2 Plot of  $\log k$  against  $\log \{ \text{Quantity of } [\text{Co}(\text{INPP})(\text{Dex})\cdot 2\text{H}_2\text{O}] \}$ .

### B) CML Co(II)/Ni(II) Complexes as Heterogenized Catalysts

It is known that a catalyst, when attached to a support [23], i.e. when heterogenized, enhances the catalytic activity. In the following section, we report the results of kinetics of disproportionation of hydrogen peroxides catalyzed by CML Co(II)/Ni(II) complexes adsorbed on alumina.

It is reported that alumina, duly processed [24], acts as a catalyst in the decomposition of hydrogen peroxides. Therefore, when experiments were carried out with alumina under identical conditions, the volume of oxygen evolved was found to be negligible. Experiments carried out using alumina treated with a solution of HINPP or saccharides revealed no activity at all. This shows that when alumina, HINPP or saccharides are used individually, they show much less or no catalytic activity in the decomposition of hydrogen peroxide. However, activity increases considerably when the complex is adsorbed on alumina. Thus it can be inferred that the CML Co(II)/Ni(II) complex adsorbed on alumina is responsible for the fast H<sub>2</sub>O<sub>2</sub> decomposition reaction.

Keeping the quantity of the catalyst and H<sub>2</sub>O<sub>2</sub> constant, when the temperature was varied in the range 35-60°C, the value of k was found to increase with increase in temperature.

The plot of log k against log {[Co(INPP)(Dex)].2H<sub>2</sub>O adsorbed on alumina} is linear with a slope of 1.0, indicating that the order of the disproportionation reaction with respect to quantity of catalyst is unity (fig. 3)

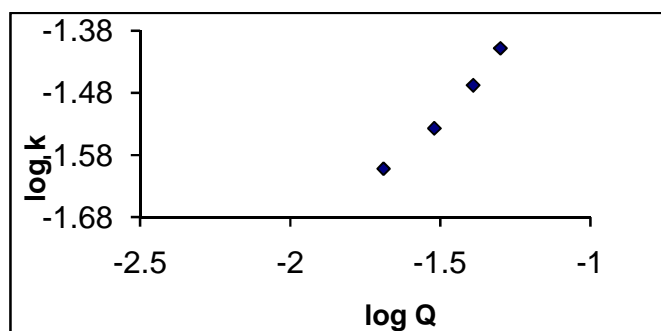


Fig. 3 Plot of log k against log {Quantity of [Co(INPP)(Dex)].2H<sub>2</sub>O adsorbed on alumina}.

Table 1. Colour, decomposition temperature, molar conductance, specific rotation and analytical data of the metal complexes

Compound	Empirical formula	Colour	Decomp Temp. (°C)	Elemental Analysis Found (Calculated)				Molar Cond. mhos.cm <sup>2</sup> .mol <sup>-1</sup>	[α] <sub>D</sub>
				%M	%C	%N	%H		
[Co(INPP)(Dex)].2H <sub>2</sub> O	CoC <sub>15</sub> H <sub>21</sub> O <sub>9</sub> N	Light yellow	277	14.22 (14.10)	42.91 (43.07)	3.52 (3.35)	5.11 (5.02)	0.24	+193.0
[Co(INPP)(Fru)].2H <sub>2</sub> O	CoC <sub>15</sub> H <sub>21</sub> O <sub>9</sub> N	Light yellow	285	14.12 (14.10)	43.00 (43.07)	3.40 (3.35)	5.27 (5.02)	0.30	-220.0
[Ni(INPP)(Dex)].2H <sub>2</sub> O	NiC <sub>15</sub> H <sub>21</sub> O <sub>9</sub> N	Green	290	14.25 (14.05)	43.01 (43.09)	3.55 (3.35)	4.89 (5.02)	0.38	+225.9
[Ni(INPP)(Fru)].2H <sub>2</sub> O	NiC <sub>15</sub> H <sub>21</sub> O <sub>9</sub> N	Green	260	14.25 (14.05)	43.01 (43.09)	3.55 (3.35)	4.89 (5.02)	0.41	-303.0

Table 2. Magnetic moments and diffuse reflectance spectral data (cm<sup>-1</sup>) for CML Co(II)/Ni(II) complexes

Compound	μ <sub>eff</sub> (B.M.)	ν <sub>1</sub> *	ν <sub>2</sub>	ν <sub>3</sub>	Dq	B'	β	ν <sub>2</sub> /ν <sub>1</sub>
[Co(INPP)(Dex)].2H <sub>2</sub> O	4.54	6,286	12,953	17,391	628.6	765.7	0.788	2.06
[Co(INPP)(Fru)].2H <sub>2</sub> O	4.61	6,339	12,853	17,543	633.9	758.5	0.781	2.02
[Ni(INPP)(Dex)].2H <sub>2</sub> O	2.96	6,874	12,658	18,867	687.4	726.6	0.697	1.84
[Ni(INPP)(Fru)].2H <sub>2</sub> O	2.82	6,901	12,706	18,939	690.1	729.4	0.700	1.84

Table 3. Some Important Infrared Spectral Bands (cm<sup>-1</sup>) of CML Complexes<sup>a</sup>

Complex	v(O-H) (Sacch)	v(O-H) (Sacch)	v(O-H) (H <sub>2</sub> O)	v(C=O) (HINPP)	v(HOH)	v(C=N) (HINPP)	v(C-OH) v(C-H <sub>2</sub> ) v(C-CH) (Sacch)	v(N→O) (HINPP)	v(C-O) v(C-C) (Sacch)	v(M-N)	v(M-O)
[Co(INPP)(Dex)]·2H <sub>2</sub> O	3500s	3395m	3315 w	1598s	1573 s	1509 s	1408	1200	1050	602 <sup>b</sup> w	420 <sup>b</sup> w
[Co(INPP)(Fru)]·2H <sub>2</sub> O	3505m	3400s	3362 w	1599m	1575 s	1510 s	1400	1197	1045	603 <sup>b</sup> w	435 <sup>b</sup> w
[Ni(INPP)(Dex)]·2H <sub>2</sub> O	3500s	3415m	3322 w	1600s	1573 s	1512 m	1395	1203	1040	595 <sup>b</sup> w	425 <sup>b</sup> w
[Ni(INPP)(Fru)]·2H <sub>2</sub> O	3495m	3400s	3320 w	1599s	1574 m	1499 m	1405	1200	1050	602 <sup>b</sup> w	425 <sup>b</sup> w

<sup>a</sup>where b: saccharides, c: HINPP, s: strong, m: medium, w: weakTable 4. Kinetics of decomposition<sup>a</sup> of H<sub>2</sub>O<sub>2</sub> in presence of CMLM complexes as heterogeneous catalysts<sup>b</sup>

Complex	T (K)	k × 10 <sup>-2</sup> (min <sup>-1</sup> )	E (kJ.mol <sup>-1</sup> )	ΔH <sup>‡</sup> (kJ.mol <sup>-1</sup> )	ΔS <sup>‡</sup> (J.K <sup>-1</sup> .mol <sup>-1</sup> )	ΔG <sup>‡</sup> (kJ.mol <sup>-1</sup> )
[Co(INPP)(Dex)]·2H <sub>2</sub> O	308	0.68	16.41	13.73	-267.68	100.19
	328	03.58				
	333	26.48				
[Co(INPP)(Fru)]·2H <sub>2</sub> O	308	37.99	41.48	38.80	-188.01	99.52
	328	1.31				
	333	1.77				
[Ni(INPP)(Dex)]·2H <sub>2</sub> O	308	0.23	46.27	43.59	-178.85	101.35
	328	0.66				
	333	0.92				
[Ni (INPP)(Fru)]·2H <sub>2</sub> O	308	0.39	30.31	27.63	-226.91	100.92
	328	0.73				
	333	1.00				

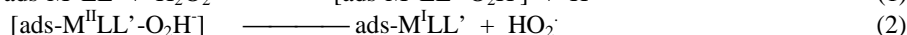
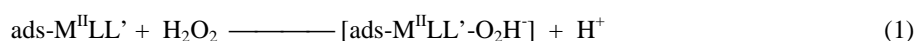
<sup>a</sup>Volume of H<sub>2</sub>O<sub>2</sub> taken : 10 cm<sup>3</sup> of 5V H<sub>2</sub>O<sub>2</sub><sup>b</sup>Amount of catalyst : 40 mgTable 5. Kinetics of decomposition<sup>a</sup> of H<sub>2</sub>O<sub>2</sub> in presence of CMLM complexes adsorbed on alumina(Alu) as heterogenized catalysts<sup>b</sup>

Catalyst	T (K)	k × 10 <sup>-2</sup> (min <sup>-1</sup> )	E (kJ.mol <sup>-1</sup> )	ΔH <sup>‡</sup> (kJ.mol <sup>-1</sup> )	ΔS <sup>‡</sup> (J.K <sup>-1</sup> .mol <sup>-1</sup> )	ΔG <sup>‡</sup> (kJ.mol <sup>-1</sup> )
Alu-Co(INPP)(Dex)	308	03.58	82.96	80.28	-35.10	91.61
	328	26.48				
	333	37.99				
Alu-Co(INPP)(Fru)	308	02.55	102.11	99.43	+24.60	91.48
	328	30.70				
	333	38.38				
Alu-Ni(INPP)(Dex)	308	00.25	31.31	28.63	-175.75	101.30
	328	00.78				
	333	01.25				
Alu-Ni (INPP)(Fru)	308	00.57	25.52	22.84	-239.58	100.20
	328	00.92				
	333	01.27				

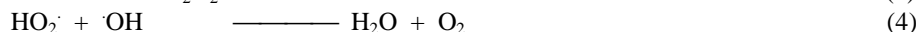
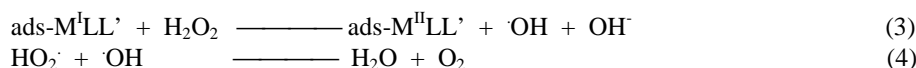
<sup>a</sup>Volume of H<sub>2</sub>O<sub>2</sub> taken : 10 cm<sup>3</sup> of 5V H<sub>2</sub>O<sub>2</sub><sup>b</sup>Amount of catalyst : 500 mg

It has been observed that heterogenized CML complexes show more activity than heterogeneous CML complexes as catalysts. This is due to the increase in the concentration of adsorbed reactant molecules on the surface of the catalyst, which according to the law of mass action, enhances the rate of the reaction. The surface-active complex, recovered during the reaction after washings, was however found to decolorize a dilute solution of potassium permanganate, indicating that it is a peroxy species.

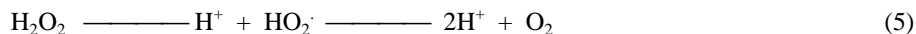
Based on the above experimental observations, the following reaction mechanism (Scheme I) may be suggested and may involve the initial steps of interaction of the surface complex with H<sub>2</sub>O<sub>2</sub> or OOH<sup>-</sup> ion. The decomposition of H<sub>2</sub>O<sub>2</sub> in presence of the catalysts may proceed through steps (1)-(6) shown in Scheme.







The mechanism in above scheme has been proposed utilizing the oxidation and reduction of  $\text{H}_2\text{O}_2$  by steps (5) and (6) respectively, as reported elsewhere.



the formation of free radicals  $\cdot\text{OH}$  and  $\text{HO}_2\cdot$  as the intermediates in homogeneous metal ion catalysed decomposition of  $\text{H}_2\text{O}_2$ .

### CONCLUSION

Based on the above discussion and information available in the literature, the following conclusions may be drawn.

1. Higher decomposition temperature and electrical conductance studies show the presence of strong metal-ligand bonding and non-electrolytic nature of the complexes, respectively.
2. Specific rotation measurement studies are indicative of the chirality of the complexes.
3. Magnetic studies are indicative of tetrahedral geometry for Co(II) complexes and octahedral geometry for Ni(II) complex, which is confirmed by crystal field transitions shown by the electronic spectra.
4. IR spectra show bonding of the metal ion through N/O and O of the two ligands and presence of water of crystallization, confirmed by thermal analysis.
5. In both the reactions, Co(II) complexes are catalytically more active than Ni(II) complexes.
6. Octahedral Co(II) complexes are catalytically more active than tetrahedral Co(II) complexes in decomposition of  $\text{H}_2\text{O}_2$  while in hydrolysis of esters tetrahedral Co(II) complexes are catalytically more active.
7. Catalytic activity of octahedral Co(II) complexes is more than octahedral Ni(II) complexes in both the reactions.
8. Generally, CML Co(II)/Ni(II) complexes adsorbed on alumina (heterogenized) are better catalysts as compared to non-adsorbed complexes (heterogeneous catalysts).

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