

Synthesis and structural properties of metal complexes prepared from 2-Hydroxy-4,5-dimethyl isonitroso acetophenone ligand

Prashant C. Chandorkar*, R.M. Patil, R.S. Lokhande

Department of Chemistry, The Institute of Science, 15, Madam Cama Road, Mumbai 400032 (M.S.), India

ABSTRACT

The present paper deals with the synthesis and characterization of metal of some substituted oximes of 2-Hydroxy-4,5-dimethylacetophenone with salts of some metals like Cobalt, Nickel, Copper and Zinc. The were characterized by elemental analysis, conductivity measurements, ESR spectra, UV-Visible and TGA analysis. The oximes act as bidentate coordinate through deprotonated nitrogen and ketonic oxygen atoms.

ARTICLE INFO

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1. Introduction

There is great interest in synthesis and characterization of oximes and their metal complexes. Oximes were synthesized by condensation of acetophenone and aromatic aldehyde in acidic [1] or basic [2] media. The importance of oximes lies in the wide range of pharmacological activities such as anti-tubercular, anthelmintic [3], fungicidal [4], antitumor [5] and antibacterial [6] activity. The bidentate oximes containing oxygen atom have been tried for complexation with transition metals. It has been reported that O-hydroxy oximes are much more reactive than the ketones and aldehydes from which they are synthesized [7]. In this paper we wish to report the synthesis of Co(II) complex with oximes and their characterization.

2. Experimental

2.1. Materials and methods

All reagents used were chemically pure and are of AR grade. Solvents were dried and distilled before use according to standard procedures. The metals salts used were in their hydrated form and are of AR grade.

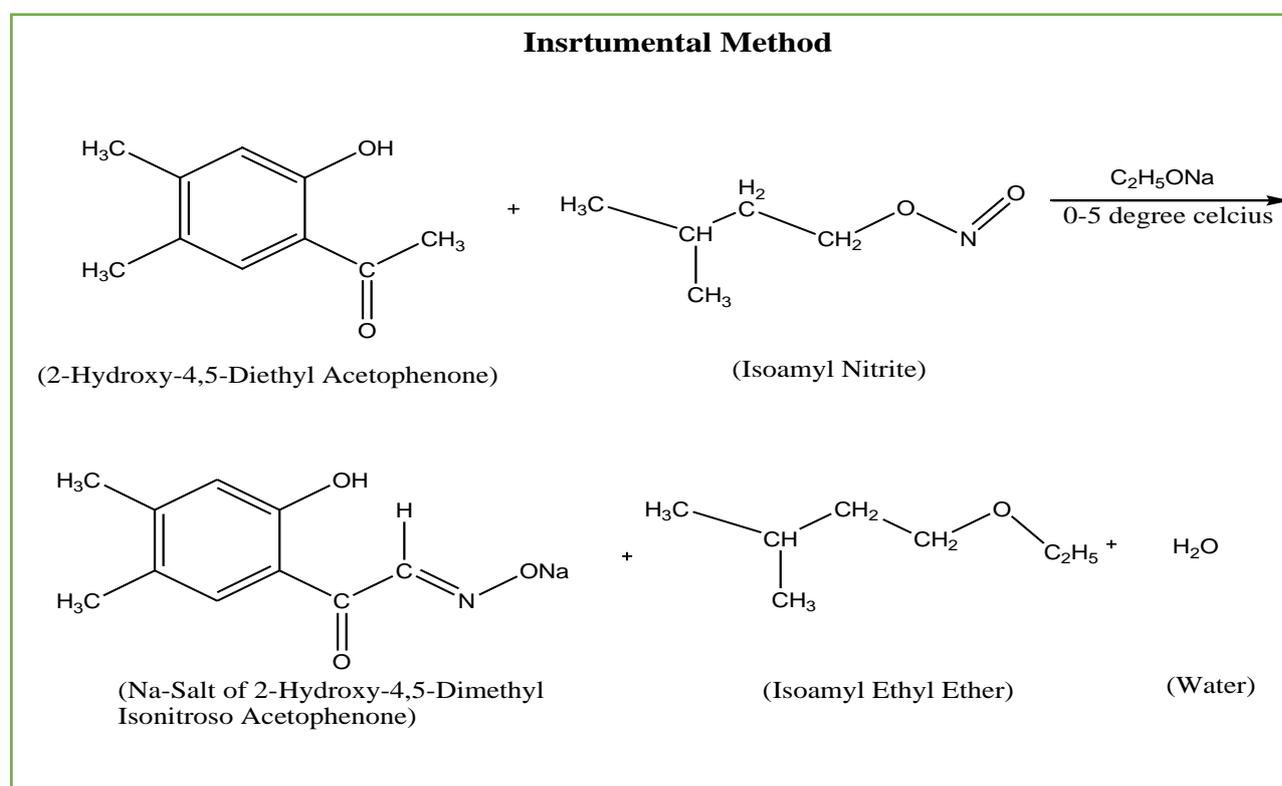
2.2. Synthesis of ligands

The oxime ligands were synthesized by the method reported [8] from our laboratory (see Fig. 1).

2.3. Preparation of complexes

The hot ethanolic solution of ligand (0.05 M) was mixed with ethanolic solution of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (0.05 M) metal salt. The resulting mixture was refluxed for about 3 hours and pH of the solution then raised up to 8 with aqueous ammonia and further refluxed for about 1 hour. The solid mass separated filtered through Whatman filter paper no. 1 and washed several times with hot ethanol until the washing was free from the excess of ligand. These complexes were finally dried under vacuum in desiccator over fused CaCl_2 .

Fig. No. 1 : Synthesis of oxime ligand:



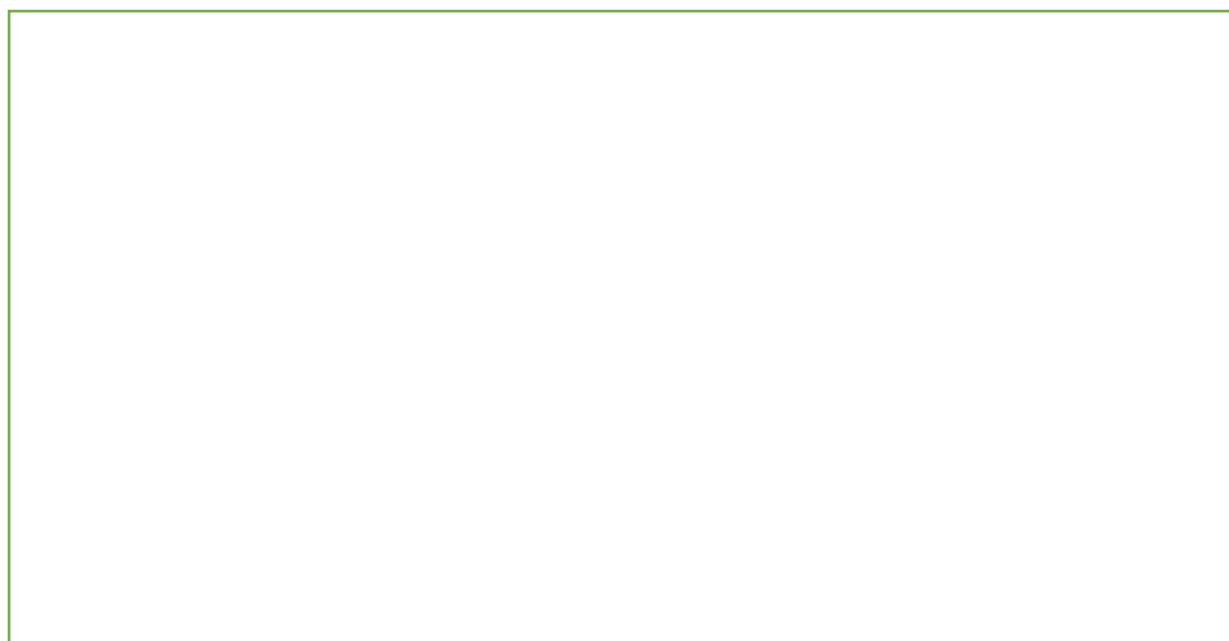
2.4. Instrumental methods

The IR spectra of complexes were recorded on a Perkin-Elmer instrument in KBr pallets in the range of $4000-400\text{ cm}^{-1}$. The conductance was measured in DMF solvent on Equiptronics Conductivity meter (EQ-664A). UV-Visible spectra were recorded using DMF as solvent on Shimadzu UV-VIS spectrophotometer in the range $200-900\text{ nm}$. Electron spin resonance spectra complexes were recorded on E-112 ESR Spectrometer as 'g' marker ($g=2.00277$) at room temperature. TGA analysis of metal complexes were carried out in nitrogen atmosphere in the range $25-900^\circ\text{C}$ on Rigaku Thermo Plus-8120 TG-DTA instrument with a heating rate $10^\circ\text{C min}^{-1}$ using Alumina as a standard.

3. Results and discussion

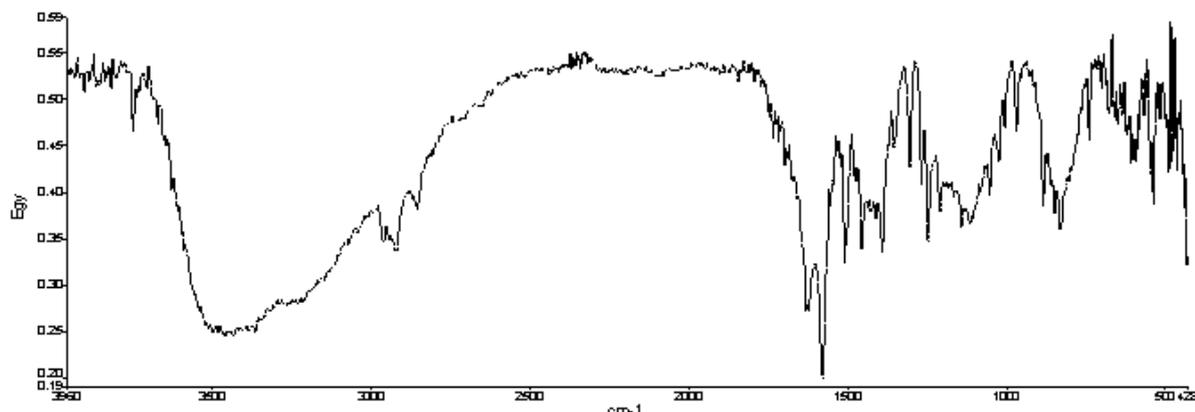
All the complexes are stable at room temperature insoluble in water and most common organic solvent but sparingly soluble in DMF. The elemental analysis shown in Table 1 indicates that, all metal complexes have 1:2 (metal : ligand) stoichiometry for all the complexes. The molar conductance values obtained for these complexes at the concentration are in the range of 0.782–0.832 mhos $\text{cm}^2\text{mol}^{-1}$ suggesting [9] their non-electrolytic nature.

Fig. 2 Preparation of metal complex



4. IR Spectral studies

The important infrared frequencies exhibited by metal complexes are given in Table 2. The ligand showed a weak broad band around $2921\text{--}3527\text{cm}^{-1}$ due to aromatic (OH) group, but IR spectra of Co(II) complexes (Fig. 2) exhibited intense broad band near $3300\text{--}3400\text{cm}^{-1}$ due to O-H of coordinated water molecule [10]. The band observed near 2980cm^{-1} in the FTIR spectrum of the ligand is ascribed to the aromatic C-H stretching vibration. In the IR spectra of all the ligands an intense band appearing around 1640cm^{-1} is attributed [11] to (C=O) group. In the complexes this band is shifted to lower wave number around 1616cm^{-1} indicating coordination through oxygen of (C=O) group. The medium intensity band appearing around $1565\text{--}1580\text{cm}^{-1}$ is due to the aromatic (C=C) vibrations. The ligand showed medium intense band around $1185\text{--}1220\text{cm}^{-1}$ which is attributed to (C-O) group but in the complexes this band shifted to higher wave number around 1250cm^{-1} indicating coordination through oxygen of (C-O) group. The (M-O) band was observed [12] in the complexes around 620cm^{-1} . The medium intensity band appeared at 1490cm^{-1} in CuL_3 is due to presence of - NO_2 group in the aromatic ring. The band appeared at 719cm^{-1} in CuL_4 complex is due to presence of C-Cl stretching vibration.

Fig. No. 3 IR spectra of $\text{Co}(\text{HDMINAP})_2(\text{H}_2\text{O})_2$ complex

5. Magnetic susceptibility measurements

The magnetic susceptibility for all the metal complexes of Co(II), Ni(II), Cu(II) & Zn(II) were recorded at room temperature by the Gouy's method using $\text{Hg}[\text{Co}(\text{SCN})_4]$ as a calibrant and reported. The effective magnetic moments were calculated [13] after applying diamagnetic corrections for the ligand components using Pascal's constants. The room temperature μ_{eff} values for the metal complexes were found in the range 1.71–1.88 B.M. The magnetic susceptibilities of the complexes are consistent with octahedral geometry around the central metal ion. The magnetic moments of the compounds investigated are in agreement with the findings of electronic absorption spectra.

6. Thermal measurements

The TGA studies of the complexes was recorded in nitrogen atmosphere on Rigaku Thermo Plus-8120 instrument by increasing the temperature from room temperature upto 900°C at the heating rate of $10^\circ\text{C min}^{-1}$. The decomposition pattern obtained for Cu (II) complexes of oxime ligands follow two major stages (Fig.2). In first stage the complex starts decomposing gradually till it attains the temperature around 150°C which corresponds to loss of co-ordinated water. After 250°C the anhydrous complex starts to decompose.

Total mass loss upto 700°C is around 80 % to 87 % which show finally formation of CoO. The residue left after 700°C is around 7 % to 13 % which resemble the theoretical values. Hence from thermal analysis it is clear that the complexes under study contains two water molecules which are coordinated to central metal ion (Table 2).

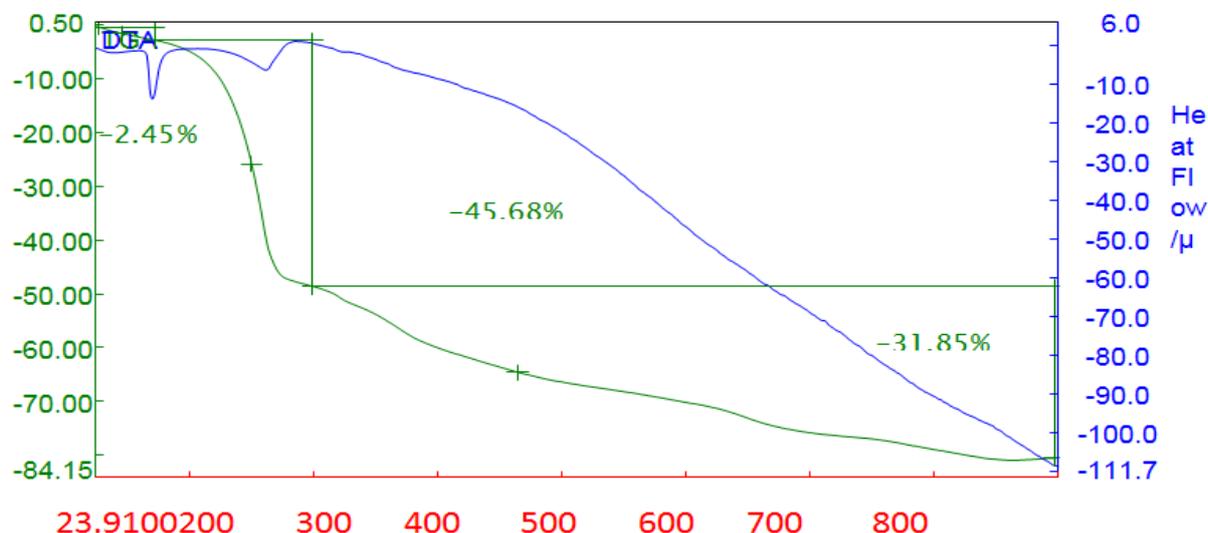


Table no. 4: TG-DTA spectra of $\text{Co}(\text{HDMINAP})_2(\text{H}_2\text{O})_2$ complex

Table1 Physical and analytical data of metal complexes.

Complex	Molecular formula	Mole. Wt. (gmol^{-1})	Yield%	% Elemental analysis Found(calculated)					Molar conductance ($\text{mhos cm}^2\text{mol}^{-1}$)
				C	H	O	N	Metal	
$\text{Co}(\text{HDMINAP})_2(\text{H}_2\text{O})_2$	$\text{C}_{20}\text{H}_{24}\text{O}_8\text{N}_2\text{Co}$	478.93	58.90	50.11	5.01	26.73	5.85	12.30	0.782
$\text{Ni}(\text{HDMINAP})_2(\text{H}_2\text{O})_2$	$\text{C}_{20}\text{H}_{24}\text{O}_8\text{N}_2\text{Ni}$	478.70	60.80	50.14	5.01	26.74	5.85	12.26	0.766
$\text{Cu}(\text{HDMINAP})_2(\text{H}_2\text{O})_2$	$\text{C}_{20}\text{H}_{24}\text{O}_8\text{N}_2\text{Cu}$	483.50	74.07	49.64	4.96	26.47	5.79	13.13	0.750
$\text{Zn}(\text{HDMINAP})_2(\text{H}_2\text{O})_2$	$\text{C}_{20}\text{H}_{24}\text{O}_8\text{N}_2\text{Zn}$	485.38	67.01	49.44	4.94	26.37	5.77	13.47	0.632

7. Electronic spectra

The electronic spectra (Fig. 3) of the metal complexes in DMF (10^{-3} M) was recorded on Shimadzu UV-VIS spectrophotometer in the range 200–900 nm. From these electronic absorption bands and paramagnetic nature, octahedral geometry suggested [15] for the oxime complexes. Reduction of

Racah parameter from 1050 cm^{-1} (free ion value) to around $508\text{--}603\text{ cm}^{-1}$ and the β value around 42%–52% indicate the covalent nature of the compound.

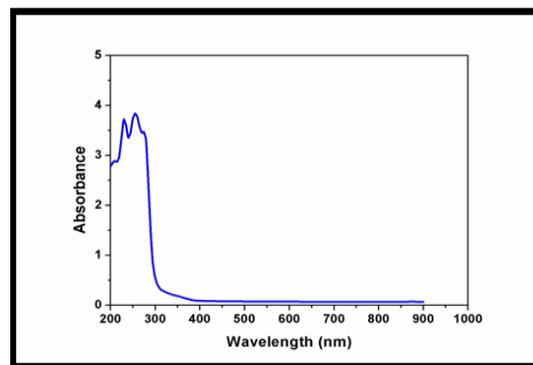
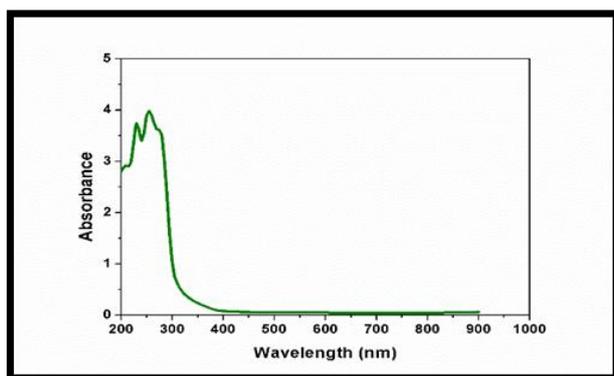


Figure 1: UV spectrum of Complex $\text{Co}(\text{HDMINAP})_2(\text{H}_2\text{O})_2$ Figure 2: UV spectrum of Complex $\text{Ni}(\text{HDMINAP})_2(\text{H}_2\text{O})_2$

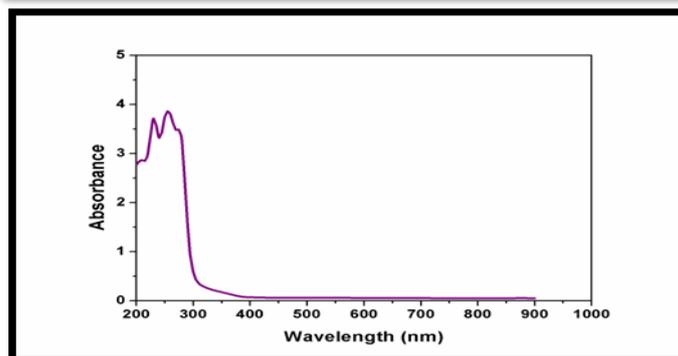
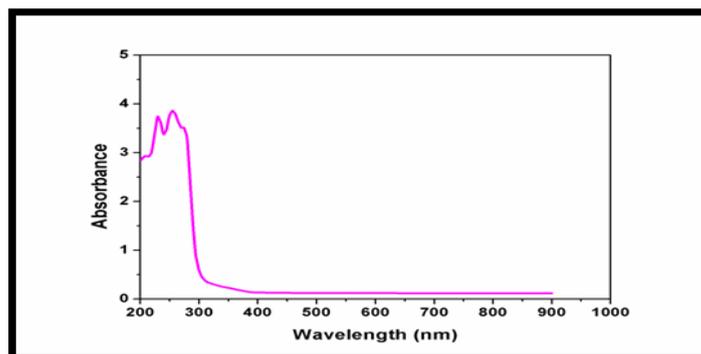
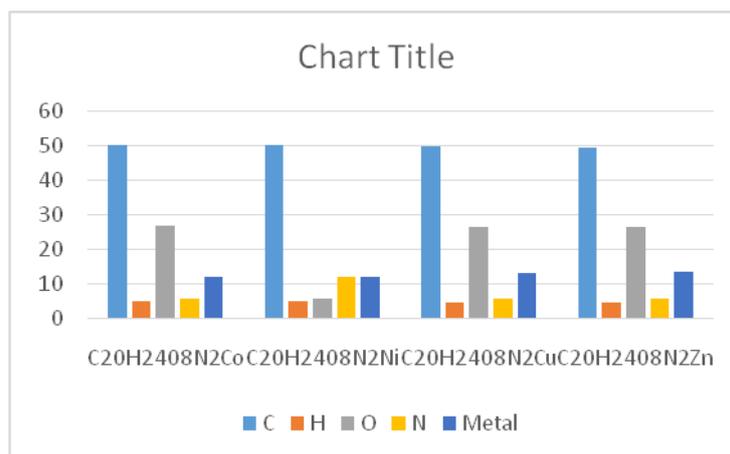


Figure 3: UV spectrum of Complex $\text{Cu}(\text{HDMINAP})_2(\text{H}_2\text{O})_2$ Figure 4: UV spectrum of Complex $\text{Zn}(\text{HDMINAP})_2(\text{H}_2\text{O})_2$

8. NMR and X-ray

All complexes are paramagnetic in nature, due to this and less solubility in CDCl_3 , well resolved spectra does not obtained. The XRD pattern do not show good peaks may be due to amorphous nature of the higher decomposition temperature and electrical conductance studies show the presence of strong metal-ligand bonding and non-electrolytic nature of the complexes, respectively. Room temperature magnetic studies are indicative of paramagnetic nature and octahedral geometry of the Co (II) complexes which is supported by the electronic spectra. The IR spectra shows bonding of the metal through O-donor atoms of the ligands. Acknowledgement Authors would like to thanks to Director, Institute of science (E) Mumbai and SAIF IIT, Powai Mumbai, for providing necessary facilities.

Fig. No. 2 Elements of different complexes:



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