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Effect Of 2-Nitrosophenol Ligand On The Antibacterial Activity Of Nickel (II) And Copper (II) Complexes

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Abstract: ***This paper aims to investigate the effect of the ligand, 2-nitrosophenol on the antibacterial activity of copper and nickel complexes. The complexes of 2-nitrosophenol with copper and nickel were synthesized and the complexes were characterized by IR spectroscopy and scanning electron microscopy. It is concluded that phenol undergoes nitrosation at position-2 and undergoes tautomerisation to its oxime form and thus acts as a bidentate ligand through N atom of the oxime group and through carbonyl oxygen. The spectral and all other data support a square planar geometry for both nickel and copper complexes. The thermal behavior of the complexes was studied using thermo gravimetric analysis. It is observed that all the complexes are thermally stable upto 190 ^{o}C and then it decomposes rapidly. The antibacterial properties of the complexes were evaluated using two types of bacteria, Staphylococcus aureus and Escherichia coli. The complexes were found to possess good anti bacterial activity.***

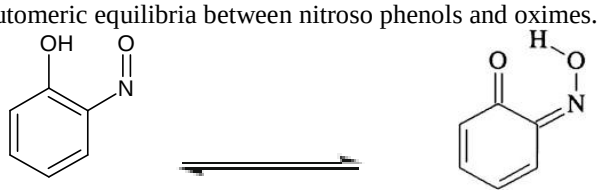
Keywords: metal complexes; copper, nickel; antibacterial activity; nirosophenol

I. INTRODUCTION

Copper and nickel play an important role in the biological life systems and in the formation of biocomplexes[1-8]. Nickel forms many bio-complexes and is the ingredient of some valuable bioactive molecules of enzymes. Bio-complexes of nickel are important bioenzymes and have key role in the biological life. Copper is necessary constituent many enzymes, is utilized for production of haemoglobin. It enhances iron absorption in gastrointestinal and transport of iron. Cu is utilized to maintain the level of myelin in nervous process, utilized for brain tissues and bone formation. Copper excess is harmful to human kind, also effects the microbiological treatment of waste water.

LIGAND (2- NITROSOPHENOL)

The molecular Formula of nitrosophenol is $C_6H_5NO_2$ and its Molecular Weight is123.1094 g/mol. Nitroso compounds are biologically active and have antibacterial - antiviral properties. These compounds have been extensively used as analytical reagents and of potential importance to the environment. Most of these compounds are subjected to the tautomeric equilibria between nitroso phenols and oximes.



In laboratory, Masoud et al [9-17] recently reported a detailed structural chemistry of azo and nitroso metal complexes based on spectral and magnetic susceptibility measurements.

The usual nitrosation of phenol with nitrous acid always leads to the p-nitroso compounds although Viebel found that o-compounds are formed as intermediate [18].

The Baudisch Reaction was discovered by Oskar Baudisch in 1939 and further developed by his colleague

Cronheim[18][19]. In the reaction a solution containing aqueous hydroxylamine hydrochloride and hydrogen peroxide reacts with benzene or phenol, with the assistance of copper(II) to give 2-nitrosophenols [20].

A large number of nitroso compounds were used as reagents for the detection and estimation of many metal ions [21]. Nitrosophenol complexes of metal salt was studied by Masoud et al.[22,23].

Georg Cronheim studied new substituted 2-nitrosophenols and characteristic properties of their inner complex metal salts. He could prepare 50 new mono and di substituted o-Nitrosophenols from benzene and phenol derivatives by Baudisch reaction [24]. A study on complexes of copper (II) with 2-nitrosophenols (monoximes of ortho benzoquinones) by Charalambous et al. [25]. The properties, magnetic susceptibilities, and electronic, IR and mass spectra of the complexes have been investigated.

A study on Nickel and cobalt chelates of some 2-nitrosophenols by Khadem [26]. The Ni (II) chelates of 2, 4-dinitrosoresorcinol, 1-nitroso-2-naphthol, 5-methoxy-2-nitrosophenol, 4-chloro-2-nitrosophenol were obtained in a crystalline form by the interaction of Ni (II) salts with the ligands or their sodium salts. The electronic spectra of nickel chelates were found to be solvent and temperature dependent.

The nitroso complexes were reported to have anti bacterial and anti viral properties. The aim of this work is to explore the scope of the chelating properties of 2-nitrosophenol compounds with nickel (II) and copper (II) based on electronic and IR spectra. The thermal behavior of the complexes was also studied.

II. EXPERIMENTAL

A. MATERIALS

Nickel complex was prepared using nickel (II) chloride (AR Grade) samples and for the preparation of copper (II) complexes, AR Grade copper (II) sulphate pentahydrate was used. Commercial grade solvents were used for the present study and all the solvents were purified by standard procedures.

B. PREPARATION OF THE METAL COMPLEXES

a. NICKEL (II) COMPLEX

A solution of 1.3 g phenol in 50 ml water was prepared and mixed with nickel (II) solution (2 g of nickel chloride in 30 ml water). To this mixture, a solution of 1 g sodium nitrite in 15 ml water was added with stirring. A sudden change in colour was observed indicating the complex formation. The mixture was refluxed for about 3 hours. Cooled, filtered, dried over anhydrous calcium chloride.

b. COPPER (II) COMPLEX

1.25 g of copper (II) sulphate was dissolved in 50 ml water. A solution of 1g phenol in 50 ml water was prepared and mixed with copper (II) solution. To this mixture, a solution of 0.8 g sodium nitrite in 12 ml water was added with stirring. The mixture was refluxed for about 3 hours, cooled, filtered, dried over calcium chloride.

C. METAL PERCENTAGE ANALYSIS

The percentage of metals was estimated according to the standard procedure [28]. Nickel present in the complex was estimated gravimetrically by precipitating as nickel dimethyl glyoximate [28].

D. CHARACTERIZATION OF METAL COMPLEXES

a. FTIR

The FTIR spectra were recorded on a on a 'Perkin-Elmer' FTIR spectrometer in the wave number range 400-4000 cm^{-1} by KBr disc method. The spectral analysis was done in Sophisticated Analytical Instrument Facility, STIC, CUSAT, Cochin.

E. THERMO GRAVIMETRIC ANALYSIS

Thermogravimetric analysis or TGA is a method of thermal analysis in which changes in physical and chemical properties of materials are measured as a function of increasing temperature. TGA measurements were done on TGA curves are recorded on Perkin Elmer Pyris. The samples were heated from 40 °C to 750 °C at 10 °C/min in the nitrogen atmosphere.

F. BIOLOGICAL ACTIVITY (ANTIBACTERIAL ACTIVITY) OF THE COMPLEXES

Antimicrobial activities of the complexes have been carried out against the pathogenic bacteria like Escherichia coli and Staphylococcus aureus using nutrient agar medium by well diffusion method.

Agar diffusion method was employed to evaluate the antibacterial activity. About 1 mg of complexes were dissolved in DMSO and well diffusion was carried out. Wells of standard size (6 mm) were incised at specified distances in Mueller Hinton agar 18 hrs old broth cultures of *Staphylococcus aureus* and *Escherichia col*i were swabbed on separate agar plates. 100 µl each of the compounds (300 µg dissolved in 1 ml DMSO) was added into separate wells. DMSO was served as control. 0.2% chlorhexidine was used as positive control. After incubation at 37 ^{o}C for 24 hrs, diameter of zone of inhibition was measured and consequently antibacterial activity was assessed. All the experiments were conducted in triplicates and the average value of the diameter of zone of inhibition exhibited by isolates were recorded.

III. RESULTS AND DISCUSSION

A. ANALYSIS OF THE COMPLEXES

a. GENERAL PROPERTIES OF THE COMPLEXES

The complexes are found to be stable and coloured crystalline substances. The nickel complex is found to be brown coloured and copper complex is black in colour. Both complexes are soluble in DMF and DMSO, but sparingly soluble in methanol, ethanol and completely insoluble in organic solvents like benzene, toluene etc.

b. METAL PERCENTAGE ANALYSIS

The metal percentages observed for NiL_2 and CuL_2 are 20.9 and 21.5 respectively comparable with those calculated (21.6 and 20.6 respectively). The metal percentage analysis confirms the formula of the complex NiL_2 and CuL_2 where L is the ligand, 2-nitrosophenol. The absence of Cl^- and SO_4^{2-} indicates that there is no anion in the complex.

B. CHARACTERIZATION

a. IR SPECTRA

The main absorptions in the IR spectrum of the complexes are given in Table 1. A close examination of the FTIR spectra shows that there is a broad absorption band appeared around 3400 cm^{-1}. This indicating the presence of hydrogen bond involving N-OH group. The carbonyl absorption in these compounds is assigned to the ketoxime structure. Normally aryl ketones are expected to give an absorption around 1670 cm^{-1} characteristic of carbonyl group. In both complexes, a very intense peak around 1630 cm^{-1} is observed and such a low value suggests that carbonyl group is involved in coordination with the metal ions. There is a strong absorption in the range 1590 cm^{-1}-1597 cm^{-1} which is attributed to the $\nu_{C=N}$ of the oxime group.(28) The absorptions in the range 1400 cm^{-1} -1500 cm^{-1} are due to C=C stretching of the aromatic ring. A strong band at around 1505 cm^{-1} is due to the stretching vibration of NO bond in the oxime group. The bands observed below 1000 cm^{-1} can be assigned to the absorption of the ortho disubstituted aromatic ring. The bands at 2790 cm^{-1} is assigned to υ(C–H) aromatic stretching. 2-nitroso phenols show a broad absorption band near 3300 cm^{-1}.The absence of such absorption in the spectra of the complexes indicates that 2-nitrosophenol is coordinated after deprotonation.

The absorptions due to N-O stretching vibration should be in the range 1000-1050 cm^{-1}.However in these complexes the increased absorption frequency indicates that the coordination is through nitrogen and not through oxygen. The prepared complexes showed weak bands in the range of 500-520 cm-1 and 416- 460 cm-1 which may be attributed to the ν(M- O) and ν(M- N) respectively.

All these observations suggest that phenol undergoes nitrosation at position-2 and undergoes tautomerisation to its oxime form and thus acts as a bidentate ligand through N atom of the oxime group and through carbonyl oxygen. The spectral and all other data support a square planar geometry for both nickel and copper complexes as shown in Fig.1 and Fig. 2.

C. THERMOGRAVIMETRIC ANALYSIS OF THE COMPLEXES

Thermogravimetric analysis of the complexes gives information concerning the thermal stability of the complex. The complexes were heated to 750 ^oC at a heating rate 10 ^oC/min in nitrogen atmosphere. The decomposition takes place in a number of stages as shown in the TG and DTG curves (Fig.4 and Fig.5). In this complex weight loss below 100 ^oC indicating the loss of absorbed water. The complex is stable upto 190 ^oC and then it decomposes rapidly. The steps are not well defined.

D. ANTIBACTERIAL ACTIVITY OF THE COMPLEXES

The newly synthesized metal complexes were screened in vitro for their antibacterial activity against bacteria: Staphylococcus aureus and E-coli. The antimicrobial activities of the compound are recorded in Table 2. 0.2 % chlorhexidine was used as positive control. The zone inhibition of bacterial growth was measured in mm and is given in Table 2. The anti bacterial activity can be assessed based on the diameter of the inhibition zone. It was observed that both the complexes show good antimicrobial activity towards Staphylococcus aureus and E-coli bacteria.

IV. CONCLUSIONS

The metal complexes of 2-nitrosophenol were synthesized with two transition metals, copper and nickel. The complexes were characterized by IR. It is concluded that phenol undergoes nitrosation at position-2 and undergoes tautomerisation to its oxime form and thus acts as a bidentate ligand through N atom of the oxime group and through carbonyl oxygen. The thermal behavior of the complexes were studied using thermo gravimetric analysis. The complex is found to be thermally stable upto 190 ^oC and then it decomposes rapidly. The steps are not well defined. The antibacterial properties of the complexes were evaluated using two types of bacteria, Staphylococcus aureus and Escherichia coli. The complexes were found to possess anti bacterial activity.

TABLES

ν (cm^{-1})	Nickel Complex	Copper Complex
$\nu_{C=O}$	1630	1627
$\nu_{C=N}$	1590	1597
$\nu_{C=C}$	1300-1350	1430-1460
ν_{C-H}	2790	2820
ν_{N-O}	1080	1105
ν_{M-O}	505	519
ν_{M-N}	410	421

Table 1: IR spectral data of the complexes

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Complex	Inhibition zone diameter (mm)	
	E. coli	S. aureus
Cu (II) complex	25 mm	39 mm
Ni (II) complex	24 mm	38 mm
Chlorhexidine 0.2%	27 mm	39 mm
Chlorhexidine 0.1%	24 mm	29 mm

Table 2: Zone inhibition diameter of the complexes

Captions to Figures

Fig.1 Bis(2-nitrosophenolato) nickel (II) complex

Fig.2 Bis(2-nitrosophenolato) copper (II) complex

Fig.3 TGA curve of Copper (II) complex

Fig.4 TGA curve of Nickel (II) complex

Fig.5 Antibacterial activity of the complexes against (a) E-coli and (b) Staphylococcus aureus.

FIGURES

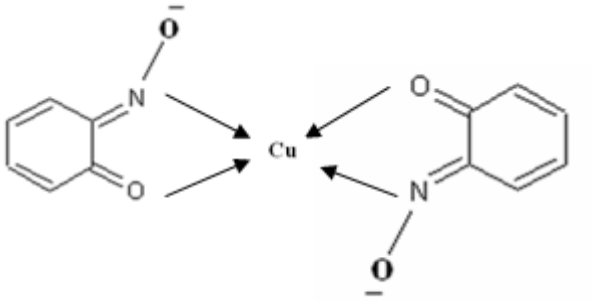

Figure 1: Bis(2-nitrosophenolato) nickel (II) complex

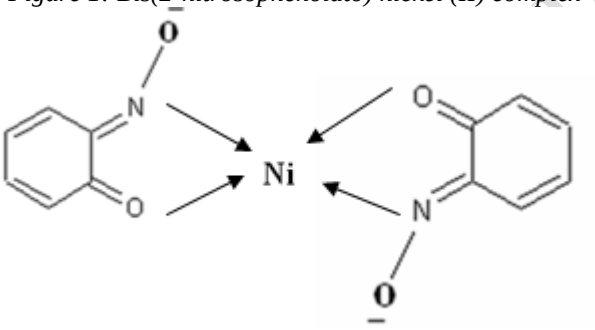

Figure 2: Bis(2-nitrosophenolato) copper (II) complex

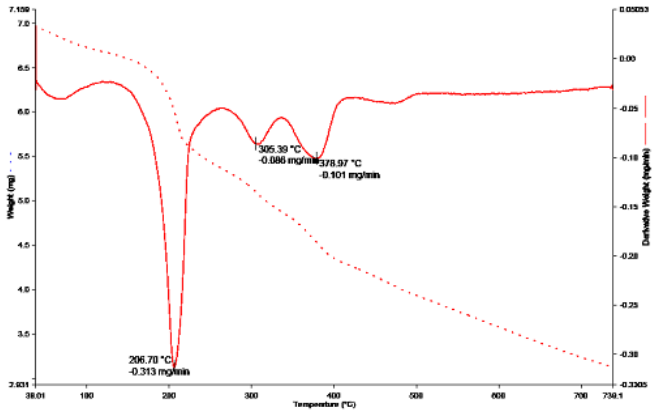

Figure 3: TGA curve of Copper (II) complex

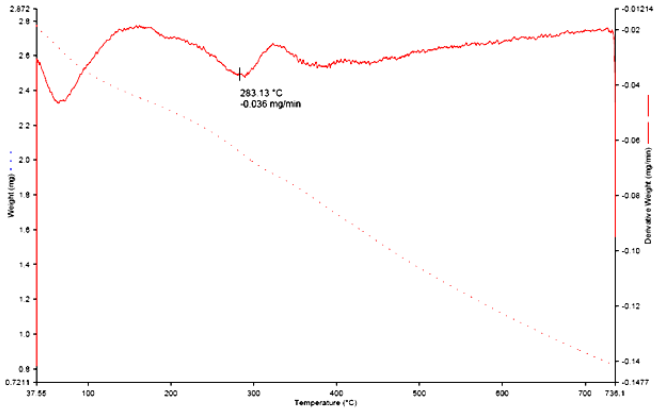

Figure 4: TGA curve of Nickel (II) complex

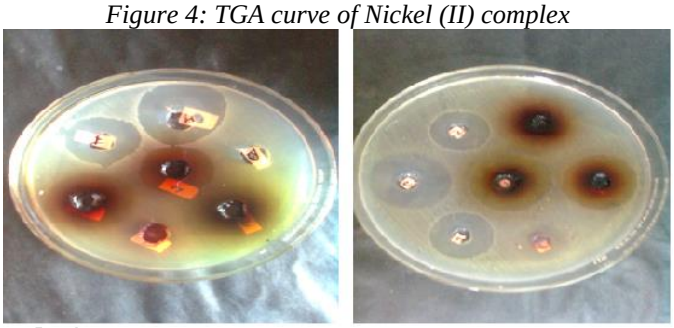

Figure 5: Antibacterial activity of the complexes against (a) E-coli and (b) Staphylococcus aureus

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