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STUDIES OF METAL COMPLEXES DERIVED FROM ISONITROSO ACETOPHENON ,BENZYL OXIMES, ACETYL ACETONATE AND AMINES

Dr. Mayuri R. Joshi
Associate Professor, Department of Chemistry,
Maharashtra College of Arts, Science and Commerce, 246 – A, JBB Marg, Mumbai-400008, India.

Abstract

The metal complexes have been screened for their antibacterial activity. Escherichia Coli, Staphylococcus, B.cereus,Bacillus Subtilis were studied on laboratory grown cultures, these yield several kinds of information which are of value in guiding and understanding their therapeutic use. The work reported here deals with the synthesis and spectroscopic studies of some Cd(II) complexes with poly dentate Schiff bases are reported here. These Schiff bases were derived by condensing carbonyl oximes-like isonitrosoacetophenone, α-benzyl monoxime, isonitroso acetyl acetone with amines like sulphanilic acid. The characterization of the complexes was done on the basis of elemental analysis, molar conductivity, spectral IR, electronic thermal analysis spectra.The metal complexes have been screened for their antimicrobial activity. The concentration required to inhibit various organisms and the effects of environmental conditions on their activity are of paramount importance. The complexes show moderate activity against (10-22 mm) against the above mentioned bacteria.This shows that besides the complex formation, the nature of the metal ion has important role in the inhibition of the pathogenic activity of the bacteria The analytical data suggests that the complexes can be formulated as $M_2L_2Cl_2$ $4H_2O$ where M=Cd. The conductivity measurement indicates that they are non-electrolyte in nature.

The complexes are thermally stable, insoluble in water but soluble in organic solvent to varying extent .The room temperature magnetic susceptibility measurements indicate their octahedral geometry which is further supported by electronic absorption /diffuse reflectance spectra.

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1. Introduction

Progress in the field of Coordination chemistry has received considerable significance because of its importance in chemical industry and life itself. Schiff bases contain azomethine (>C=N) group as functional group and hence act as an effective ligand. Transition metal complexes of Schiff bases have witnessed a great deal of interest in the recent years because of their chemical, pharmacological[1-3] and analytical applications[4] In addition the presence of nitrogen and oxygen donor atoms in the complexes act as stereospecific catalyst for many reactions like oxidation,[5] reduction,[6] hydrolysis and possess antibacterial activity[7]. In this paper, the synthesis, Spectral studies, , Thermal, and Antibacterial of some Cd(II) complexes with polydentate Schiff base ligands are reported.

2. Material & Methods

All chemicals used were of A. R. grade purchased from S. D. Fine chemicals (Mumbai) & used without further purification. Distilled solvents were used throughout the experiments.

Metal content was determined in the laboratory by the reported methods[8] C, H and N analysis were performed at the IIT Mumbai. The infra-red spectra of the ligands and of their metal complexes were recorded in KBr pellets in the 4000-400 cm-1 region using a FTIR spectrum one supplied by Perkin Elmer instrument. The electronic spectra were recorded on Beckman Spectrophotometer, diffuse reflectance spectra of solid complexes taken on

Carl-Zeiss VSU -2P spectrophotometer. The ^{1}H NMR spectra were recorded on a VXR-300S Varian Super TGA analysis was carried out using a Shimadzu DT-30 recording thermal analyser in an inert atmosphere of nitrogen, from room temperature to 900^0c. Antimicrobial studies: The in vitro biological screening effects of the investigated compounds were tested against the bacteria Escherichia coli, Staphylococcus, B.cereus, Bacillus subtilis were studied on laboratory grown cultures. Stock solutions were prepared by dissolving the compounds in DMSO and serial dilutions of the compounds were prepared in sterile distilled water to determine the minimum inhibition concentration (MIC). The nutrient agar medium was poured into Petri plates. A suspension of the tested microorganism (0.5 ml) was spread over the solid nutrient agar plates with the help of a spreader. Different dilutions of the stock solutions were applied on the 10 mm diameter sterile disc. After evaporating the solvent, the discs were placed on the inoculated plates. The Petri plates were placed at low temperature for two hours to allow the diffusion of the chemical and then incubated at a suitable optimum temperature for 30 – 36 hrs. The diameter of the inhibition zones was measured in millimetres.

2.1 Synthesis of **1**-phenyl 1-hydroimino ethylidine iminobenzene 4-sulphonic acid (HPEIBSA) of Hg(ll) complex. [L_1]

The Metal complexes of Schiff base were synthesized *in situ* condensing ethanolic solution of 0.01 mol of carbonyl oximes, namely HINAP[9], with 0.01 mol of aqueous solution of sulphanilic acid and metal chloride in 1:1:1 stoichiometric ratio and pH of the solution was raised to ~8 with 0.1 N NaOH solution when solid complexes were obtained, they were digested on water bath for about half an hour and filtered, washed with hot water repeatedly followed by 50% alcohol and dried in vacuum.

2.2 Synthesis of 1,2diphenyl 1-hydroxyimino ethylidine iminobenzene 4 – sulphonic acid (HBEIBSA) Of Hg(ll) complex. [L_2]

An alcoholic solution of α –benzilmonoxime[9] was mixed with aqueous solution of sulphanilic acid and metal chloride solution in 1:1:1 molar proportions .The pH of the solution was raised 8 with dilute alkali solution when chelates separated out, The solids left overnight and filtered next day, they washed thoroughly with hot water, 50% alcohol and dried in vacuum.

2.3 Synthesis of 1-acetyl 2-methyl 1-hydroimino ethilidine imino benzene 4-sulphonic acid (HAMEIBSA) complex of Hg(ll). $[L_3]$

An alcoholic solution of isonitrsoacetylacetone[9] was mixed with aqueous solution of sulphanilic acid and aqueous alcoholic metal chloride in 1:1:1molar proportion. The pH of the solution was raised to 8.0 with dilute alkali solution when solid chelate was obtained. They were digested on water bath for about half an hour and kept overnight .They were filtered on net day, washed several time with hot water followed by 50% alcohol and dried in vacuum.

3. Results & Discussion

All the metal complexes are intensely coloured. They are thermally quite stable, as shown by their high decomposition temperatures, which indicate strong metal to ligand bonding solids. The complexes are insoluble in water, ethanol, methanol, chloroform, carbon tetrachloride etc. but soluble in DMF and DMSO. The complexes dissolve in alkali like sodium hydroxide giving colour, indicating the presence of a free oxime group, suggesting oximino proton is not replaced during complexation. The elemental analysis show 1:1 ligand metal stoichiometry for all the complexes. The analytical data along with some physical properties of the ligand and metal complexes are reported in Table 1.

The molar conductivities of 1×10^{-3} mhos cm^2 mol^{-1} solutions of the complexes in nitro benzene indicate their non-electrolytic nature.[10]

The elemental analysis suggest 1:1 (metal: ligand) stoichiometry for all the metal complexes. They are formulated as M_2L_2 Cl_2. Here L represents HPEIBSA, HBEIBSA and HAMEIBSA. The infrared spectra of the free carbonyl oximes were compared with those of their Hg(II) complexes to determine the bonding corresponding ligands. The observations confirm the successful replacement of carbonyl oxygen by imino nitrogen during Schiff base formation prior to the *in situ* formation of the complexes.The spectra of the parent carbonyl oximes shows strong and broad absorption band in the region 3300 cm-1, which is due to $^{\nu}$O-H band due to =NOH. The FT-IR spectra of the metal complexes reveal a band in the region 3246-3398 attributed to O-H stretching may be concluded that sulphonic group is deprotonated on the basis of Pk values of $–SO_3$ vibrations of free =NOH group. It is also corroborated by PMR spectra of complexes. The N-O stretching vibrations in the spectra pf complexes are in the range of 883-1024 cm^{-1} indicating a shift bonding through deprotonated free oxime. The coordination of azomethine nitrogen is confirmed by the presence of bands in the 1590-1598 cm^{-1} region in the ligand which underwent a shift to a lower frequency after complexation[11]. All complexes show extra bands in the 515-618 cm-1 and 413-492cm-1 region assigned to υ(M-N)[12] and υ(M-O)[13] stretching vibrations. The medium or weak intensity bands at 355-380 cm-1 is due to terminal M-Cl. This data is in good agreement with literature values[14]. Thus these Schiff bases behave as multi-dentate ligand coordinating through the deprotonated sulphonic group and azomethine nitrogen azomethine nitrogen the presence of an ionised $–SO_3$[15] is indicated by 1120-1160 cm^{-1}. Selected IR bands for the ligands and their metal complexes are represented in Fig. 1 along with the IR spectral data (cm^{-1}) in Table 2.

The metal complexes indicate that oximino proton of HINAP observed at 11.4δ in dioxan or at 9.06 δ in $CDCl_3$ is shifted to 12-12.6δ this positive shift indicates the proton of the =NOH is not replaced.

The thermal studies of the complexes show that they are thermally stable to varying degree. The complexes show loss in weight up to about 100 – 110°C. This observation suggests (1-1.5%) the absence of any lattice water or water of crystallization. It clearly indicates the nature of water molecules present as being coordinated to the central metal ion by loss of coordinated water in the temperature range 120-220°C with further increase in temperature the complexes show decomposition by fragmentation and thermal degradation of the organic part of the metal complexes, finally resulting into corresponding metal oxide[16].

The result of the preliminary study on antimicrobial activity of Hg(ll) complexes screened against B.subtilis, B.cereus, E.coli and S.aureus are tabulated in table 5.the test for complexes carried out in DMF solution using the agar cup method with DMF as blank control. They show resistance to most of the complexes. S.aureus and E.coli are fair to moderately sensitive to Zn (ll) complexesThey show varying action towards these bacteria.

Table shows result of agar cup method for the antibacterial activity of the Hg(ll) complexes in (DMF).

COMPOUND	B.subtilis(mm)	B.cereus(mm)	S.aureus(mm)	E.coli(mm)
Hg$_2$(HPEIBSA)$_2$Cl$_2$	17	14	17	16
Hg$_2$(HBEIBSA)$_2$Cl$_2$	16	11	22	16
Hg$_2$(HAMEIBSA)$_2$Cl$_2$	12	13	12	16

Synthesis and characterisation of mercury complexes with sciff base ligand s

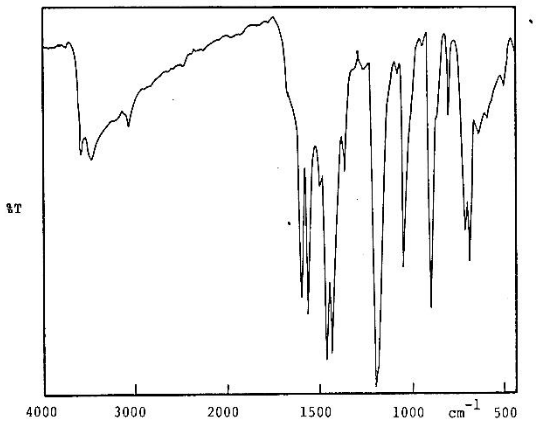

Fig 1 Infrared absorption Spectrum of Hg$_2$(HPEIBSA)$_2$Cl2

Table 1. Physical and Analytical Data of the metal complexes

COMPLEX	Colour	M.P. (^{0}C)	M	C	H	N	S	Cl	Molar conductance

$Hg_2(L_1)_2Cl_2$ $4H_2O$	yellow	178	34.0 (30.83)	36.2 (36.89)	2.2 (2.92)	5.0 (4.30)	5.0 (5.59)	5.9 (6.1)	.89
$Hg_2(L_2)_2Cl_2$ $4H_2O$	yellow	225	30.2 (30.83)	36.2 (36.89)	2.2 (2.9)	5.0 (4.30)	4.3 (4.92)	4.6 (5.46)	..840
$Hg_2(L_3)_2Cl_2$ $4H_2O$	pale yellow	178	36.0 (36.17)	23.2 (23.80)	2.0 (2.70)	4.9 (5.04)	6.2 (5.77)	5.8 (6.40)	.820

Table 2. I.R. Spectral data of Cd (ll) complexes (cm^{-1})

Complexes	$^{\upsilon}$O-H H$_2$O/NOH (cm^{-1})	$^{\upsilon}$C=N Azomethine (cm^{-1})	$^{\upsilon}$C=N Oximino (cm^{-1})	$^{\upsilon}$N-O (cm^{-1})	$^{\upsilon}$M-N (cm^{-1})	$^{\upsilon}$M-O (cm^{-1})
Hg_2 $(L_1)_2Cl_2$ $4H_2O$	3540/3395	1597	1560	886	532	488
Hg_2 $(L_2)_2Cl_2$ $4H_2O$	3540/3385	1597	1560	886	532	488
Hg_2 $(L_3)_2Cl_2$ $4H_2O$	3520/3378	1597	1540	1000	510	462

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