SYNTHESIS, MAGNETO-SPECTRAL CHARACTERIZATION AND ANTIMICROBIAL ACTIVITY OF ALKALI METALS WITH 4-CHLOROISONITROSOACETOPHENONE (4-CIINAP)

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Abstract

Studies of the complexes of alkali metal such as Li, Na, K, Rb and Cs with the ligand isonitroso-4-chloroacetophenone (4-CIINAP) have been performed. Complexes have been assigned the formula M(4-CIINAP)2 (where M= alkali metals) on the basis of elemental analysis, magnetic properties, conductance measurement, spectral studies and antimicrobial activity.

Keywords

Alkali metals, Schiff's bases, I.R., N.M.R. spectroscopy ,antimicrobial properties.

Introduction

Schiff bases have wide range of applications. Some are known to be used in many potential drugs and many are used in number of biological activities. A Schiff base bis(2-pyridyl carboxyl aldehydes)ethylene diamine was studied for few transition metals1. The ligand p-methyl isonitrosoacetophenone (HIMAP) also been used for few analytical applications2-3.Some transition metal complexes were also been synthesized using Schiff base 1,2-propylenedimmine o-hydroxy-acetophenone and their antimicrobial study have been performed4.The ligand Isonitroso phenyl-2-propanone have also been studied for few transition metals 5-6. Spectroscopic study of the ligand p-chloroisonitrosoacetophenone was also been performed with Cu, Co and Ni 7.Some alkali metals were also been studied using the above ligand8.However, spectroscopic study including magnetic properties of the complexes of all the alkali metals with isonitroso-4-chloroacetophenone using various aspects have not been reported so far. The present paper describes the synthesis,

characterization and determination of structural formula of complexes of alkali metals with 4-chloroisonitrosoacetophenone on the basis of elemental analysis, magnetic properties, microbial activity and spectral analysis such as electronic, I.R. and NMR.

Material and Methods

Experimental- Chemicals- The chemicals were used of A.R. grade. The ligand was prepared using the method described in the literature9. Preparation of metal complexes with p-chloroisonitrosoacetophenone:- Solutions of salts of Alkali Metals and the ligand p-chloroisonitrosoacetophenone were prepared in the molar proportion of 1: 2 Preparation of Li(p-ClINAP)2 Complex- Lithium nitrate solution was prepared by dissolving 0.689 g. in a minimum quantity of distilled water. Similarly 3.670 g. of p-ClINAP was dissolved in a minimum quantity of alcohol. These solutions were mixed together. The pH of the solution was maintained at 6.5 by adding few drops of con. HCl. The suspension mixture was heated on a water bath for 7 hours by applying a water condenser. Then the reaction mixture was kept in vacuum desiccators for 12 hours. A lithium salt of ligand p-Chloroisonitrosoacetophenone was precipitated out. Preparation of Na(p-ClINAP)2 Complex- A solution of sodium nitrate was prepared by dissolving 0.850 g. in a minimum quantity of distilled water. Similarly 3.67 g. of p-ClINAP was dissolved in a minimum quantity of alcohol. These solutions were mixed together. The pH of the solution was maintained at 6.5 by adding few drops of conc. HCl. The suspension mixture was heated on a water bath for 8 hours by applying a water condenser & then kept in vacuum desiccators for 12 hours. A sodium salt of ligand p-chloroisonitrosoacetophenone was precipitated out. Preparation of K(p-ClINAP)2 Complex- A saturated solution of Potassium Nitrate was prepared by dissolving 1.015 g. in a minimum quantity of water. Similarly 3.67 g. of p-ClINAP was dissolved in a minimum quantity of alcohol. These solutions were mixed together. The pH of the solution was maintained at 6.5 by adding few drops of conc. HCl. The above mixture was heated by applying a water

condenser on a water bath for 8 hours. The resultant mixture was kept in vacuum desiccators throughout night for cooling. A potassium salt of p-Chloroisonitrosoacetophenone was precipitated out. Preparation of Rb(p-ClINAP)2 Complex- A solution of Rubidium Chloride was prepared by dissolving 1.209 g. in a small amount of water and obtained its saturated solution. Similarly 3.67 g. of p-ClINAP was also dissolved in a minimum quantity of alcohol. Both these saturated solutions were mixed together. The pH of the solution was maintained at 6.0 by adding few drops of conc. HCl. The above mixture was heated on a water bath for 10 hours by applying a water condenser. The resultant mixture was kept in vacuum desiccators for 12 hours. A rubidium salt of p-Chloroisonitrosoacetophenone was precipitated out. Preparation of Cs(p-ClINAP)2 Complex: A saturated solution Cesium Chloride was prepared by dissolving 1.950 g. in a minimum quantity of water. Similarly 3.67 g. of p-ClINAP was dissolved in a minimum quantity of alcohol. Both these solutions were mixed together. The pH of the solution was maintained at 6.0 by adding few drops of conc. HCl. The above mixture was heated on water bath for 10 hours by applying a water condenser. After heating, the resultant mixture was kept in vacuum desiccators for 14-15 hours. A Cesium salt of p-Chloroisonitrosoacetophenone was precipitated out . All the complexes were dried, washed with alcohol and then recrystallized from ether and subjected to melting point determination and analyzed for Li, Na, K, Rb, Cs, C, H, N and Cl separately as given in literature10.

Result and Discussion

On the basis of analytical data (table no.1), complexes of Li, Na, K, Rb and Cs can be represented M(ClINAP)2 . All the compounds are genuine complexes and not stoichiometric mixtures. They are colored and thermally stable. It is cleared from the fact their decomposition temperatures were much higher (2020 C - 2480 C) than the melting point of the ligand (1580 C). Molecular weights of the complexes were determined by using Rast's method. The values of molecular

weights calculated on the basis of molecular formulae of the complexes are found to be close to those obtained by Rast's method. The molecular weight of the complexes could not be determined by the cryoscopic method due to the limited solubility of the complexes in nitrobenzene and other organic solvents. Magnetic properties- The magnetic moment values of alkali metal complexes of p-ClINAP lies in the range 3.90-5.08 B.M. are usually expected to be indicative of the distortion from square planer geometry11. It could be therefore, informed that magnetic moment of potassium in the complex is broadly within the range of square planar or tetragonally distorted octahedral stereochemistry. The observed values at room temperature show that there is no interaction between separate potassium atoms in the complex12. Magnetic moment values obey the Curie-Weiss law indicating neither inter nor intra molecular M-M interaction. Magnetic moment values of alkali metal complexes with p-ClINAP support square planar geometry and same is supported when examined in the light of the literature data. Conductivity Measurements:- Conductivities of the complexes are found to be in the range of 9.4-11.7 mhos cm2 respectively in 10-4 Molar solutions. These are very close to those reported for non-electrolyte in nitrobenzene. I.R.Spectra: IR spectra have been measured in the region 4000-400 cm-1 in KBr pellets (table no. 5). The (O-H) of the oxime group observed at 3190.17 cm-1 in p-ClINAP absent in the spectra of the complexes suggesting replacement of the oxime proton by the metal ion during complexation13.It shows a broad band around 3190.17 cm-1 is known to be lowered due to the hydrogen bonding 14,15 The peak observed near 1608.48 cm-1 in the spectrum of Li(p-ClINAP)2 may be assigned to the perturbed C=O and/or C=N stretching vibration involving bonding through oxygen and nitrogen donor atoms. Na(p-ClINAP)2,K(p-ClINAP)2,Rb(p-ClINAP)2 and Cs(p-ClINAP)2 show perturbed C=O and/or C=N bands at 1606.10, 1607.96, 1606.60 and 1607.96 cm-1 respectively. The I.R. spectra of above ligand also shows two picks at 1640.40 cm-1 and 1602.44 cm-1 which may be attributed to the C=O and C=N respectively. The strong absorption band at 1261 cm-1in

the ligand is assigned to poor N-O stretching frequency. Rb complex shows it at 1052 cm-1 due to the bonding of the metal ions through O of N-O. These peaks could be due to two unequally N-bonded N-O groups or they could be assigned to the coupled vibrations of N- bonded N-O.Rubidium and Cesium complexes show two new bands at 1260 and 1150 cm-1 due to N-bonded N O. Appearance of new distinct sharp 5-6 peaks in the alkali metal complexes in the range 670-300 cm-1 due to the presence of M-N and M-O stretches strongly supports the coordination of the ligands to the metal ions .In the present study, I.R. spectra reveal the presence of strong hydrogen bonding .Further they indicate that Li attached to the ligand through the oxygen of N-O group and oxygen of the C=O .The ligand molecules in the Rb and Cs complexes are attached to the metal ion through the nitrogen of oxime groups. Their structures can be represented as shown in fig.1.From the partial ionic nature of Rubidium and Cesium complexes, they can be considered to have polymeric structures similar to that of sodium hydrogen bis and potassium hydrogen bisisonitrosoacetophenonate16-17. N.M.R.Spectra-Nuclear magnetic resonance spectra of these complexes in DMSO solution (table no.6) are similar to the spectra given by Lacey et.al.18 A peak around 8.30 δ due to =NOH group, aromatic ring is observed at 7.18 δ. The proton signal due to –CH group appears at 6.74 δ. This is also supported from the nmr spectra studied by Pathak and Halder19. R. D. Raut and coworker20 have also been shown a peak around 8.64 δ due to =NOH group, two groups of bands corresponding to –CH and aromatic ring at 2.72 and 7.62 δ respectively. NMR Spectra of Li(p-ClINAP)2,Na(p-ClINAP)2 , K(p-ClINAP)2, Rb(p-ClINAP)2 and Cs(p-ClINAP)2(fig.no.1-6) exhibit peaks due to C-H group & aromatic ring protons & do not show any proton signal due to =NOH group. This suggest that these complexes have been formed by the replacement of the proton of the =NOH group by the metal ion. Antimicrobial Activity- Antibacterial activity of these metal complexes was examined against E. coli, S. aureus, P. aeruginosa, B. subtilis, B. cereus and K. pneumonae. Antifungal activity of the same

compounds was evaluated against C. albicans, A. niger and F. oxysporium. Assays were performed in agar media with final concentration of 500 µg/mL.The results showed that the ligand (ClINAP) and synthesized complexes of ClINAP exhibited poor to good antibacterial and antifungal activities against all the tested strains. Complexes of Rb (ClINAP)2 and Cs (ClINAP)2were shown maximum zone of inhibition and hence were found to inhibit the growth of all tested strains of bacteria and fungi. It may be due to the more penetrating power of Rb and Cs complexes to the cell wall of bacteria, which prevents the biosynthesis of peptidoglycan or may find better fit at the receptor site as compared to other compounds. Though the ligand exhibited antibacterial and antifungal activity against all the tested strains, its activity is less when compared with its metal complexes and hence suggested its unsuitability against all the strains. None of the synthesized complex showed more activity as compared to the standard drug.(table no.5 & 6)

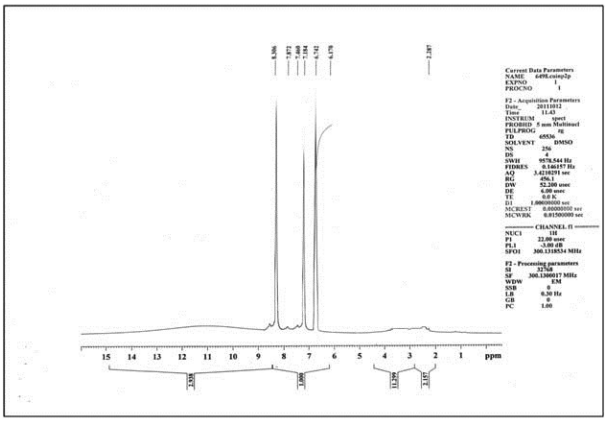

Fig.no.1- nmr spectrum of p-HClINAP

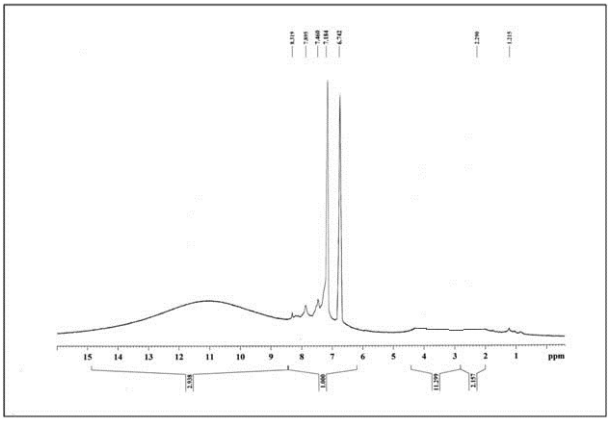

Fig.no.2- nmr spectrum of Li(p-ClINAP)$_2$

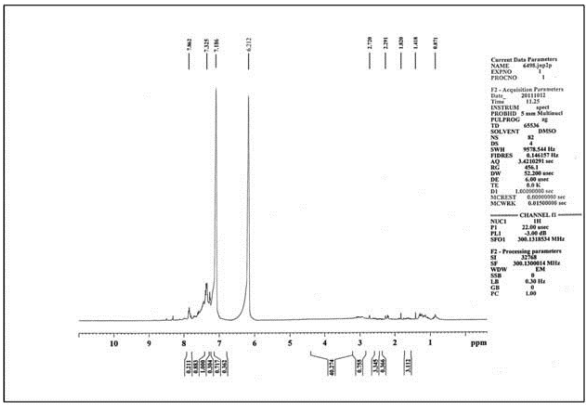

Fig.no.3- nmr spectrum of Na(p-ClINAP)$_2$

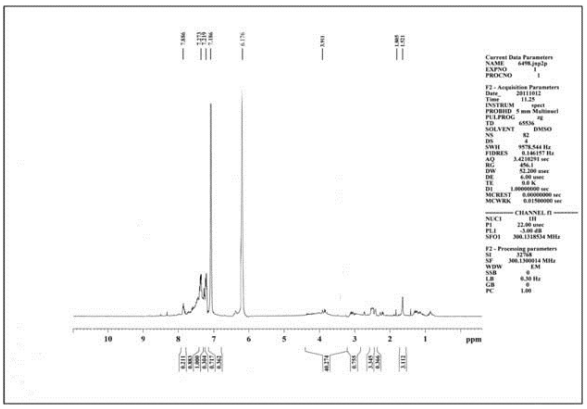

Fig.no.4- nmr spectrum of K(p-ClINAP)$_2$

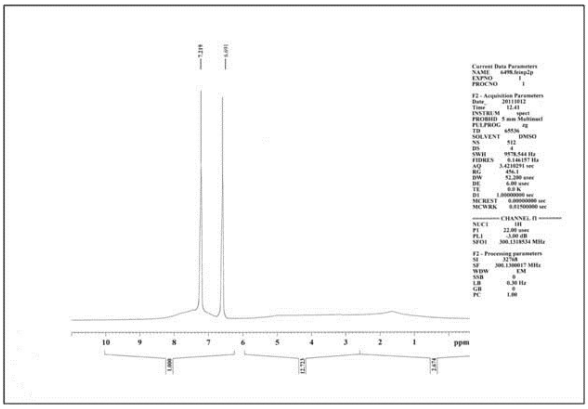

Fig.no.5- nmr spectrum of Rb(p-ClINAP)$_2$

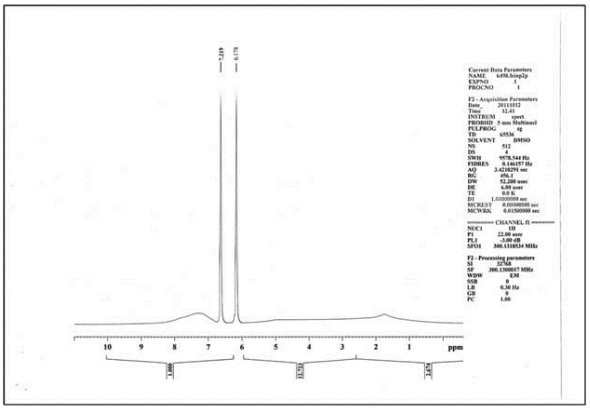

Fig.no.6- nmr spectrum of Cs(p-ClINAP)$_2$

Table No. 1- Analytical data and mol. wt. of complexes

Complex	Mol.wt	% C	% H	% N	% M	% Cl
p-ClINAP		52.01 52.32	3.05 3.29	7.25 7.63	----- -----	19.43 19.35
$Li(p\text{-}ClINAP)_2$	372.15 (371.94)	51.40 (51.62)	2.45 (2.69)	7.40 (7.53)	1.75 (1.87)	18.95 (19.05)
$Na(p\text{-}ClINAP)_2$	388.24 (387.98)	49.41 (49.50)	2.47 (2.58)	7.10 (7.22)	5.80 (5.93)	18.10 (18.30)
$K(p\text{-}ClINAP)_2$	405.12 (404.09)	47.45 (47.52)	2.40 (2.48)	6.80 (6.93)	9.50 (9.65)	17.42 (17.57)
$Rb(p\text{-}ClINAP)_2$	449.50 (450.47)	42.40 (42.62)	2.10 (2.22)	6.12 (6.22)	18.70 (18.97)	15.65 (15.76)
$Cs(p\text{-}ClINAP)_2$	496.75 (497.90)	38.80 (38.95)	1.90 (2.01)	5.40 (5.63)	26.55 (26.69)	14.20 (14.26)

(Theoretically calculated values are given in parenthesis.)

Table No. 2 -Molar Conductance of Alkali Metal complexes of p-ClINAP

Metal Complex	**Concentration Mol/dm^3**	**Molar Conductance (mho cm^{2}mol^{-1})**
$Li(p\text{-}ClINAP)_2$	1 x 10^{-4}m	9.4
$Na(p\text{-}ClINAP)_2$	1 x 10^{-4}m	10.5
$K(p\text{-}ClINAP)_2$	1 x 10^{-4}m	11.2
$Rb(p\text{-}ClINAP)_2$	1 x 10^{-4}m	11.4
$Cs(p\text{-}ClINAP)_2$	1 x 10^{-4}m	11.7

Table no.3: Infra Red Spectra of metal complexes and the ligand

Assign.	p-ClINAP	$Li(ClINAP)_2$	$Na(ClINAP)_2$	$K(ClINAP)_2$	$Rb(ClINAP)_2$	$Cs(ClINAP)_2$
OH	-------	3475.62	3475.62	3474.22	3474.22	3474.22
OH of NOH	3190.17	-----	-----	-----	-----	-----
C=O	1640.40	-----	-----	-----	-----	-----
C=O, C=N	-------	1608.48	1608.48	1607.98	1607.98	1607.98
CH	------	1381.87	1419.20	1420.50	1420.50	1420.50
N---O	------	1258.98	1258.98	1261.83	1261.83	1261.83
N-O	1047.75	1052.21	1052.21	1052.41	1052.41	1052.41
N-O	924.19	937.88	937.88	937.98	937.96	937.96
M-N	-------	624.68	624.68	624.78	624.78	624.78

Table No. 4- N.M.R.in Metal Complexes and in the ligand (values are in δ scale)

Ligand/Complex	=NOH	Aromatic ring	-CH group
p-ClINAP	8.30	7.18	6.74
$Li(p\text{-}ClINAP)_2$	-----	7.18	6.74
$Na(p\text{-}ClINAP)_2$	-----	7.18	6.21
$K(p\text{-}ClINAP)_2$	-----	7.18	6.17
$Rb(p\text{-}ClINAP)_2$	-----	7.12	6.69
$Cs(p\text{-}ClINAP)_2$	-----	7.12	6.59

Table No 5:Antibacterial Activity Data of p-ClINAP & Synthesized Complexes

(bacteria with zone of inhibition in mm)

Comp.	***S. aureus***	***E.coli***	***B. Subtilis***	***p. aeruginosa***	***K. Pneumonae***	***B. Cereus***
L	12	10	11	11	10	12
III a	16	14	14	15	16	17
III b	15	14	13	16	16	17
III c	16	13	14	14	17	16
III d	18	15	17	16	18	18
III e	17	15	17	17	17	19
Gentamycin	20	17	15	18	19	20

L = p-ClINAP , III a = $Li\ (ClINAP)_2$ III b= $Na\ (ClINAP)_2$

III c= $K\ (ClINAP)_2$ III d= $Rb\ (ClINAP)_2$ III e= $Cs\ (ClINAP)_2$

Table No. 6:- Antifungal Activity Data of p-ClINAP & Synthesized Complexes

(fungi along with zone of inhibition in mm)

Compound	*C.albicans*	*A. niger*	*F.oxysporium*
L	13	11	12
IIIa	19	18	19
IIIb	18	16	19
IIIc	19	17	18
IIId	21	19	20
IIIe	20	18	21
Miconazole	22	21	22

L = p-ClINAP , III a = $Li\ (ClINAP)_2$ III b= $Na\ (ClINAP)_2$

III c= $K\ (ClINAP)_2$III d= $Rb\ (ClINAP)_2$III e= Cs (ClINAP)

Conclusion

On the basis of elemental analysis, molar conductance measurement, IR and UV-VIS spectral studies complexes of 4-chloroisonitrosoacetophenone with the alkali metals Li, Na, K, Rb and Cs have square planar geometry

Acknowledgement

I am thankful to the principal,anand niketan,warora,all my friends,my spouse sharda,my son aniket and daughter ashlesha.I am very much thankful to my guide dr.r.d.raut and co-guide dr s.z.jadhav for their nice cooperation.I am also thankful to the director institute of science for allowing me to work in chemistry lab.

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