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Characterization and biological studies of neutral complexes of the ligand isonitroso-4-chloro-acetophenone with alkali metals

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ABSTRACT

A Ligand Isonitroso-4-chloroacetophenone (4-CIHINAP) has been synthesized by using n-Amyl Nitrate and 4-Chloroacetophenone. Alkali metal complexes of this Ligand have been synthesized and studied on the basis of elemental analysis, molar conductivities, NMR spectroscopy and biological properties.

Key words: Isonitroso-4-chloroacetophenone, Schiff's bases, molar conductivities, biological properties and NMR spectroscopy.

INTRODUCTION

Ligand Isonitrosophenyl-2-propanone[1] and Isonitroso-4-Bromoacetophenone[2] (p-BrHINAP) have been studied for few transition metals for possible complex formation. However, spectroscopic studies and biological evaluation of the complexes of alkali metals with the Ligand Isonitroso-4-chloroacetophenone have not been reported so far. The present paper describes the characterization of the complexes of Li, Na and K using the Ligand Isonitroso-4-chloroacetophenone on the basis of elemental analysis, molar conductivities, NMR spectroscopy and biological studies.

MATERIALS AND METHODS

All the solvents and chemicals used were of A.R. grade. They were purified by using the methods given by Vogel[3]. The Ligand Isonitroso-4-chloroacetophenone was synthesized by the procedure described by Muller and Pechmann[4]. The crude product was recrystallized from benzene. Its melting point was found to be equal to 157^0 C.

Synthesis of Li, Na and K complexes of Isonitroso-4-chloroacetophenone

Preliminary experiments have shown that all the complexes could be prepared by same general procedure by refluxing the mixture of aqueous solutions of salts of alkali metals such as Lithium Chloride, Sodium Chloride and Potassium Chloride with alcoholic solutions of the Ligand 4-HClINAP in 1:2 molar proportions. After cooling and standing for some time precipitates of complexes were formed. These precipitates were filtered, washed with alcohol and dried at 110^0 C.

During isolation of the complexes, it was observed that, the complex of potassium was precipitated immediately after mixing of alcoholic solutions of the Ligand. The complex of sodium required nearly half an hour after standing for precipitation and the complex of lithium required nearly two hours for precipitation.

RESULTS AND DISCUSSION

Chemical analysis data (Table no.1), molecular weight determination (Table no.2) and conductance measurements in Nitrobenzene (Table no. 3) have indicated that, the complexes of alkali metal ions with Isonitroso-4-chloro-acetophenone (4-HClINAP) may be represented by the molecular formula $M(4\text{-ClINAP})_2$, where M = alkali metal ions such as Lithium, Sodium, Potassium.

Molecular weights of these complexes were determined by using Rast method[5]. Melting points of these complexes were determined by using electrically heated melting point apparatus. Molecular weights of complexes determined by using above method were found to be very close to the molecular weights calculated theoretically on the basis of molecular formulae

a) Conductivity Measurements

Dilute solutions of these complexes were prepared in Nitrobenzene and measured their conductivities. Molar conductivities of these complexes in this solvent were obtained in the range of 1-80 mho cm^2mol^{-1} in 10^{-4} M concentration which is very close to the molar conductivities reported for non-electrolytes[3] (Table no.3).These values are very low as compared to the values for electrolytic solutions (i.e.150 mho $cm^2\ mol^{-1}$ in 10^{-4} M). From the values of molar conductivities of above complexes, it was observed that Li complex is almost nonionic but Na and K complexes have partial ionic characters.

b) Magnetic Properties

Magnetic moment and magnetic susceptibility values of alkali metal complexes of 4-ClHINAP have been determined using Gouy's method. Effects of temperature on the magnetic susceptibilities of these complexes have also been studied. It was observed that, the magnetic moment values of these complexes were equal to zero. When the magnetic susceptibility of these complexes was measured then it was observed that, these complexes have small negative values in the order of $10^{-6}g^{-1}$.When the effect of temperature on the magnetic susceptibility values of above complexes was observed in the range from 80 K to 300 K then, these values were almost constant. Magnetic susceptibility values of these complexes were found to be independent of temperature. They do not obey the Curie-Weiss law indicating neither inter nor intra molecular interaction[7]. Magnetic moment values of all these complexes with p-ClHINAP have supported tetrahedral geometry and all these complexes have found to be diamagnetic in nature.

c) NMR spectroscopic study

NMR spectra of the Ligand Isonitroso-4-chloro-acetophenone (4-ClHINAP) have been studied using DMSO as a solvent (Fig.1). In all, four NMR signals were observed for the above Ligand. NMR signals due to presence of protons of =NOH group, aromatic ring, -CH group and OH group were observed at 8.65, 7.60, 6.29 and 2.87 ppm respectively. (Table no.4)

NMR spectra of $Li(p\text{-ClINAP})_2$, $Na(p\text{-ClINAP})_2$ and $K(p\text{-ClINAP})_2$ (fig.no.1 to 4), complexes in DMSO solution have shown signals due to the protons of–CH group, aromatic ring &-OH group but not any signal due to the presence of proton of=NOH group. This suggests that, these complexes have been formed by the replacement of proton of =NOH group by the alkali metal ions[8].

It is interesting to note that, peaks due to the proton of –CH group in the above complexes appear at lower value as compared to the peak due to the proton of –CH group in the Ligand 4-ClHINAP. Further, NMR signals due to the protons of aromatic ring in these complexes occur at higher field side with respect to the NMR signals due to the protons of aromatic ring in 4-ClHINAP. It is also observed that, peaks due to the protons of -OH group in the complexes are observed at lower side with respect to peak due to the protons of –OH group in the Ligand. A chemical shift of resonance & position of peaks suggests that structure of these complexes should have been formed by five member rings.

d) Antimicrobial and antifungal testing

The Ligand Isonitroso-4-chloroacetophenone and its alkali metal complexes were tested against antibacterial activity *S. Aureus, C. Coli, B. Subtilis, P. Aeruginosa, K. Pneumonae and B. Cereus* and against antifungal activities *F. Oxysporium, A. Niger* and *C. Albicans.*

From the results, it was concluded that, the complexes from III a to III c exhibited poor to good antibacterial and antifungal activities against all the tested strains. The complexes IIId have shown maximum zone of inhibition (table 5 and 6) and hence they were found to inhibit the growth to all tested strains of bacteria and fungi. It may be due to more penetrating power of these complexes to the cell wall of bacteria, which prevent biosynthesis of peptidoglycan or may find better fit at the receptor site as compared to other complexes. In addition, complexes IIIa, IIIb have shown moderate to good activity against all the tested strains of bacteria and fungi.

Though the ligand p-Chloroisonitrosoacetophenone exhibited satisfactory antibacterial and antifungal activity against all the tested strains, its activity was less when compared with the alkali metal complexes and hence it was suggested that, the above Ligand cannot be suitable against all the strains. When synthesized complexes were compared for their antibacterial and antifungal activities against the standard drugs Gentamycin and Miconazole, then it was observed that, none of these complexes have shown more antibacterial and antifungal activities than these standard drugs.

Table -1 Analytical data of the metal complexes

Complex	Color	M.P	% C	% H	% N	% M	% Cl
Li(p-ClINAP)$_2$	Yellow	204	51.40 (51.62)	2.45 (2.69)	7.40 (7.53)	1.75 (1.87)	18.95 (19.05)
Na(p-ClINAP)$_2$	Dark Yellow	211	49.41 (49.50)	2.47 (2.58)	7.10 (7.22)	5.80 (5.93)	18.10 (18.30)
K(p-ClINAP)$_2$	Yellowish Brown	226	47.45 (47.52)	2.40 (2.48)	6.80 (6.93)	9.50 (9.65)	17.42 (17.57)

(Theoretically calculated values are given in parenthesis.)

Table - 2 Table showing molecular weight of complexes

Metal Complexes	Calculated mol. weight	Observed mol. Weight
Li(p-ClINAP)$_2$	371.94	372.15
Na(p-ClINAP)$_2$	387.98	388.24
K(p-ClINAP)$_2$	404.09	405.12

Table- 3 Molar Conductivities of Alkali Metal complexes in Nitrobenzene

Metal Complexes	Conc. of solution (mol/dm^3)	Molar Conductivities (mho cm^{2}mol^{-1})
Li(p-ClINAP)$_2$	1 x 10^{-4}M	9.4
Na(p-ClINAP)$_2$	1 x 10^{-4}M	19.5
K(p-ClINAP)$_2$	1 x 10^{-4}M	39.2

Table -4 Assignments of NMR Signals in 4-ClHINAP& its Alkali Metal Complexes (in ppm)

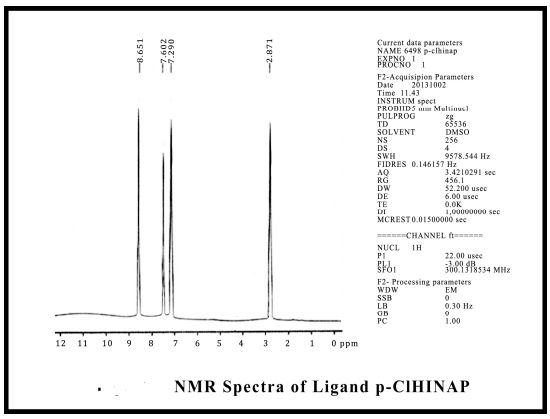
Ligand/Complex	=NOH	Aromatic ring	-CH group	-OH group
p-ClHINAP	8.65	7.60	6.29	2.87
Li(p-ClINAP)$_2$	-----	7.62	6.28	2.85
Na(p-ClINAP)$_2$	-----	7.64	6.27	2.86
K(p-ClINAP)$_2$	-----	7.63	6.28	2.84

Table -5 Antibacterial activity data of 4-ClHINAP & its synthesized complexes (Bacteria along with zone of inhibition in mm)

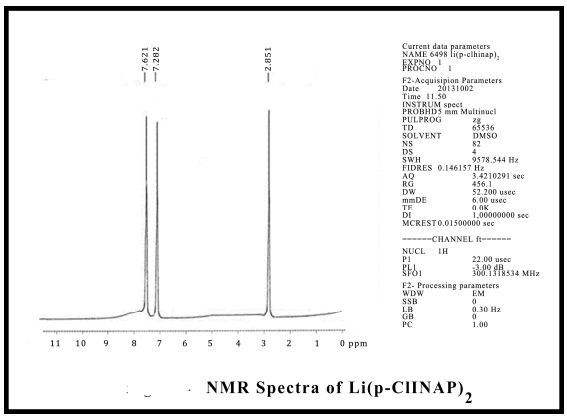
Ligand/ Complex	*S. Aureus*	*E. Coli*	*B. Subtilis*	*P. Aeruginosa*	*K. Pneumonae*	*B. Cereus*
p.ClHINAP	14	12	13	13	12	14
Li(ClINAP)$_2$	18	16	16	17	18	19
Na(ClINAP)$_2$	17	16	15	18	18	19
K (ClINAP)$_2$	18	15	16	16	19	18
Gentamycin	22	19	20	20	21	22

Table-6 Antifungal activity data of 4-ClHINAP & its synthesized complexes (Fungi along with zone of inhibition in mm)

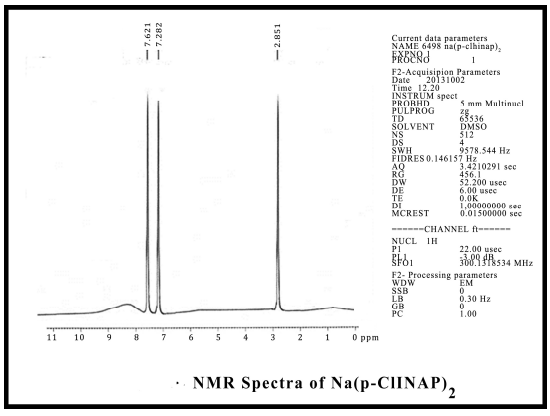
Ligand/ Complex	*F. Oxysporium*	*A. Niger*	*C. Albicans*
p-ClHINAP	14	13	13
Li $(ClINAP)_2$	21	20	21
Na $(ClINAP)_2$	20	18	21
K $(ClINAP)_2$	20	19	22
Miconazole	24	23	24



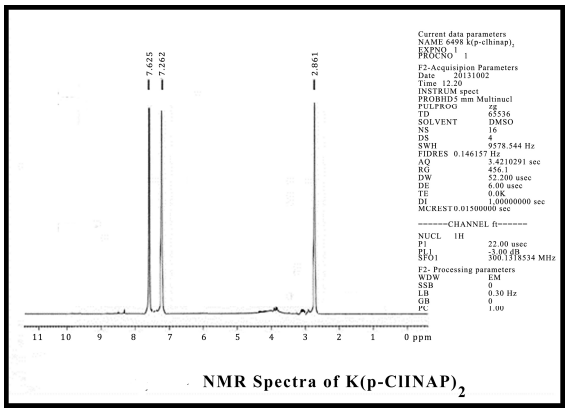
NMR Spectra of Ligand p-ClHINAP



NMR Spectra of Li(p-ClINAP)$_2$



NMR Spectra of Na(p-ClINAP)$_2$



NMR Spectra of K(p-ClINAP)$_2$

CONCLUSION

On the basis of elemental analysis, molar conductance measurement, magnetic properties, biological and NMR spectroscopic studies and from various discussions, these alkali metal complexes of this Ligand may be having tetrahedral geometry. From conductometric measurements, the above complexes have been found to be non electrolytic in nature. From magnetic properties, all these complexes were found to be diamagnetic in nature. From antibacterial and antifungal activities it was observed that all the complexes were found to possess moderate to good activity against all the tested strains of bacteria and fungi.

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