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Research Article

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Physicochemical and spectroscopic study of lithium, sodium and potassium with p-chloroisonitroso-acetophenone(P-ClINAP)

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ABSTRACT

Neutral complexes of alkali metals such as Lithium, Sodium and Potassium with isonitroso-p-chloroacetophenone have been synthesized and characterized on the basis of elemental analysis, molar conductivities and uv-visible and infrared spectroscopy.

Key words: Alkali metals, p-chloroisonitrosoacetophenone, Schiff's bases, I.R., U.V. visible spectroscopy, molar conductivity.

INTRODUCTION

The ligand p-methyl isonitrosoacetophenone (HIMP) have been used for few analytical applications [1,2]. The ligand p-bromoisonitrosoacetophenone have also been studied for few transition metals[3].The structural studies of ligand p-chloroisonitrosoacetophenone (P-ClINAP) have already been studied with transition metals for possible complex formation[4]. However, structural studies of the complexes of alkali metals with p-chloroisonitrosoacetophenone have not been reported so far. The present paper describes the isolation and characterization of complexes of alkali metals such as Li, Na and K with p-chloroisonitrosoacetophenone on the basis of elemental analysis, spectroscopic study, magnetic properties and molar conductivities.

EXPERIMENTAL SECTION

All the chemicals used were of A.R. grade. The ligand p-chloroisonitrosoacetophenone (P-ClINAP) is commercially available in the market. The basic principle underlying this preparation is that of Claisen[5].It was synthesized by dissolving 11.5 g of sodium in 230 ml of absolute alcohol and to this solution small portions of 58 ml amyl nitrate and 77 ml of p-chloroacetophenone was added with constant stirring and cooling in the freezing mixture containing ice and sodium chloride at about zero degree Celsius. The mixture was kept for three days in a well stoppard bottle in a refrigerator. At the end of this time, the yellowish green color mixture of sodium salt was obtained. It was filtered and dried in air. The dried sodium salt was dissolved in minimum quantity of ice cooled water and treated with equal volume of water-ethanol mixture. Precipitated p-chloroisonitrosoacetophenone was then filtered through suction and dried in vacuum .The crude product was recrystallized from benzene .Its melting point was found to be 158^0 C.

Procedure for preparation of complexes Lithium, Sodium and Potassium:-
Solutions of salts of Alkali Metals and the ligand p-chloroisonitrosoacetophenone were prepared in the molar proportion of 1: 2.

Preparation of Li(ClINAP)$_2$ Complex:
Lithium nitrate solution was prepared by dissolving 0.689 g. in a minimum quantity of water. Similarly 3.670 g. of ClINAP was dissolved in a minimum quantity of alcohol. These solutions were mixed together. The pH of the solution was maintained at 6.0 – 6.5 by HCl/NH_4OH. The suspension mixture was refluxed on water bath for 9 hours by applying a water condenser & then kept in vacuum desiccator for overnight. A bluish green colored lithium metal salt of ligand p-Chloroisonitrosoacetophenone was precipitated out .It was filtered, washed with alcohol, recrystallized from ether, dried and subjected to melting point measurement and analyzed for Lithium, Carbon, Hydrogen and Nitrogen.

Preparation of Na(ClINAP)$_2$ Complex:
A solution of sodium chloride was prepared by dissolving 0.585 g. in a minimum quantity of water. Similarly 3.67 g. of ClINAP was dissolved in a minimum quantity of alcohol. These solutions were mixed together. The pH of the solution was maintained at 5.5–6.5 by HCl/NH_4OH. The suspension mixture was refluxed on water bath for 8 hours by applying a water condenser & then kept in vacuum desiccator for overnight. A green colored sodium metal salt of ligand p-chloroisonitrosoacetophenone was precipitated out. It was filtered, washed with alcohol, recrystallized from ether, dried and subjected to melting point measurement and analyzed for Sodium, Carbon, Hydrogen and Nitrogen.

Preparation of K(ClINAP)$_2$ Complex:
A saturated solution of Potassium Chloride was prepared by dissolving 0.745 g. in a minimum quantity of water. Similarly 3.67 g. of ClINAP was dissolved in a minimum quantity of alcohol. These solutions were mixed together. The pH of the solution was maintained at 6.0 – 6.5 by HCl/NH_4OH. The above mixture was refluxed by applying a water condenser on the water bath for 8 hours. The resultant mixture was kept in vacuum dessicator through out night for cooling. A light green colored potassium salt of p-Chloroisonitrosoacetophenone was precipitated out .It was filtered, washed with alcohol, recrystallized from acetone, dried and determined its melting point and analyzed for Potassium, Carbon, Hydrogen and Nitrogen.

RESULTS AND DISCUSSION

Analytical data (table 2) reveals that the complexes which are isolated have the compositions Li(ClINAP)$_{2,}$ Na(ClINAP)$_2$ and K(ClINAP)$_2$. All these compounds are genuine complexes and not stoichiometric mixtures. It is also cleared from the fact their decomposition temperatures were much higher (202^0 C -248^0 C) than the melting point of the ligand (158^0 C)

Conductivity Measurements :- Molar conductivities of the complexes of Li, Na and K in acetone are found to be 6,18 and 41 mhos cm^2 respectively at 10^{-3} M. These values are very low as compared to the value,150 for 1:1 electrolyte in acetone[6].The values 1.6,41 and 73 mhos cm^2 respectively at 10^{-4} M in acetone suggest that Li complexes as almost non-ionic, but Na and K complexes have partial ionic character .

Electronic Spectra: Electronic spectra of the metal complexes and the ligand (table 3) show internal $\pi \rightarrow \pi^*$ transition of the ligand at 250 nm and 310 nm. The band observed in the range 365-400 nm are due to the charge transfer transition.

I.R. Spectra: In the infra-red spectrum of the ligand in KBr pellet ,a broad band is observed in the range 3250-2840 cm^{-1} due to hydrogen bonded OH of =NOH. Weak broad bands which appear in the Li, Na and K complexes at around 3150,2400 and 2300 cm^{-1} respectively are attributed to the hydrogen bonded OH of the =NOH of one of the ligand molecules. This order of these bands represent that the hydrogen bonding in complexes increase from lithium to potassium. It may be concluded that hydrogen bonding is one of the structures forming features of the alkali metals complexes of the type ML.HL[7].The increase in decomposition temp. of complexes from Lithium to Potassium (table 1)also confirms the increasing hydrogen bond strength.

The strong absorption at 1705 cm^{-1} is assigned to C=O of the pyrazolone in the spectrum of ligand .Two peaks at 1690 and 1630 cm^{-1}are found in the Li complex. Na and K complexes show two peaks at 1705 and 1600 cm^{-1} .This indicates that perturbation of one of the C=O is less as compared to the other in the Li complex and in the Na and K complexes one is almost unperturbed and the other is perturbed.

The strong absorption band at 1050 cm^{-1}in the ligand is assigned to poor N-O stretching frequency .Li complex shows it at 1030 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[8-9] .Sodium and potassium complexes show two new bands at 1260 and 1150 cm^{-1} due to N- O bonded atoms.

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 (table 3) 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 indicates that Li attached to the ligand through the oxygen of N-O group and oxygen of the C=O .The ligand molecules in the Na and K 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 Sodium and Potassium complexes, they can be considered to have polymeric structures similar to that of sodium hydrogen bis and potassium hydrogen bisisonitrosoacetophenonate[10].

Table No.1: Analytical data p-Chloroisonitrosoacetophenone (by difference)

Elements	% C	% H	% N
Found	52.01	3.05	7.25
Required for	52.32	3.29	7.63

Table -2 Analytical data of the metal complexes

Compound	% C	%H	%N	% M	m.p.(^{0}C) @
(ClINAP)$_2$ Li	51.80	2.71	7.58	1.91	201
	(51.62)	(2.69)	(7.53)	(1.87)	
(ClINAP)$_2$ Na	49.51	2.61	7.25	5.98	212
	(49.49)	(2.58)	(7.22)	(5.93)	
(ClINAP)$_2$ K	47.55	2.54	6.98	9.75	249
	(47.52)	(2.48)	(6.93)	(9.65)	

**observed values are given in parenthesis @ meltings point of complexes*

Table 3- Electronic spectral data of the metal complexes in methanol

Compound	max(nm)	max	Tentative assignment
p-ClINAP	250	32,000	π→π*
	310	29,500	π →π*
	390	5,950	charge transfer
(ClINAP)$_2$ Li	250	58,000	π→π*
	300	17,500	π →π*
	400	1300	charge transfer
(ClINAP)$_2$ Na	250	45,500	π →π*
	310	22,600	π →π*
	365	3,500	charge transfer
(ClINAP)$_2$ K	250	50,500	π→π*
	310	19,000	π →π*
	365	3,400	charge transfer

Structure and bonding

On the basis of elemental analysis, molar conductance measurement, IR and UV-VIS spectral studies, following two (A and B) probable structures of the complexes are possible but on the basis of presence of hydrogen bonding between hydrogen and oxygen atoms of two N-O-H groups, the probable structure of the alkali metal complex with p-chloroisonitrosoacetophenone may be as given in fig. B .

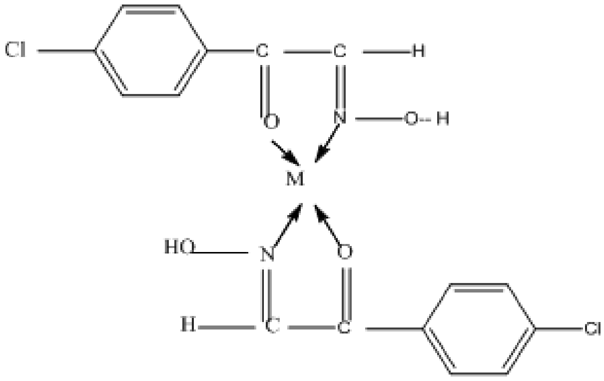
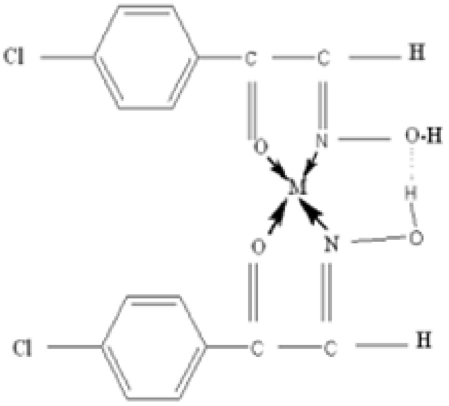


Fig. A



M= alkali metals Li,Na and K

Fig. B

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