



NOVEL NUTRAL COMPLEXES OF ALKALI METALS THE SYNTHETIC AND STRUCTURAL STUDY

Nandeshwar S. T.¹, Jadhao S. Z.², Raut R. D.³

^{1, 2} Deptt .of Chemistry, Institute of Science, Nagpur

³Deptt. of Chemistry J. B. College of Science, Wardha

Email : s.nandeshwar14@yahoo.in, ravishankar.raut@gmail.com

ABSTRACT

The complexes of alkali metals [Li, Na, K, Rb & Cs] with the ligand p-bromoisoinitrosoacetophenone [P-BrHINAP] have been synthesized and characterized by Elemental analysis, Conductivity measurement, Magnetic susceptibility, Nuclear magnetic, Electronic (Ultra Violet , Visible) and Infrared spectral studies.

Keywords: Alkali Metals, p-bromoisoinitrosoacetophenone, Conductivity, Magnetic, Electronic and Infrared spectra.

1. INTRODUCTION

P-bromoisoinitrosoacetophenone has already been investigated for possible complex formation with transition metals¹. Here, in this announcement we are synthesize ligand and exposing the neutral complexes of this ligand with alkali metals which have been characterized by techniques like elemental analysis, molecular weight determination, conductivity measurements, magnetic susceptibility, nuclear magnetic resonance, electronic and infra red spectra.

2. EXPERIMENTAL

The Experimental work has been carried out by using all chemicals and solvents were of analytical reagent grade. The ligand [p-BrHINAP] was synthesized from the basic principle claisen² and the formula described by Muller and pechmann³ using isoamylnitrate⁴ as a reagent. The reagent isoamylnitrate was prepared from isoamylalcohol and sodium nitrate. The recrystalised light cream coloured complex was



obtained entitled as p-bromoisonitrosoacetophenone which was used for the synthesis of alkali metal complexes performing as a ligand.

Synthesis of alkali metal complexes with ligand:-

A mixture of saturated aqueous solution of alkali metal nitrates of Li, K & Cs and acetates of Na & Rb with the alcoholic solution of ligand [p-BrHINAP] in the molar fraction of 1:1, 1:2 & 1:3 respectively, were taken in a separate five round bottom flask accordingly and refluxed under water condenser on boiling water bath for 5-7 hours with intermittent shaking. The volume and the pH 5.5-6.5 of mixture solution were maintained by adding equal quantity of water with alcohol and HCl or NH₄OH respectively. The solid product obtained was immediately removed from the flask and kept in vacuum desiccators. On cooling respective coloured complexes were obtained. It was filtered, dried in air, recrystallised from ether, acetone or chloroform, dehydrated in air, subject to the melting point measurement and analyzed for alkali metal [Li, Na, K, Rb & Cs], carbon, hydrogen & nitrogen of the corresponding metal complex.

3. RESULTS AND DISCUSSION

Almost all the alkali metal salts and their respective complexes were found to be coloured and stable in air but stability decreased on exposure to moisture leading ultimately to decomposition, hence all the salts and complexes made were kept in a desiccators over solid anhydrous calcium chloride, most of the complexes were soluble in polar organic solvents such as ethanol but insoluble in water and non-polar solvents like benzene, ether etc.

Melting point, molar conductance & percentage of elements.

The decomposition of the complex was carried out by slanted method described by Vogel⁵. Nitrogen present in metal complexes [M



(BrINAP)] was estimated by Kjeldahl's method and the molecular weight by Rast method.

Molar conductance:

The molar conductance was resolute in acetone, the values were found to be to be in between 7.9 to 76 mhos⁻¹cm²mol⁻¹ at the molar concentration of 10⁻⁴ to 10⁻⁵ M. These values were very low as compared to 150 for 1:1 electrolyte in acetone⁶ recommended that Lithium, Rubidium & Cesium complexes were almost non-ionic while Sodium & potassium complexes were have partial ionic character. In the table number 1.1 listed the above mention properties.

Electronic spectra:

The absorption spectrum of [Li(BrINAP)₂] discloser $\pi - \pi^*$ transitions at 224 nm and 227 nm, it also exhibits a broad maximum at 359 nm and a shoulder at 298 nm which appear to be due to charge transfer transitions⁷. The absorption spectrum of [Na(BrINAP)₂] shows a band at 223 nm & 237 nm which is attributed to $\pi - \pi^*$ transition and a shoulder at 348 nm which may be attributed to the charge transfer transitions. The absorption spectrum of [K (BrINAP)₂] exhibits bands at 216 nm, 345 nm and 348 nm. The band at 216 nm shows $\pi - \pi^*$ transition and the band at 345 nm may be assigned to a charge transfer transition on the basis of its position and intensity. The absorption spectrum of [Rb(BrINAP)₂] could be examined in chloroform and observed that the band at 203 nm exhibits $\pi - \pi^*$ transition . It appears to be charge transfer band at 214 nm. The absorption spectrum of [Cs(BrINAP)₂] complex shows peaks at 232 nm which may attributed due to $\pi - \pi^*$ transitions.

Infra red spectra:

The IR spectra of all the alkali metal complexes of [p-BrINAP] differ from lignd by the absence of a medium broad hydrogen

bonded-OH stretching absorption bands in the region 3300-2600 cm^{-1} . A new broad band of weak to medium intensity in the region $\nu_{2300} \text{ cm}^{-1}$ in all the complexes may be attributed to O--H...O absorption. This suggests the hydrogen bonding to be essential feature of these complexes.

Table 1.1

Type of Complex	MP /DT /TT in $^{\circ}\text{C}$	Molar conductance [$\text{mhos}^{-1} \text{ cm}^2 \text{ mol}^{-1}$]	% Elements with calculated values.			
			%C	%H	%N	%M
[Li(BrINAP) ₂]	297 D	7.9	64.27 (64.16)	5.27 5.21	8.14 (8.19)	14.43 (14.41)
[Na(BrINAP) ₂]	284 D	47	62.50 (62.07)	4.92 (4.89)	7.92 (8.05)	16.68 (16.61)
[K(BrINAP) ₂]	186 D	76	59.80 (59.34)	4.70 (4.67)	7.58 (7.69)	10.72 (10.71)
[Rb(BrINAP) ₂]	115 D	9.9	52.72 (52.68)	4.22 (4.15)	6.90 6.83	20.79 (20.73)
[Cs(BrINAP) ₂]	110 D	11.5	46.85 (47.16)	4.42 (3.71)	6.05 (6.11)	29.28 (29.04)

¥ Theoretically calculated values are given in parentheses.

The IR spectra of the ligand shows characteristic absorption at 1650, 1600 and 980 cm^{-1} which may be assigned to $\nu_{\text{C=O}}$, $\nu_{\text{C=N}}$ and $\nu_{\text{N-O}}$ modes respectively. In complexes these bands splits and giving two or more than two peaks. These splitting of bands or the presence of additional bands in C=O, C=N and N-O region point out to the probability of a structure having trans configuration of the two ligands with respect to each other. None of the neutral complexes show anomalous broad absorption band between 1300-700 cm^{-1} as such the acid salt structure⁷ with very short O...H--O.

4. STRUCTURE AND BONDING:

The IR spectra of these complexes suggested that, in case of ligand being used as first, alkali metals replace the hydrogen atom attached to the oxygen atoms of the Isonitroso groups, thereby attaching themselves to nitrogen atom of isonitroso group and are coordinated through oxygen atom of the adjacent keto group forming five member chelation ring necessary for stabilization of the salt. In the case of ligand being used as second, coordination was through the oxygen atom of the keto group forming five member chelating ring. The IR spectra also indicated the presence of hydrogen bonding in the complexes, thereby giving additional stability to the complexes.

On the basis of elemental analysis, molecular weight determination, Molar conductivity measurement, electronic and infra red spectral studies, following two A & 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 alkali metal with p-bromoisonitrosoacetophenone complex may be given in fig. B.

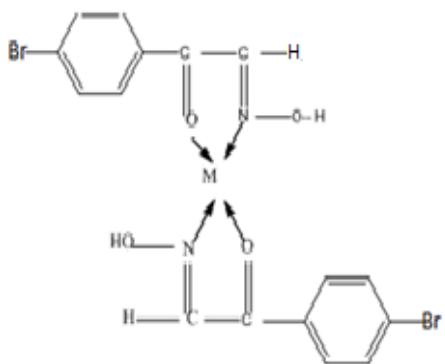


Fig. A

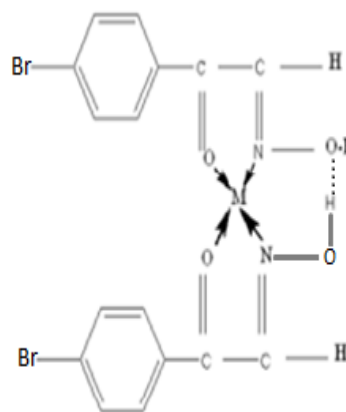


Fig. B

M= Alkali metal Li, Na, K, Rb & Cs.



Conclusion:

The synthesis of alkali metal complexes with ligand p-bromoisonitrosoacetophenone requires extensive interval at boiling temperature of water. Out of the synthesized complexes, some were ionic and remaining was non-ionic.

Acknowledgment:

We are very thankful to the Director of the Institution and Head Department of Chemistry, Institute of Science, Nagpur for providing necessary laboratory facilities and also thankful to the Deptt. of chemistry, university of Mumbai and CDRI Lucknow for carrying out spectral analysis.

References:

- Natrajan and Hussain A nazeer, (1981). *Indian J Chem*, 20A, 307.
- Muller and Penchmann V, (1888). *Ber*, 22, 2560.
- Victor Meyer, Zunlin J, (1978). *Ber*, 11, 695.
- Blatt, *Organic Syntheses, Coll. Vol II*, P. 108
- Vogel A. I. "A text Book of quantitative Inorganic Analysis", Longman Green & company limited, III Ed. London, ELBS (1964).
- Cotton F A & Mayere M D, (1960). *Jour. Amer. Chem. Soc.* 82, 5023.
- Lord R. C. and Merrifield R. E., (1953). *J. Chem. Phys.*, 21, 166.