Microwave Synthetic and Structural Studies of Cesium Complexes with P-Bromoisonitrosoacetophenone

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Abstract

The Complexes of alkali metals like Cesium with the ligandp-bromoisonitrosoacetophenone[P-BrHINAP] have been synthesized and characterized by Elemental analysis, Conductivity measurement, Molecular weight determination and Melting point determination, Nuclear magnetic resonance, Electronic/Absorption and Infrared spectral studies as well as Thermo gravimetric analysis.

Keywords: Synthesize, characterize, resonance, analysis, determination and measurement.

Introduction:

For the formation of complexes of transition metals[1], the ligand P-bromoisonitrosoacetophenone has previously been investigated. Here in the present work of study we are reporting the synthesis of ligand and its neutral complexes with alkali metals like Rubidium and Cesium. The purity of ligands has been check and confirmed by elemental analysis and melting point determination. Solid complexes of alkali metals have been synthesized and characterized by techniques such as elemental analysis, molecular weight determination, conductivity measurements, nuclear magnetic resonance and thermo gravimetric analysis.

Materials and Method:

The method for synthesis of ligand P-bromoisonitrosoacetophenone was described by Muller and pechmann[2]. The basic principle used for the synthesis of this ligand is that of claisen[3]. The reagent isoamylnitrate[4] was needed for the synthesis, which was prepared from isoamylalcohol and sodium nitrate. The precipitates so formed were filtered, washed with ethanol or ether as the case needed and subjected to molecular weight and melting point determination, Conductivity measurement , Elemental analysis, ESR, IR, NMR spectrum and Thermo gravimetric analysis.

Experimental

The Experimental work has been carried out by using all the chemicals and solvents were of analytical reagent grade. Double distilled water was obtained by distilled water containing potassium permanganate and alkali in glass apparatus.

Synthesis of [Cs (P-BrINAP)$_2$]complex:

Cesium acetate (.1mole, .192gm) and [P-BrINAP] (.3mole, .684gm) in the molar proportion of 1:3was dissolved in the minimum quantity of alcohol separately. Then the mixture of both solutions with equal volume of water were taken in a round bottom flask and refluxed under water condenser on sand bath at 100°C for an

hour with occasional shaking. The pH 6.0-7.0 of mixture solution was maintained by adding HCl or NH_4OH. The solid product obtained was immediately removed from the flask as soon as the reaction period was over and kept in vacuum desiccators. On cooling a bright yellow coloured complex was obtained. It was filtered, dried in air, recrystallised from chloroform and analyzed for the elements carbon, hydrogen and nitrogen.

Results and Discussion:

All 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. For decomposition of the complex, every time about 200 mg of the sample was taken and heated with a mixture of perchloric acid and nitric acid till the clear solution was obtained. Then this clear solution was diluted with water and the analysis of metal ion in complexes was carried out by slandered method described by Vogel[5]. Nitrogen present in the complex [Cs $(BrINAP)_2$] was estimated by Kjeldahl's method.

General Characteristics:

The complex [Cs (P-BrINAP) $_2$]is bright yellow in colour which is insoluble in water but it is partially soluble in common organic solvents and completely soluble in pyridine. The elemental analytical data of the complex shows, rubidium and ligand proportion is in the ratio 1:3. The molar conductivity value of the complex shows the solution of complex in nitrobenzene is non-electrolyte.

Molecular Weights of Complex:

The molecular weights of above complexes were determined by Rast method. The molecular weight of complexes could not be determined by cryoscopy method due to limited solubility of the complexes in nitrobenzene and other organic solvents. The molecular weights determined by Rast method are found to be comparable with the molecular weights calculated theoretically on the basis of molecular formula of the complex.

Alkali Metal Complex	Calculated Values	Observed Values
[Cs(P-BrINAP)2]	588.88	588.7

Molar Conductance of the complexes:

Molar conductance of the complexes of [Rb $(P\text{-}BrINAP)_2$] in nitrobenzene is found to be analogous witrh that of reported for non-electrolyte in nitrobenzene which are expose in the following table.

Alkali Metal Complex	Concentration in moles	Molar Conductance (Ohm^{-1} cm^2 $mole^{-1}$)
[Cs(P-BrINAP)2]	1 x 10-4m	11.3

Percentage of elements, colour and melting point of complex:

From the table given below it was observed that all the alkali metal salts and their complexes undergo transformation at a temperature which were considerably higher than the melting point of the ligand (98-99^{0}C) used , most of the complexes were soluble in polar solvents such as ethanol but insoluble in non-polar solvents like benzene, ether etc. The molecular weights of the complexes of [Rb (P-BrINAP)] in nitrobenzene were determined by Rast method which were found to be close to the molecular weights calculated theoretical on the basis of molecular formulae and molar conductance were found to be close to that of reported for non-electrolyte in nitrobenzene[6].

Type of Complex	Complex Colour	M P/ DT / TT in ^{0}C	% Elements with calculated values.			
			% C	% H	% N	% M
$[Cs(BrINAP)_2]$	Bright yellow	110 D	46.85 (47.16)	4.42 (3.71)	6.05 (6.11)	29.28 (29.04)

¥ Theoretically calculated values are given in parenthes.

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NMR spectrum of the complex:

NMR Spectra of $[Cs(P\text{-}BrINAP)_2]$ in DMSO solution exhibit peaks due to –CH group & aromatic ring protons , it does not show any proton signal due to =NOH group. This suggest that the complexes have been formed by the replacement of proton of =NOH group by metal ion. Further signals of aromatic ring protons in the cesium complexes occur at extremely lower side with respect to that of aromatic ring signal in [P-BrINAP]. The shift of –CH group & aromatic ring protons signals 6.317 and 7.231 respectively may be interpreted that, the donor atom is closest to the metal ion which involved in the formation of metal ligand bond. The assignments of NMR Signals of cesium alkali metal complex are shown in the following table.

Complex	=NOH	Aromatic Ring	-CH Group
$[Cs(P\text{-}BrINAP)_2]$	--	7.231	6.317

*** All Values in δ scale

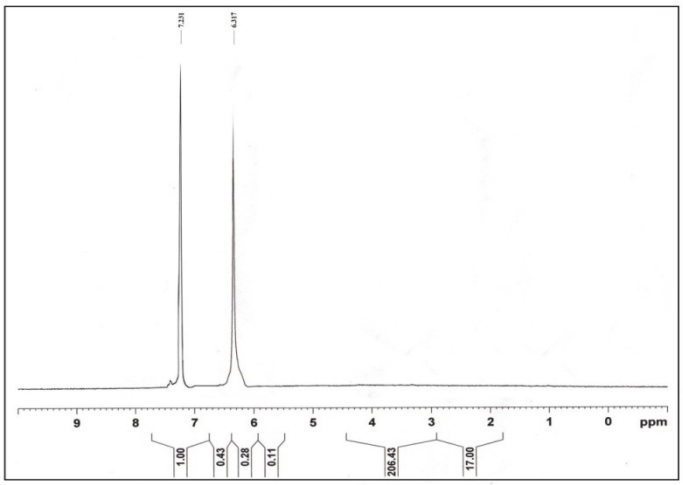
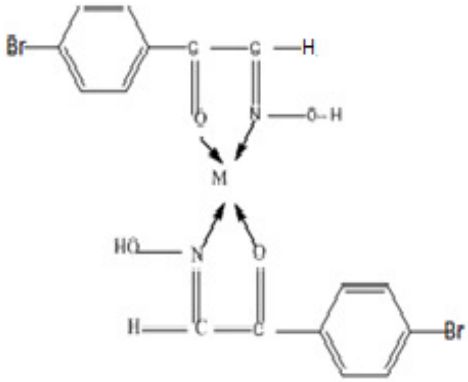


Figure.1- NMR SPECTRA OF [Cs (P-BrINAP)$_2$]

5. STRUCTURE AND BONDING:

On the basis of elemental analysis, molecular weight determination, Molar conductivity measurement, nuclear magnetic resonance spectra following probable structure of the complex is possible.



M= Alkali Metal Cesium

Conclusion:

The cesium complex with ligand p-bromoisonitrosoacetophenone has been synthesized by the above discussed condensation method is very simple. The purity of newly synthesized complex has been experienced and established by special physico-chemical and experimental techniques.

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