

Study, Synthesis and Characterisation of Mixed Ligand Complexes of Alkali Metal Salt of Some Organic Acids with 3-Nitro-1,5-O-Tolyl Formazanes

Ranveerkumar*, Kalyan Singh** and Bijay S. Singh*

*Dept of Applied Chemistry, CIT, Ranchi, Jharkhand, India

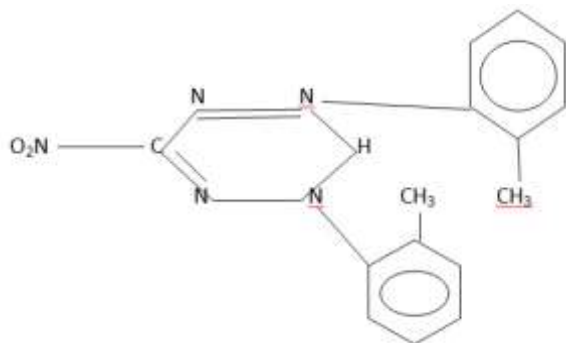
**Department of Chemistry, B.S. College, Lohardaga, Ranchi University, Jharkhand, India

Abstract:-The design, synthesis and characterization of suitable mixed ligand around a metal center is important task for effective reaction. A number of mixed ligand complexes of alkali metal salt of o-nitro phenol, 1-nitroso-2-naphthol, 8-hydroxy quinolone and salicylic acid has been synthesized and characterized. IR studies indicate the presence of hydrogen bonding. Ease of complexation as well as the yield has been found to increase with the increase in radius of alkali metal cations. Low value of molar conductivities suggests that the mixed ligand complexes are covalent in nature. The complexes have stimulated intense interest because of their unique molecular architecture and biological properties.

Key Words: Mixed ligand complexes, NOTF, IR-spectra

I. INTRODUCTION

Metal complexes of poly azo ligands have been important Metal derivatives of aryl formazans are coloured and are of great interest as pigments and analytical reagents. Formazanes are known to possess anticancer, antifungal and antiviral properties^{1,2} in an attempt to explore the study of formazanes further, we have synthesized and characterised a number of alkali metal complexes with the ligand 3-nitro-1,5-di-o-tolyl formazan. A literature survey³⁻⁷ reveals that the ligand 3-nitro-1,5-di-o-tolyl formazan (NOTF) which has two possible coordination sites, has remained its chelating ability. The present investigation has been undertaken to examine the behavior of these formazans towards alkali metal salts.



We have prepared a number of mixed ligand complexes having general formula $ML.HL'$, where $M=Li, Na$ or K ; $L =$ deprotonated O-nitrophenol, 1-nitroso-2-naphthol, 8-hydroxy quinolone and salicylic acid, $HL' = NOTF$.

II. EXPERIMENTAL

Preparation of NOTF

The ligand 3-nitro -1,5-o-tolyl formazans was prepared by the methods as described below:

O-toluidine (21.4g) was dissolved in a mixture of 75 ml of conc. HCL and 40ml of water. The resulting solution was cooled to $0^{\circ}C$. The solution was diazotized by adding an ice cold solution of $NaNO_2$ (15g). Nitro methane 6g was dissolved in aqueous solution of NaOH (8g) in minimum quantity of water while the temperature was maintained below $10^{\circ}C$. The alkaline solution of nitro methane was then added to the diazotized solution of o-toluidine in small amounts and with constant stirring.

The red coloured material formed was filtered, washed with water, crystallized from ethanol and recrystallized with $CHCl_3$ -hexane mixture. The authenticity of the sample was established from analytical data, melting point determination and its IR spectra. The melting point of the ligand that we obtained was $141^{\circ}C$, which is almost identical with that ($143^{\circ}C$) reported previously¹⁰.

III. PREPARATION OF COMPLEXES

The complexes were synthesized¹²⁻¹³ by refluxing equimolar proportions of the alkali metal (ML) of organic acid and the ligand (HL), 3-nitro -1, 5-di-tolyl formazans in propanone on a hot for about half an hour. The mixture was concentrated and then cooled. Red coloured adduct separated out almost instantaneously which was filtered, washed with propane and then dried in an electric oven at $80^{\circ}C$.

IV. RESULT AND DISCUSSION

The complexes of these ligands with alkali salts are characteristically coloured. Ease of their complexation with these salts was found to increase with increase in radius of alkali metal ions. Yield too showed similar trend. The colours,

the decomposition/ transition temperature, conductivity values as well as analytical data of these complexes are listed in table -1

Table-1

COMPOUNDS	COLOUR	M.P./decomposition temp(0°C)	Conductivity ($\text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$)	%Found				%calculated			
				C	H	N	M	C	H	N	M
NOTF	Red	141m	-	60.20	5.00	23.47	-	60.60	5.05	23.57	-
LiONP.NOTF	Deep brown	205t	1.8	57.80	4.50	19	-	57.01	4.30	19	-
NaONP.NOTF	Deep brown	190t	1.8	55.58	4.50	18.00	4.80	55.02	4.15	18.34	5.02
KONP.NOTF	Deep brown	160t	3.0	5300.0	4.00	17.50	8.00	53.16	4.01	17.72	8.23
Li1N2N.NOTF	Deep brown	220d	2.0	63.08	4.58	17.88	-	63.03	4.41	17.65	-
Na1N2N.NOTF	Deep brown	210d	0.5	61.28	4.38	17.00	4.88	60.98	4.27	17.07	4.67
K1N2N.NOTF	Deep brown	205d	8.5	59.16	4.38	16.50	7.77	59.06	4.13	16.54	4.68
Li8HQ.NOTF	Grey	215d	2.5	64	4.95	18.85	-	64.29	4.68	18.75	-
Na8HQ.NOTF	Grey	200d	2.5	62.08	4.58	18.00	4.98	62.07	4.53	18.1	4.96
K8HQ.NOTF	Greenish Grey	188d	4.8	60.00	4.50	17.56	8.25	60.00	4.37	17.5	8.13
LiSalA.NOTF	Light pink	205d	0.5	59.20	4.50	15.80	-	59.36	4.54	15.57	-
NaSalA.NOTF	Light pink	200d	0.5	57.70	4.50	15.00	5.00	57.77	4.38	15.32	5.03
KSaI.NOTF	Light pink	190t	4.0	55.65	4.26	14.84	8.25	55.81	4.23	14.8	8.25

These complexes are soluble in most solvents but are insoluble or sparingly soluble in polar solvents such as chloroform, toluene and n-hexane. They are soluble when kept in vacuum or in desiccators over anhydrous CaCl_2 . On exposure to moisture they appear to decompose rapidly to give free ligand and alkali metal salt. They are found to either decompose or undergo a transformation at a temperature which is considerably higher than the melting point of corresponding ligand indicating thereby their greater thermal stability.

V. CONDUCTIVITIES

Molar conductivities of the alkali metal salts as well as those of the higher unknown alkali metal complexes of these ligands were measured in DMF at 25°C at a concentration of 10^{-3}M .

A value of approx. $35\text{-}40\ \text{Ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ appears characteristic of a electrolyte. From the result, it is evident that the molar conductivities of none of these complexes approach either ideal or 1:1 electrolyte⁸. However, significantly low value for potassium complexes suggests that they have undergone partial dissociation in the solvent.

VI. INFRARED SPECTRA

Infrared spectra measurement for the title ligands and their hitherto unknown mixed ligand complexes with alkali metals were made between $4000\text{-}650\ \text{cm}^{-1}$ in Nujol with the help of a Perkin Elmer spectro photometer, model 257. Pertinent IR data for these complexes are recorded in table 2. The symmetric and asymmetric -NO_2 frequencies generally appear around 1550 and $1250\ \text{cm}^{-1}$ respectively in the spectra of nitro compound¹¹. But in conjugated nitro compounds, these shifts to lower regions. For example in nitro phenyl hydrazone¹⁴, these frequencies occur at 1490 and $1280\ \text{cm}^{-1}$.

In the IR spectra of alkali metal salts, these bonds remain unaffected. Obviously, the nitro group does not participate in or add to chelating ability of the title ligand molecule NOTF exhibits the stretching -NH frequency at $2850\ \text{cm}^{-1}$ as a broad band medium intensity⁹⁻¹⁰. In the spectra of the complexes, this band appears as poorly resolved weak band, exhibiting metal atom with the ligand through nitrogen atom of the -NH group.

Table-2

compound	$\sqrt{\text{NH}}$	2400-1800	$\sqrt{\text{NO}_2(\text{SYM})}$	$\sqrt{\text{NO}_2(\text{ASYM})}$
NOTF	2850	2350br	1550	1250
LiONP.NOTF	2830	2350br	1550	1250
NaONP.NOTF	2834	2350br	1550	1250
KONP.NOTF	2835	2350br	1550	1250
Li1N2N.NOTF	2840	2350br	1550	1250
Na1N2N.NOTF	2835	2350br	1550	1250
K1N2N.NOTF	2835	2350br	1550	1250
Li8HQ.NOTF	2832	2350br	1550	1250
Na8HQ.NOTF	2835	2350br	1550	1250
K8HQ.NOTF	2830	2350br	1550	1250
LiSalA.NOTF	2835	2350br	1550	1250
NaSalA.NOTF	2835	2350br	1550	1250
KSal.NOTF	2834	2350br	1550	1250

A weak band appears in the region 1640-1650 cm^{-1} in the spectra of the title ligand NOTF which may be attributed to the stretching $\text{C}\equiv\text{N}$ vibrations. IR spectra of the adduct shows no considerable change either in intensity or in the position of $\text{C}\equiv\text{N}$ vibrations.

A new broad band of weak to medium intensity in the region 2400-1800 cm^{-1} in the IR spectra of all these complexes may be attributed to the O-H.....O-N.....H-O absorption. This suggests hydrogen bonding to be an essential in the complex of alkali metal salts of organic acid with the ligands 3-nitro-1, 5-di-o-tolyl formazan comes out to be $\text{ML.HL}'$ where $\text{M}=\text{Li}$, $\text{Na}\&\text{K}$; L = deprotonated O-nitrophenol, 1-nitroso-2-naphthol, 8-hydroxy quinoline or salicylic acid and HL' = 3-nitro-1, 5-di-o-tolyl formazan. The structure of these complexes which supported by the IR spectra can be suggested as fig 2.

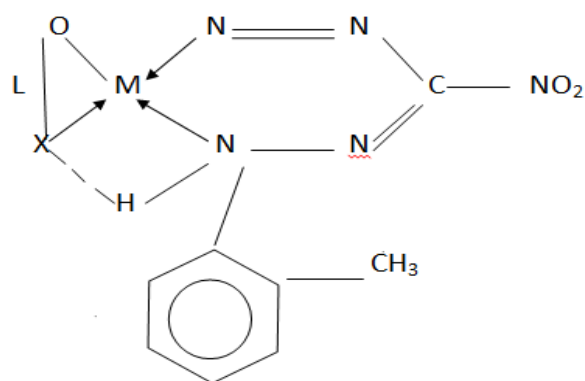


Figure 2

VII. CONCLUSION

We prepared alkali metal salts of organic acid with 3-nitro-1, 5-di-o-tolyl formazan and characterized on the basis of IR and conductometric. It is however evident that the biological properties /behavior of complex is less than ideal and additional study is required to improve the stability and other action.

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