

SYNTHESIS, CHARACTERIZATION AND ^1H -NMR STUDIES OF SOME BIS- LIGANDS OF P-CHLOROPHENYL UREA

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ABSTRACT

Different ligands of p-chlorophenyl urea with adipic acid, azelaic acid, succinic acid, and suberic acid have been prepared in benzene medium by condensation method. The structural composition has been determined from elemental analyses, ^1H -NMR and IR spectra. The spectral assignment of NMR has been done with the help of distortionless enhancement by polarization transfer and the H-H coupling is explained with the help of total correlated spectroscopy.

Key words: - ^1H -NMR studies, p-chlorophenyl urea, ligands, IR spectra

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INTRODUCTION

Polymeric coordinating reagents are a novel type of ligand giving complexes having a mixture of physical properties of a polymer and the chemical properties of the ligand. The coordination polymers i.e. metal complexes derived from polymeric coordinating ligands may also enjoy such advantageous features such as general thermal stability, insolubility in common solvents and multiactive sites available within the molecule¹⁻². Now a days proton nuclear magnetic resonance spectroscopy (^1H -NMR) is a powerful technique that can be used for determination of stereochemical structure and conformational analysis of polymeric compounds³. Coordination of ligand to a metal ion can make appreciable changes in ^1H -NMR chemical shift and reactivity of the ligand, which may be important for understanding of certain biological processes. Nuclear magnetic resonance (NMR) is a technique which has been used widely to study these changes⁴⁻⁸.

A literature survey however reveals that ligands of p-chlorophenyl urea with adipic acid, azelaic acid, succinic acid, and suberic acid can be used for the preparation of chelate polymers of first row transition metal ions. These ligands have been synthesized in our laboratory and characterized by various instrumental techniques.

EXPERIMENTAL

Materials

All the chemicals used were of A. R. grade. Solvents were purified by the usual method before used.

Instruments

The analysis of carbon, hydrogen and nitrogen were performed on a Carlo Erba 1108 elemental analyzer. ^1H -NMR spectra were recorded on Bruker DRX-300 NMR spectrometer 300 MHz FT NMR using TMS as internal standard (δ ppm). FTIR spectra were recorded on Nicolet magma IR 550 series 2 spectrophotometer, USA using KBr pellets in the 400-4000 cm^{-1} range at Regional Sophisticated Instrumentation Centre, Lucknow. Chlorine contents were analyzed at National Chemical Laboratory Pune.

Preparation of p-chlorophenyl urea⁹

A quantity of 25.6 gm (0.2 m mol) of finely powdered p-chloroaniline dissolved in a mixture of 100 ml. glacial acetic acid and 200 ml. distilled water at 35 $^{\circ}\text{C}$. The solution of 13 gm (0.2 m mol) sodium cyanate in 100 ml distilled water at 35 $^{\circ}\text{C}$ added gradually with constant stirring. Solid obtained was filtered and recrystallized from 90 % aqueous ethanol. Melting point of the product was 238 $^{\circ}\text{C}$.

Preparation of dichloride of adipic, azelaic, succinic, and subaric acid

It was prepared by the reaction of (0.1 m mol) dry acid and (0.2 m mol) double distilled thionyl chloride placed in a 100 ml. dry round bottomed flask filled with a perfectly dry Liebig water condenser provided with calcium chloride guard tube. The reaction mixture then refluxed on a water bath till clear solution was obtained. To remove SO_2 , HCl and unused SOCl_2 , reaction mixture was refluxed under reduced pressure for about 30 minutes.

Preparation of ligand

The ligand adipyl bis p chlorophenyl urea (ADPCPU), azelaoyl bis p chlorophenyl urea (AZPCPU), succinyl bis p chlorophenyl urea (SUPCPU), and suberoyl bis p chlorophenyl urea (SBPCPU) was prepared by the condensation of acid dichloride (0.1 m mol) with p chlorophenyl urea (0.2 m mol) in sodium dried benzene for about 4-5 hours. The ligand was filtered and washed with hot ethanol to remove unused p chlorophenyl urea and dried in oven at 100°C then it was characterized by elemental analyses and infrared spectra.

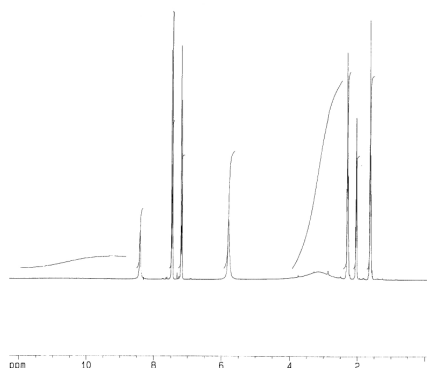


Fig.-1: ^1H NMR spectra of ADPCPU ligand

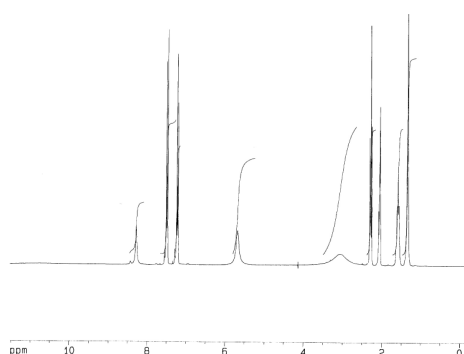


Fig.-2: ^1H NMR spectra of AZPCPU ligand

RESULTS AND DISCUSSION

The ^1H -NMR spectrum of ADPCPU, AZPCPU, SUPCPU, and SBPCPU in acetone solvent along with complete assignment of resonances signals for aliphatic and aromatic protons are shown in figs.1-4

The NMR signals around δ (chemical shift) 2.00-2.50 ppm is assigned to the overlap of $-\text{CH}_2$ proton of ligand¹⁰. The aromatic proton of two phenyl groups appeared around δ 7.44-7.67 ppm due to the presence of $(-\text{NH}-\text{C}=\text{O})$ amide groups attached directly to benzene ring¹¹, and other NMR signal around δ 7.16-7.30 ppm is assigned due to two proton of benzene ring at which chlorine is attached¹²⁻¹³. The resonance weak signal around δ 5.58-5.79 ppm is assigned to NH proton of ligand and other weak signal around δ 8.20-8.40 ppm is assigned to two proton of amide group $(-\text{NH}-\text{C}=\text{O})$ ¹⁴.

In the infrared spectrum of the ligands a weak band observed in the region $3314\text{--}3427\text{ cm}^{-1}$ may be due to the presence of $-\text{NH}$ group¹⁵. A sharp band observed in the region $1606\text{--}1656\text{ cm}^{-1}$ is due to $\nu(\text{C}=\text{O})$ of the carbonyl group¹⁶ and a weak band appeared in the region $2935\text{--}2958\text{ cm}^{-1}$ may be assigned to stretching vibration of $-\text{CH}_2$ group¹⁷. The table 1, 2 & 3 shows ^1H -NMR, elemental analyses and infrared spectral assignment of ligands. Fig.5 shows IR spectrum of ligands.

Table- 1: ^1H NMR spectra of p chlorophenyl urea ligands (δ ppm)

Observed Chemical Shift (δ ppm)				Nature of Proton Assigned	Experimental Chemical Shift
ADPCPU	AZPCPU	SUPCPU	SBPCPU		
2.00-2.32	2.03-2.49	2.00-2.55	2.03-2.31	Methylene proton of $-\text{CO}-(\text{CH}_2)_n-\text{CO}-$	1.4 - 2.4

5.79	5.68	5.58	5.60	Proton of Nitrogen of —C— NH—CO—	5.16
7.16-7.48	7.20-7.55	7.17-7.48	7.20-7.67	Aromatic proton of Ar – H	7.41

Table-2: Elemental Analyses of ligands

S. No.	Ligands	Formula weight	% Carbon		% Hydrogen		% Nitrogen		% Chlorine	
			Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
1	ADPCPU	450.8	52.20	53.21	4.45	4.43	13.19	12.41	16.00	15.74
2	AZPCPU	492.89	55.62	56.00	5.26	5.31	11.43	11.36	13.92	14.40
3	SUPCPU	422.81	50.73	51.19	3.87	3.81	12.87	13.25	16.58	16.79
4	SBPCPU	478.87	54.66	55.13	5.02	5.05	11.50	11.70	15.4	14.82

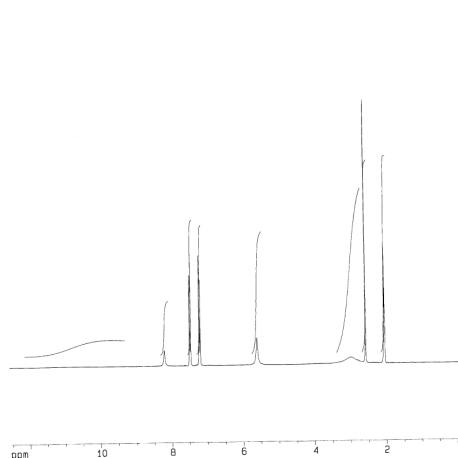
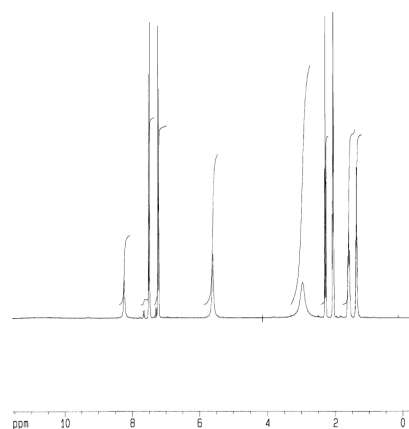
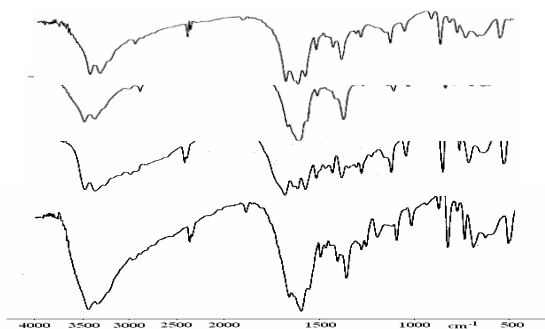
Fig.-3: ^1H NMR spectra of SUPCPU ligandFig.-4: ^1H NMR spectra of SBPCPU ligand

Fig.-5: IR spectrum of ligands

Table-3: IR Spectral Assignment of Ligands (cm^{-1})

S. No.	Ligands	Colour	Solubility	-NH-	-CH ₂ -	=C=O
1	ADPCPU	White	Ethyl alcohol, hot DMF, Acetic acid and Acetone	3425(s)	2958(w)	1658(s)
2	AZPCPU	White	Ethyl alcohol, hot DMF, Acetic acid and Acetone	3314(s)	3938(m)	1656(s)
3	SUPCPU	White	Ethyl alcohol, hot DMF, Acetic acid and Acetone	3427(s)	2831(m)	1606(s)

4	SBPCPU	White	Ethyl alcohol, hot DMF, Acetic acid and Acetone	3427(s)	2937(m)	1655(s)
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ACKNOWLEDGEMENTS

The author would like to thank the Head, Department of Chemistry, Rashtrasant Tukadoji Maharaj, Nagpur University, Nagpur, for providing the laboratory facilities to carry out this work.

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[RJC-896/2012]

International Journal of
Chemical, Environmental and Pharmaceutical Research

www.ijcepr.com

ISSN: 2229-3892(Print); ISSN: 2229-5283(Online)

[Abstracted in : Chemical Abstracts Service , American Chemical Society, USA and CAB(I) , UK]

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