

Study on the Complexation of Macromolecule Cucurbituril with Metals and Acetamide

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Abstract

Cucurbituril is a remarkably robust macro cyclic host molecule that has a rigid cavity capable of binding small guests under a variety of conditions. In the present study, macromolecule cucurbit[6]uril (CB[6]) and its complexes with metal ions lithium, cerium were synthesized. Mixed ligand complexes containing CB[6] and acetamide with central metal ions such as lithium were also prepared. The UV – visible spectrum of the complex of lithium with CB[6] shows a peak at 225nm. The mixed ligand complex of lithium with CB[6] and acetamide shows a sharp peak at 220nm which indicates the presence of amide functional group. The peak at 274nm indicates the presence of – NO₂ group. UV-visible spectrum of the complex of cerium with CB[6] shows a peak at 213.17nm, which indicates the presence of – CONH₂ group. The IR spectrum of Cucurbituril shows the following peaks 3436.96 cm⁻¹, 2931.16 to 2372.15 cm⁻¹ and a sharp peak at 1726.39 cm⁻¹ these frequencies indicate the presence of CO - N, C-H and C=O stretching respectively.

The IR spectra of the complex of Lithium with CB[6] and Cerium with CB[6] show significant variations especially around 3000 cm⁻¹ and between 1700 to 1200 cm⁻¹ indicating prevalence of enhanced hydrogen bonding. Our studies reiterate the versatility of CB[6] as a host macromolecule and it forms stable complexes with cerium and lithium this stability is largely attributed to the strong interaction of carbonyl oxygen donor atoms of cucurbituril with the cations. IR spectroscopic studies reveal the presence of such polar oxygen portals.

Keywords: Cucurbituril, Macrocyclic ligand, mixed ligand complexes and molecular containers.

Introduction

Cucurbituril is a remarkably robust macro cyclic host molecule that has a rigid cavity capable of binding small guests under a variety of conditions^[1]. It is a barrel-shaped macrocyclic cavitand (Fig -1). The two carbonyl fringed portal of this molecule has six carbonyl oxygen atoms located in a plane which can interact with metal cations in such a way that cucurbituril behaves like a macrocyclic ligand. These portal atoms have a higher electric charge compared with crown ether oxygen atoms and consequently stronger interactions between carbonyl groups and positively charged ions take place. Due to the presence of polarized carbonyl groups, Cucurbit[6]uril forms strong complexes with alkali, alkaline earth and rare earth metal ions and hydrogen bonded complexes of transitional metal ions.^[2-4]

The cavity of Cucurbit[6]uril has nanoscale dimensions with an approximate height of 9.1pm, outer diameter 5.8pm and inner diameter 3.9 pm^[5-6].

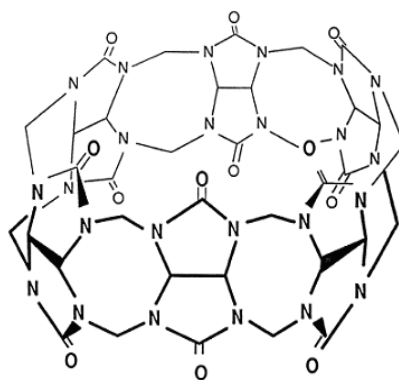


Figure 1: Chemical Structure of Cucurbituril

These compounds are particularly interesting to chemists because they are molecular containers that are capable of binding other molecules within their cavity^[7]. Host-guest chemistry (Fig -2) is the study of complexes that are composed of two or more molecules held together in unique structural relationships by non-covalent bonds^[8].

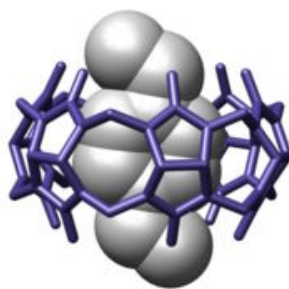


Figure 2: A model for Host-guest complex

The present work aims to synthesize the macromolecule ligand cucurbit[6]uril, to prepare CB[6] complexes with metal ions such as lithium, cerium, as guest molecules and to prepare mixed ligand complexes containing CB[6] and acetamide with central metal ion lithium, the physical and chemical properties of the complexes are also determined. Formation of complex is studied by absorption spectroscopy and IR spectroscopic methods.

Materials and Methods

Glyoxal, urea, formaldehyde, concentrated hydrochloric acid, lithium carbonate, acetamide and ceric ammonium sulphate used for the study were of analytical grade and hence they were used as such.

UV-Visible spectroscopy was recorded with various concentrations of cucurbituril keeping stock 0.025M in aqueous HCl solution. Cucurbituril is not soluble in many common solvents but it is found to be soluble in ionic and acidic solutions^[9, 10]. Water and HCl mixture at the ratio of 1:4 was used as the solvent throughout the work.

Complex of lithium with Cucurbit[6]uril

A complex of lithium with cucurbituril was prepared in the ratio of 1:2 using aqueous HCl as solvent. The amount of the ligand was in excess. The final solution was mixed thoroughly and allowed to stand at room temperature. Slow evaporation was carried out by keeping the mixture in water bath. After two days pale yellow crystals separated out. The crystals obtained were filtered off, dried and the yield of the complex obtained was found to be 70%.

Mixed Ligand complex of Lithium with Cucurbit[6]uril and Acetamide

A mixed ligand complex of lithium with cucurbituril and acetamide was prepared in the ratio of 1:2:1 using aqueous HCl as solvent. The amount of the ligand, cucurbituril, was taken in excess. The final solution was mixed thoroughly and allowed to stand at room temperature. Slow evaporation was carried out by keeping the mixture in water bath. After two days pale yellow crystals separated out. The crystals obtained were filtered off, dried and yield of the complex obtained was about 50%.

Complex of Cerium with Cucurbit[6]uril

A complex of cerium with cucurbituril was prepared in the ratio of 1:2 using aqueous HCl as solvent. The final solution was mixed thoroughly and allowed to stand at room temperature. Slow evaporation was carried out by keeping the mixture in water bath. Bright yellow crystals separated out after two days. The crystals obtained were filtered off, dried and yield of the complex obtained was about 60%.

Results and Discussion

Cucurbituril was obtained as white solid in 30% yield. The sample was found to be

soluble only in aqueous solution of HCl and was insoluble in common solvents like water, acetone, chloroform, carbontetrachloride, diethylether, alcohol and benzene. The solubility of cucurbit[6]uril in aqueous acidic solution is believed to be due to the complex formation between the portal oxygen atoms on cucurbituril and the hydronium ions in the acidic solution. The synthesized cucurbituril did not have a sharp melting point but it underwent decomposition at 260⁰C.

The complex of lithium with cucurbit[6]uril was obtained as pale yellow crystals and the yield of complex was 70%. The substance did not show a sharp a melting point. The mixed ligand complex of lithium with cucurbit[6]uril and acetamide was obtained as pale yellow crystals and the yield of complex was found to be 50%. The mixed ligand complex did not show a sharp melting point. The complex of cerium with cucurbit[6]uril was obtained as bright yellow crystals and the yield of complex was found to be 60 %. The complexes did not have sharp melting points. They underwent decomposition at 250 ⁰C, 270 ⁰C and 240 ⁰C respectively

UV – Absorption Spectroscopy

UV- Visible spectroscopy is used to study the absorption spectrum of cucurbituril complexes. Absorption spectroscopy was carried out by keeping the concentration of metal and acetamide constant and varying the concentration of cucurbituril. From the stock solutions of 0.025M, different ratios were prepared 1:1:1, 1:2:1, 1:3:1, 1:4:1, 1:5:1 and 1:6:1. All UV, visible spectrophotometric measurements were carried out using Perkin Elmer UV – Visible spectrophotometer

Complex of lithium with cucurbit[6]uril

The UV – Visible spectrum of the complex of lithium with cucurbit[6]uril shows a peak at 225nm (Figure 3). Such a type of peak is not seen in the spectrum of cucurbit[6]uril which shows a peak at 215.89nm and lithium carbonate which shows a peak at 230nm.

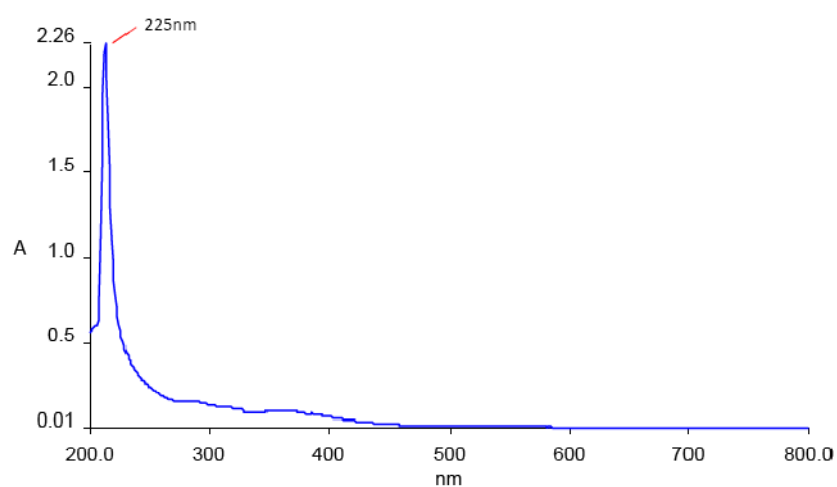


Figure 3: UV Absorption spectrum of, Lithium with cucurbit[6]uril

Mixed Ligand complex of Lithium with Cucurbit[6]uril and acetamide

The UV - visible spectrum of complex of Lithium with cucurbit[6]uril and acetamide shows a sharp peak at 220nm (Figure 4) which indicates the presence of amide functional group. The peak at 274nm indicates there is a $-\text{NO}_2$ group. These two characteristic peaks are not observed in the UV-visible spectrum of both the ligand and the metal.

Complex of Cerium with Cucurbit[6]uril

UV-visible spectrum of the complex of cerium with cucurbit[6]uril shows a peak at 213.17nm (Figure 5), which indicates the presence of $-\text{CONH}_2$ group due to $(n - \pi^*)$ transition. In addition to this peak two other peaks are also seen at 242.97nm & 256.03nm. Such characteristic peaks are not seen in both the individual spectra of cucurbit[6]uril and ceric ammonium sulphate

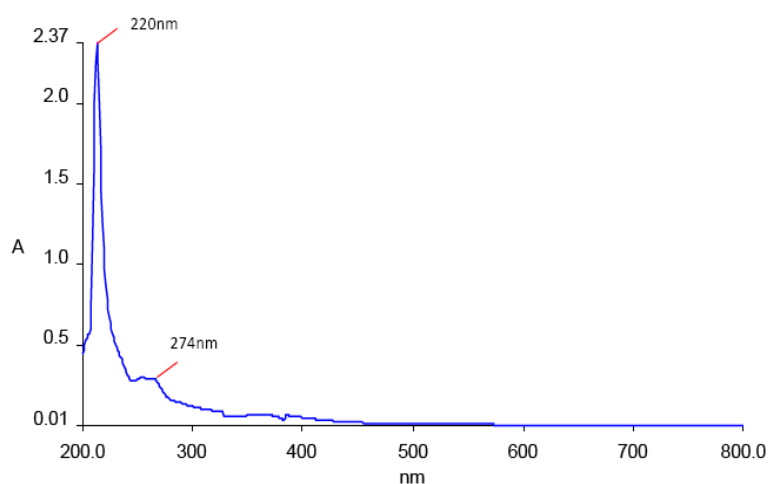


Figure 4: UV Absorption spectrum of lithium with cucurbit[6]uril and Acetamide

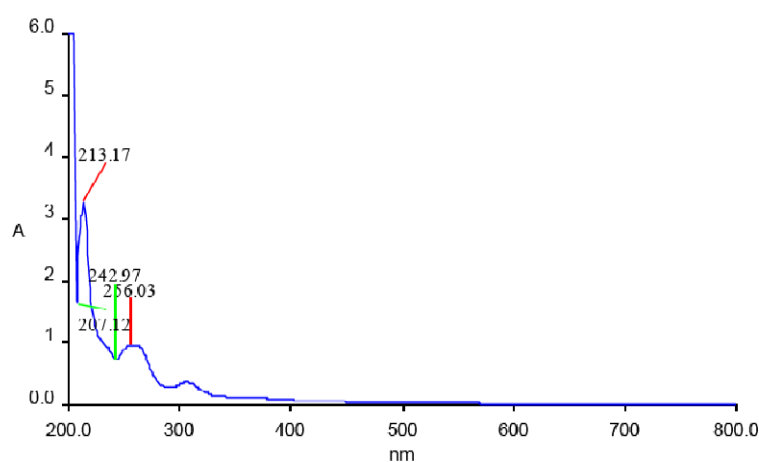


Figure 5: UV absorption spectrum of cerium with cucurbit[6]uril

IR Spectrum of complex of lithium with cucurbit[6]uril

The IR spectrum of lithium with cucurbit[6]uril shows significant variation especially in 3000cm^{-1} and between 1700 to 1200cm^{-1} indicating prevalence of enhanced hydrogen bonding which are shown in (Figure 6).

In this spectrum a peak is seen at 3432.99cm^{-1} which indicates the presence of $-\text{CO-N}$ bond, the C-N stretching gives a small absorption peak ^[8] at 2927.65cm^{-1} .

The sharp peak at 1729.34cm^{-1} indicates C=O stretching, transition due to $=\text{C}=\text{O}$ bond gives a peak at 1641.79cm^{-1} . Such a peak is not seen in the IR spectrum of CB[6]. Another new peak is seen at 1192.06cm^{-1} in the spectrum of the complex.

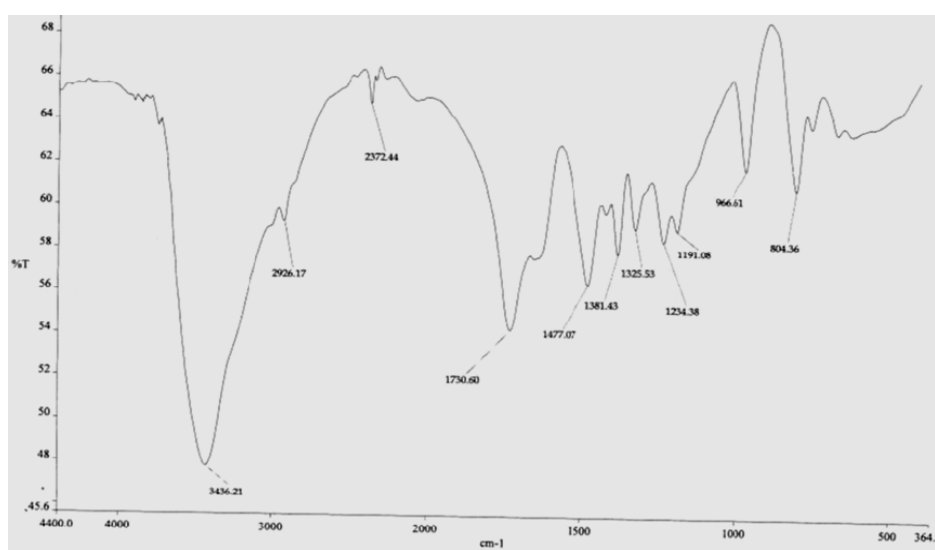


Figure 6: IR spectrum of mixed ligand complex of lithium and cucurbit[6]uril and acetamide

IR Spectrum of Complex of Cerium with Cucurbit[6]uril.

The IR spectrum of Cerium with Cucurbit [6]uril shows significant variation especially in 3000cm^{-1} region and between 1700 to 800cm^{-1} indicating prevalence of enhanced hydrogen bonding which are shown in Fig. 7

In the spectrum, a peak at 2370.27cm^{-1} is due to C-H stretching, and absorption peaks at 1480 , 1383 , 1325.80 , 1230.81 , 1191.68 , 1048.08cm^{-1} are due to S=O and S-O stretching. O-S-O bond gives a sharp peak at 963.49cm^{-1} .

Peak at 3435.26cm^{-1} indicates N-H stretching and the peak at 1727.76cm^{-1} is due to C=O stretching.

Previous studies support this proposition and have suggested the formation of coordination of transition metals by the macrocycle through hydrogen bonding between portal oxygen atoms and coordinated water molecules of the aqua complexes. In this type of complexes, cucurbituril acts as an outer sphere ligand ^[11, 12].

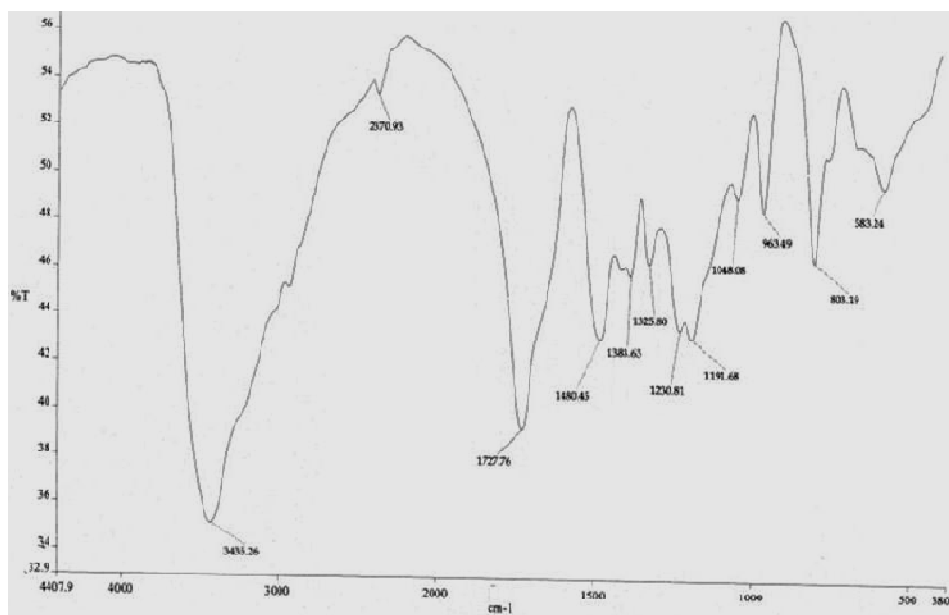


Figure 7: IR Spectrum of complex of cerium and cucurbit[6]uril

Conclusion

Cucurbituril is a remarkably robust macro cyclic host molecule that has a rigid cavity capable of binding small guests under a variety of conditions. It is an acid soluble, crystalline product, with a decomposition temperature of 260⁰ C. Cucurbit[6]uril's ability to act as a host molecule is explored in this work, from the simple and the mixed ligand complexes which were prepared with metal ions as guest and acetamide as another ligand. Simple complexes such as lithium with cucurbit[6]uril and cerium with cucurbit[6]uril, and mixed ligand complexes such as lithium with cucurbit[6]uril and acetamide and cerium with cucurbit[6]uril and acetamide were prepared.

This study reveals that for the formation of a strong complex, the host and guest must have complementary sizes. The geometric and functional complementarity of carbonyl oxygen donor atoms of cucurbituril and water molecules of the complexes leads to very stable hybrid organic – inorganic compounds. The hydrophobic cavity of cucurbituril increases the stability of the complex by providing a barrier of decomplexation of charged species.

Acetamide was chosen as the guests because it has the capability to reside in the cavity as it is relatively small.

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