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# HOST-GUEST COMPLEXES OF CUCURBITURIL WITH BENZAMIDE AND CATIONS IN AQUEOUS SOLUTION

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**Abstract:**

*Cucurbituril is a macrocyclic host molecule which is recently studied under the field of chemistry called "supramolecular chemistry". Cucurbit [6]uril is used as a host molecule, where 1:4 concentrated HCl was used as a solvent. Cucurbit [6]uril is mixed with benzamide in 1:1 ratio to form host-guest molecule. Mixed ligand complexes of cucurbituril and benzamide with metals lanthanum nitrate and gadolinium oxide were prepared. These huge robust molecular complexes helps in adsorbing effluents from industries and as a drug delivery vehicle due to their lesser cytotoxicity, the complexes have various other valuable applications in variety of fields. Physicochemical properties of the synthesized samples was studied, there was notable change in the appearance and decomposition temperature. Cucurbituril was soluble only in aqueous HCl but the host-guest complexes were soluble in most of the common solvents. Infrared spectroscopy for cucurbituril and mixed ligand complexes, gives information about the changes in carbonyl absorption band at 1708.08 $cm^{-1}$ for cucurbituril, and significant variation was observed for metal complexes i.e. for gadolinium 1701.09 $cm^{-1}$ and for lanthanum 1698.46 $cm^{-1}$. The IR studies also accounts for other non-covalent interactions between the atoms in that encircled molecular knots and helps in the comparison and variation of cucurbituril structural feature with its guest benzamide and with encapsuled rare earth metal ions.*

*The Powder X-ray diffraction studies show sharp peaks in the molecule and the mixed ligand complexes with specific 2θ values, this indicates that crystallinity is maintained in the complexes. Thus involving cucurbituril as the host molecule with benzamide and metal ions as guest molecules may also have potential applications and can be reached to greater extent with valuable outputs.*

**Key Words:** Cucurbituril, Host-guest complexes & Supramolecular Chemistry

## 1. Introduction:

Supramolecular chemistry, a term introduced by Jean-Marie Lehn, is "chemistry beyond the molecule", that is the chemistry of molecular assemblies using non-covalent bonds[1-3], i.e its entities being constituted of molecular components held together by non-covalent interactions.

The supramolecular chemistry of cucurbituril, is fascinating because of the remarkable guest binding behavior of the host. Over the past decade, a wide variety of supramolecular species such as polyrotaxanes, molecular necklaces, rotaxane dendrimers, and rotaxane-based molecular switches are synthesized using CB [6] as a molecular bead.[4-6]

Cucurbit [6]uril or CB[6] is a hexameric macrocyclic containers self-assembled from an acid-catalyzed condensation of n glycouril units with formaldehyde. In cucurbit [6]uril the two carbonyl fringed portal at two openings of the host cavitand, each 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 thus forming a host-guest inclusion complexes. 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.[7]

Cucurbituril involves the chemistry where association is seen between host and the guest, and their interaction leads to the clear understanding of the term "Supramolecular chemistry".

Host-guest chemistry (Fig. 1) is the name given to the study of the encapsulation of one compound (the guest) by a second compound (the host) through non-covalent interactions. To get a productive interaction, the host is chosen to be complementary to a particular guest such that in solution a complex is formed spontaneously.

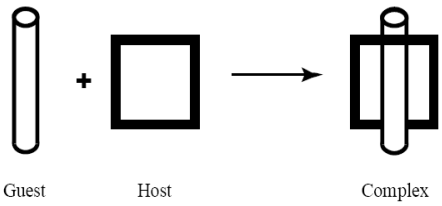



Figure 1: Host guest Chemistry.

Cucurbituril has diverse applications in various fields some of their enhancing utilizations are,

- Cucurbituril is a potential sorbent for the removal of reactive dyes from solutions and wastewaters. It can encapsulate metal ions in effluent treatment and its solubility is low in pure water but increases in the presence of salts.[8]
- It can also detect environmental contaminations such as nitrates, phosphates, chromate, uranyl and heavy metals.
- Used as a drug delivery vehicle, biomimetic systems and as an adsorbent.[9]

## 2. Scope of the Work:

- This work aims to synthesise host guest complexes and a structural study was carried out using analytical techniques
- The synthesized cucurbituril acts as a host molecule with benzamide and metal cations (lanthanum nitrate and gadolinium oxide) which acts as guest molecules prepared at 1:1 concentration, to form macrocyclic complexes.
- The physical and chemical properties of synthesized cucurbituril and the host guest complexes were studied and the overall understanding of the samples about their structure, binding nature was obtained from the characterization techniques.
- A structural study was carried out for the synthesized cucurbituril and host guest complexes, using analytical tools like Infrared spectroscopy, powder x-ray diffraction studies, thermogravimetric analysis and mass spectroscopy.

From this work better knowledge about the host guest complexation between metals (Ln, Gd), benzamide and the host macrocyclic cucurbituril can be attained.

## 3. Experimental Methods:

### Chemicals Used:

Glyoxal, urea, formaldehyde, concentrated hydrochloric acid, lanthanum nitrate, gadolinium oxide, and benzamide were of analytical grade and used without further purification.

The solubility of cucurbit [6]uril in aqueous acidic solution may be due to the complex formation between the portal oxygen atoms on cucurbituril and the hydronium ions in the acidic solution. So water and concentrated HCl mixture at the ratio of 1:4 was used as solvent throughout the work.

**Experimental Description:**

**Preparation of Glycouril:**

Cucurbituril is a cyclic condensation product of glycouril and formaldehyde. Glycouril is prepared by mixing 15g of urea with 5.8mL of glyoxal with 10mL of water under constant stirring. The pH was adjusted to 0-1 by adding concentrated hydrochloric acid. The solution was heated to 75˚C to get a creamy white precipitate which is insoluble in water. The yield was about 3g of glycouril. The white precipitate was collected by filtering in a Buckner flask.

**Preparation of Cucurbituril:**

About 3g of glycouril was dissolved in 12.5mL of hydrochloric acid. The solution was cooled to 0˚C and 4mL (40%) formaldehyde was added. The solution was mixed and then allowed to gel for 1 hour. The mixture was heated at 100˚C for about 3 hours. The mixture was allowed to cool to room temperature and then was evaporated to remove hydrochloric acid. The mixture was stirred with water and again evaporated.

A fractional crystallisation was performed by dissolving the solid in a minimum amount of concentrated hydrochloric acid and then adding water until the solution started to precipitate. The mixture was left over night and precipitate collected. The filtrate was then evaporated and then recrystallization step was repeated until all solid was collected. The product obtained was Cucurbit [6]uril. Ordinarily multifunctional monomer such as cucurbituril undergoes a step-growth polymerisation that would give a distribution of products, but due to favourable strain and abundance of hydrogen bonding, the cucurbit [6]uril is the only reaction product isolated after precipitation .

Decreasing the temperatures of the reaction between 75˚C and 90˚C can be used to access other sizes of cucurbituril including cucurbit[5]uril, cucurbit[7]uril, cucurbit[8]uril, cucurbit[9]uril, cucurbit[10]uril, although other ring sizes are still formed in smaller percentages than cucurbit[6]uril. The isolation of sizes other than cucurbit [6]uril, requires fractional crystallization and dissolution. Cucurbit[5]uril, cucurbit[7]uril, and cucurbit[8]uril are all currently commercially available. The largest sizes are particularly active area of research since they can bind larger and more interesting guest molecules thus expanding their potential applications.

The reaction can be represented as follows:

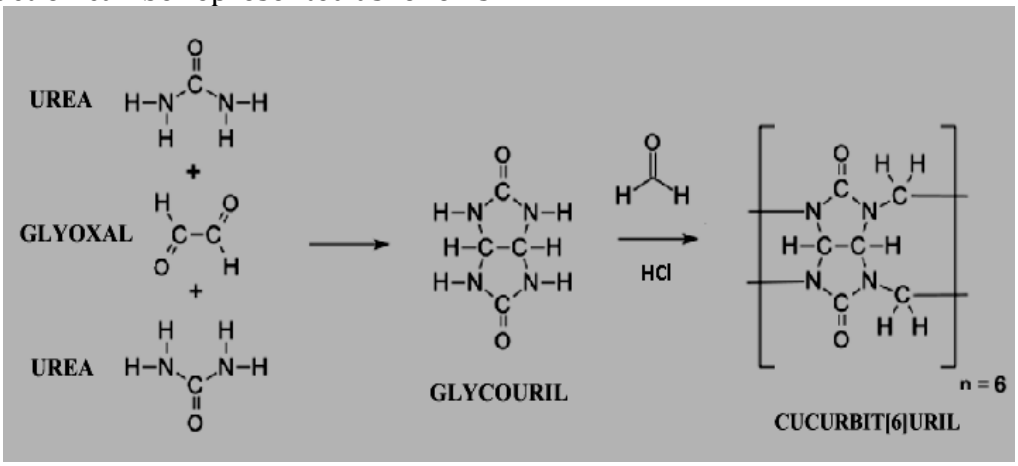



Figure 2: Synthesis of cucurbituril.

**Preparation of Host-Guest Molecule:**

**Host-Guest Molecule of Cucurbituril with Benzamide**

20mL solution of 0.05M cucurbituril, 20mL solution of 0.05M benzamide was mixed. Aqueous HCl solution was used as the solvent. The amount of ligands is in the same ratio (1:1). The final clear solution was mixed thoroughly and allowed to stand at above room temperature in heating mantle. The sample was obtained as dry powder.

**Preparation of Complexes:**

**Mixed Ligand Complex of Lanthanum with Cucurbituril and Benzamide**

20mL solution of 0.05M cucurbituril, 20mL solution of 0.05M lanthanum nitrate and 20mL solution of 0.05M benzamide was mixed. Aqueous HCl solution was used as the solvent. The amount of ligands and metal are in the same ratio (1:1:1). The final clear solution was mixed thoroughly and allowed to stand at above room temperature in heating mantle. The complex was obtained as dry powder.

**Mixed Ligand Complex Gadolinium with Cucurbituril and Benzamide**

20mL solution of 0.05M cucurbituril, 20mL solution of 0.05M gadolinium oxide and 20mL solution of 0.05M benzamide was mixed. Aqueous HCl solution was used as the solvent. The amount of ligands and metal are in the same ratio (1:1:1). The final clear solution was mixed thoroughly and allowed to stand at above room temperature in heating mantle. The complex was obtained as dry powder.

The physical properties like appearance, solubility and decomposition temperature of the bare cucurbituril, cucurbituril with benzamide and the complexes were noted down. The decomposition temperature was found using Meltemp apparatus in open capillary tubes and all the samples was analysed using IR spectroscopy (Bruker instrument), Powder XRD analysis (Bruker D8 advance ).

**4. Results and Discussion:**

The macrocyclic cavitand Cucubituril, due to its easy synthesis, rigid structure and chemical and thermal stability makes it very attractive for complexation of cations in aqueous solution. Cucurbituril was obtained as a yellow solid the sample was found to be soluble only in aqueous solutions of HCl and was insoluble in common solvents like water, acetone, chloroform and diethyl ether. The solubility of cucurbituril in aqueous acid solution is believed to be, due to a complex forming between the portal oxygen atoms on CB[n] and the hydronium ions in the acid solution. The synthesized material did not have a sharp melting point but it underwent decomposition at $230^0$C.

**Table 1: Physico-Chemical Study of the Samples**

| Properties | Cucurbituril | Cucurbituril and Benzamide | Mixed Ligand Complexes of Lanthanum with Cucurbituril and Benzamide | Mixed Ligand Complexes of Gadolinium with Cucurbituril and Benzamide |
|---|---|---|---|---|
| Appearance | Yellow solid | Yellow solid | Yellow solid | Pale yellow solid |
| Solubility | 1:4 aqueous HCl | 1:4 aqueous HCl | $CHCl_3$, $H_2O$, aqueous HCl | $CHCl_3$, $H_2O$, aqueous HCl |
| Decomposition temperature | 230˚C | 240˚C | 235˚C | 248˚C |

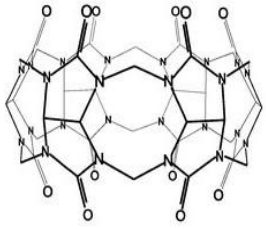
**Characterization Techniques:**

The Structural techniques involves,

- IR Spectroscopy
- Powder X-ray diffraction studies

**IR Spectroscopy:**

- IR spectroscopy helps to know the functional groups present in the sample from its stretching and bending frequencies.
- IR spectrum for cucurbituril involving following structure (Fig. 3) is analysed.



CB6

Figure 3: Cucurbituril

- IR spectrum for the following are recorded,
  - Cucurbituril with benzamide host guest molecule,
  - Host-guest complexes of lanthanum with cucurbituril and benzamide
  - Host-guest complexes of gadolinium with cucurbituril and benzamide.
- IR spectrum of cucurbituril and other synthesized complexes shows changes in the carbonyl absorption band where we can observe significant variation and come to a conclusion host guest complexes are formed

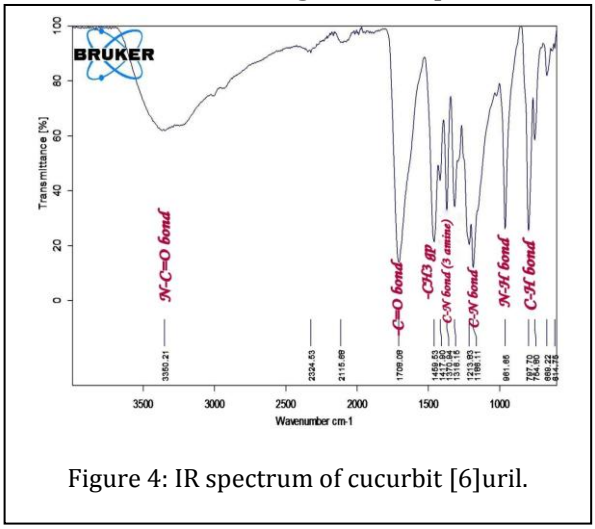



Figure 4: IR spectrum of cucurbit [6]uril.

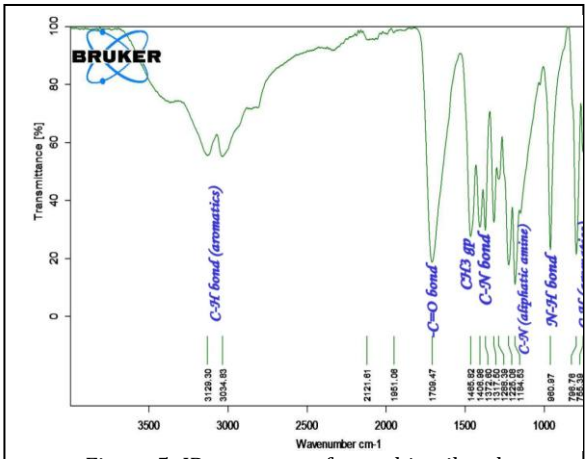



Figure 5: IR spectrum of cucurbituril and benzamide.

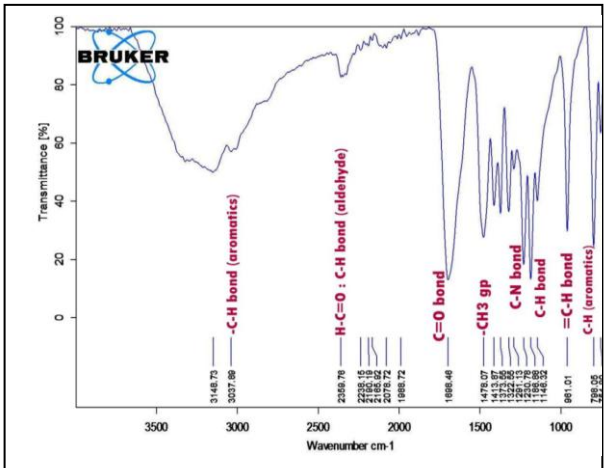



Figure 6: IR spectrum of cucurbituril, benzamide and lanthanum nitrate.

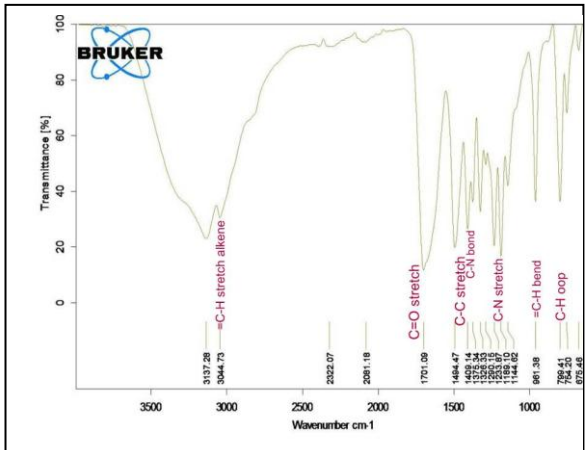



Figure 7: IR spectrum of cucurbituril, benzamide and gadolinium oxide.

**Table 2:** Comparison of IR frequencies for prepared samples

| IR Frequencies | Cucurbituril | Cucurbituril and Benzamide | Mixed Ligand Complexes of Lanthanum with Cucurbituriland Benzamide | Mixed Ligand Complexes of gadolinium with Cucurbituril and Benzamide |
|---|---|---|---|---|
| C=O stretch | 1708.08 | 1709.47 | 1696.48 | 1701.09 |
| Methyl group | 1459.53 | 1485.82 | 1478.07 | 1494.47 |
| C-N bond | 1370.94 | 1372.60 | 1322.55 | 1326.33 |

Stretching frequencies in the complex is significantly shifted towards lower wave number (Table- 2) as a result of M-O coordination. The formation of M-O bonds, leads to a decrease in the π-character of C=O bond. Previous studies support this proposition and have suggested the formation of coordination of transition metal by the macrocycle through hydrogen bonding between the portal oxygen atoms and coordinated water molecules of the aqua complexes.[6]

**Powder X-Ray Diffraction Studies:**

Powder XRD is analysed and compared with the literature for the following samples,

- cucurbituril.
- cucurbituril and benzamide.
- cucurbituril, benzamide and lanthanum nitrate.
- cucurbituril, benzamide and gadolinium oxide.

The sharp peaks in the graph for intensity vs 2θ values indicate the crystalline structure in the samples. X-ray powder diffraction patterns show numerous reflections in low to high angle regions indicative of crystalline phases.

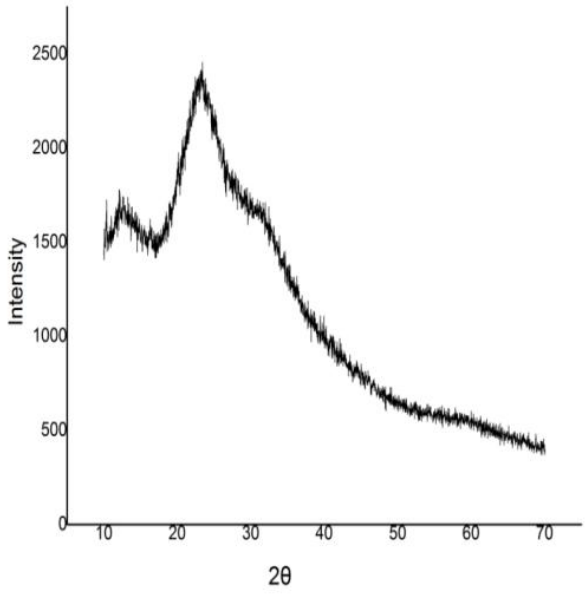



Figure 8: Powder XRD of cucurbit [6]uril.

There are two peaks at 2θ = 14˚ and 23˚

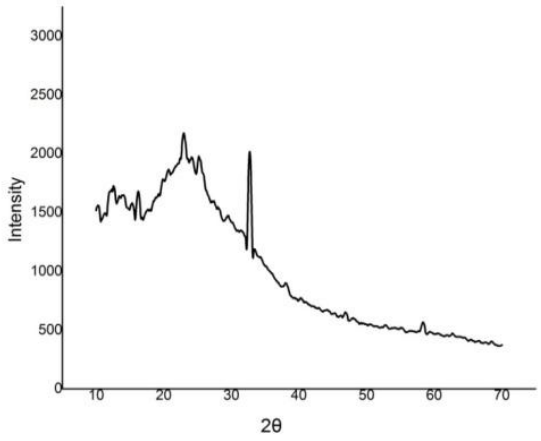



Figure 9: Powder XRD of cucurbituril and benzamide.

The sharp peaks are at 2θ = 24˚ and 34˚.

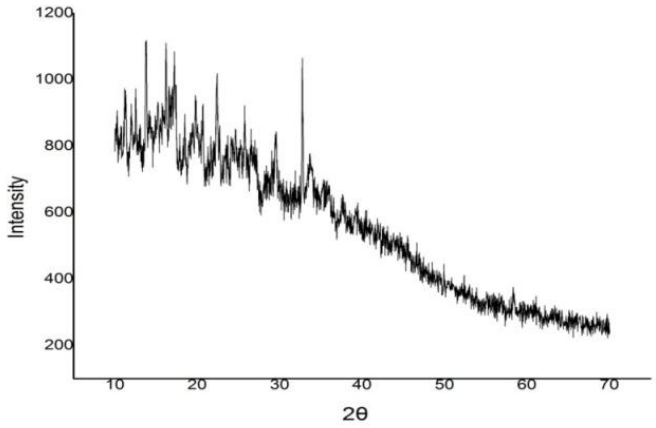



Figure 10: Powder XRD of cucurbituril, benzamide and lanthanum nitrate.

In this complex, sharp peaks are at 2θ = 16˚, 24˚ and 34˚.

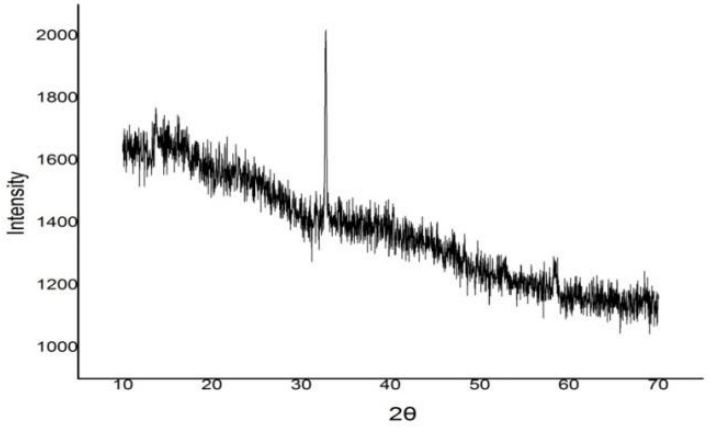



Figure 11: Powder XRD of cucurbituril, benzamide and gadolinium oxide.

Sharp peak for this complex is at 2θ = 35˚.

**5. Conclusion:**

This work reiterates the versatility of cucurbituril as a host macromolecule. The following important aspects emerge from the studies

- The present work reveals that the large modulation in physico-chemical properties of cucurbituril is based on supramolecular assemblies through non-covalent interactions like hydrogen bond and ion-dipole interactions.
- The host plays a desirable role in modulating the guest properties. There is a sharp increase in the decomposition temperature.
- The host CB [6] which was insoluble in common solvents after forming stable host-guest complexes is found to be soluble in most of the common solvents.
- IR, TG–DTA, XRD studies and mass spectroscopic studies was employed to determine these interactions. We observed a remarkable change in these studies and they reveal stable host-guest complexation has been achieved.
- Cucurbituril forms stable complexes with Lanthanum and Gadolinium, and 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.
- Powder x-ray diffraction denotes the crystalline structure is maintained in the samples from peaks obtained.

Thus the present work provides information about the structural encapsulation of cucurbituril.

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