Synthesis and Characterization of Host-guest Complexes of Cucurbituril with Gadolinum and Lanthanum

T. Jaba Priya¹, R. Wilfred Sugumar² and N. Santhosh

¹Assistant Professor, Department of Chemistry, Madras Christian College, Chennai – 600 059, INDIA.
²Professor and Head (Retd.) Department of Chemistry, Madras Christian College, Chennai – 600 059, INDIA.

email: wilfmcc@gmail.com, nanc_smily@yahoo.com

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ABSTRACT

Cucurbit[6]uril a macromolecule forms robust molecular complexes with metals and organic moieties which have wide applications in adsorbing effluents from industries and as drug delivery vehicles due to their lesser cytotoxicity. In this study, an attempt is made to synthesize and characterize host guest complexes of cucurbituril with metal ions and benzamide using various analytical techniques. Cucurbit[6]uril was mixed with benzamide in 1:1 ratio to form a host-guest molecule. Mixed ligand complexes of cucurbit[6]uril and benzamide with lanthanum and gadolinium were prepared, aqueous HCl was used as the solvent throughout the study.

Physical characteristics of the synthesized samples were studied; there was a notable change in the appearance and decomposition temperature. Cucurbit[6]uril was soluble only in aqueous HCl but the host-guest complexes were soluble in most of the common solvents. Infrared spectroscopy for cucurbit[6]uril and mixed ligand complexes, gives information about the changes in carbonyl absorption band at 1708.08 cm⁻¹ for cucurbit[6]uril. Significant variation was observed for metal complexes i.e. for gadolinium complex it is at 1701.09 cm⁻¹ and for lanthanum complex at 1698.46 cm⁻¹. The IR studies also account for other non-covalent interactions between the atoms in that encircled molecular knots and help in the comparison and variation of cucurbit[6]uril structural feature with its guest benzamide and with encapsulated rare earth metal ions.

The Powder X-ray diffraction studies illustrate sharp peaks in the molecule and the mixed ligand complexes with specific 2θ values, this indicates that crystallinity is maintained in the complexes.
The TG and DTA analysis indicate the loss of water is followed by the decomposition of cucurbit[6]uril. Formation of host-guest complexes is further confirmed by mass spectroscopic studies.

**Keywords**: Cucurbit[6]uril, Host-guest complexes, mixed ligand complexes, benzamide, lanthanum, gadolinium.

**INTRODUCTION**

Supramolecular chemistry, also known as “chemistry beyond the molecule”, focuses on the study of molecular recognition and high-order assemblies formed by noncovalent interactions. Supramolecular systems are made from building blocks that are linked together by noncovalent interactions; they can show stimuli-responsive behavior.\(^1\)

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 cucurbit[n]uril (CB[n]) as a molecular bead.\(^2-7\)

Cucurbit[6]uril (CB[6]) is a hexameric macrocyclic container formed by an acid-catalyzed condensation of glycouril units with formaldehyde. In CB[6], each of the two carbonyl fringed portal at two openings of the host cavitation has six carbonyl oxygen atoms located in a plane which can interact with metal cations in such a way that CB[6] behaves like a macrocyclic ligand thus forming host-guest inclusion complexes. Due to the presence of polarized carbonyl groups, CB[6] forms strong complexes with alkali, alkaline earth and rare earth metal ions and hydrogen bonded complexes with transitional metal ions.\(^8\)

Host-guest chemistry (Figure. 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.](image)

It was shown that the interactions between cucurbiturils are favored by many attractive interactions, CH···O intermolecular hydrogen bonds, which are more efficient for
Cucurbiturils with an even number of glycouril units, like CB[6] and CB[8], than for cucurbiturils with an odd number, such as CB[5] and CB[7].

Cucurbit[6]uril is a potential sorbent for the removal of reactive dyes from solutions and wastewaters. Hydrophobic interactions or the formation of insoluble cucurbituril dye-cation aggregates are responsible for the removal of dyes since adsorption occurs reasonably fast. It can encapsulate metal ions in effluent treatment and its solubility is low in pure water but increases in the presence of salts.

It can also detect environmental contaminations such as nitrates, phosphates, chromate, and heavy metals. It can be used as a drug delivery vehicle.

From this work better knowledge about the host-guest complexation between metals, benzamide and the host macrocyclic cucurbit[6]uril can be attained.

MATERIALS AND METHODS

Chemicals used

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

Preparation of glycouril

CB[6] 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 cucurbit[6]uril

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 crystallization 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 overnight and the 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 cucurbit[6]uril undergoes a step-growth polymerisation that would give a distribution of products, but due to favorable strain and abundance of hydrogen bonding, the CB[6] is the only reaction product isolated after precipitation.

The reaction scheme and the structure of CB[6] are shown in Figure-3 and Figure- 4.

Preparation of host-guest molecule: Host-guest molecule of cucurbit[6]uril with benzamide

20mL solution of 0.05M CB[6] was mixed with 20mL solution of 0.05M benzamide. Aqueous HCl solution was used as the solvent. The final clear solution was mixed thoroughly and allowed to stand above room temperature using a heating mantle. The sample was obtained as a dry powder.

Preparation of complexes

Mixed ligand complex of lanthanum with cucurbit[6]uril and benzamide

20mL solution of 0.05M CB[6] in 2.2 N HCl was mixed with 20mL solution of 0.05M lanthanum nitrate in 2.2 N HCl and 20mL solution of 0.05M benzamide in 2.2 N HCl. The metal and the ligands were in the molar ratio of 1:1:1. The final clear solution was mixed thoroughly and allowed to stand above room temperature using a heating mantle and evaporated slowly. The complex was obtained as a dry powder.

Mixed ligand complex of gadolinium with cucurbit[6]uril and benzamide

20mL solution of 0.05M CB[6] in 2.2 N HCl, 20mL solution of 0.05M gadolinium oxide in 2.2 N HCl and 20mL solution of 0.05M benzamide in 2.2 N HCl were mixed. The final clear solution was mixed thoroughly and allowed to stand above room temperature using heating mantle. The complex was obtained as a dry powder on slow evaporation.

The physical properties like appearance, solubility and decomposition temperature of CB[6], CB[6] with benzamide and the complexes were noted down. The decomposition
results and discussion

The synthesised CB[6] was acquired as a white solid and it was soluble only in aqueous solutions of HCl and was insoluble in common solvents. This solubility nature of CB[6] in aqueous acid solution might be due to a complex forming between the portal oxygen atoms on CB[n] and the hydronium ions in the acid solution. Sharp melting point was not observed for CB[6] but it decomposed at 230°C. The physical characteristics of the synthesized CB[6] and its complexes with respect to appearance, solubility and decomposition temperature is illustrated in Table 1.

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<tbody>
<tr>
<td>Appearance</td>
<td>White solid</td>
<td>Yellow solid</td>
<td>Yellow solid</td>
<td>Pale yellow solid</td>
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<tr>
<td>Solubility</td>
<td>1:4 aqueous HCl</td>
<td>1:4 aqueous HCl</td>
<td>CHCl₃, H₂O, aqueous HCl</td>
<td>CHCl₃, H₂O, aqueous HCl</td>
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<tr>
<td>Decomposition temperature</td>
<td>230°C</td>
<td>240°C</td>
<td>235°C</td>
<td>248°C</td>
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Characterization techniques

The mixed ligand complexes were analysed using IR Spectroscopy, Powder X-ray diffraction studies (Bruker D8 advance), Mass spectroscopy (JEOL GCMATE II GC-MS). Thermogravimetric analysis and differential thermal analysis (SWI TG/DTA, 6200 Thermal analyser) were also carried out.

IR spectra

IR spectrum for the following samples were recorded CB[6](synthesized), host guest molecule of CB[6] with benzamide, mixed ligand complexes of lanthanum with CB[6] and benzamide and mixed ligand complex of gadolinium with CB[6] and benzamide. IR spectrum of the mixed ligand complexes show substantial changes in the carbonyl absorption band when compared with host CB[6] which indicates the formation of host-guest complexes.

Benzamide is a primary amide, two N-H stretches are observed at 3360 and 3170 cm⁻¹, C=O stretching band of benzamide is observed between 1680-1630 cm⁻¹(Figure 4-b) but for inclusion complex of cucurbit[6]uril benzamide N-H stretching is observed at 3129 and 3034cm⁻¹ which is not seen for host cucurbit[6]uril (Figure 4-a). This confirms the formation...
host-guest complex of cucurbit[6]uril-benzamide. Stretching frequencies in the complex are significantly shifted towards lower wave number (Table 2) as a result of M-O coordination. The formation of M-O bond leads to a decrease in the π-character of C=O bond. Coordination of transition metal by the macrocycle CB[n] through hydrogen bonding linking the portal oxygen atoms and coordinated water molecules of the aqua complexes is supported by earlier studies too.

Table 2- IR frequencies of cucurbit[6]uril and its complexes

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<tr>
<td>C=O stretch</td>
<td>1708.08</td>
<td>1680</td>
<td>1709.47</td>
<td>1696.48</td>
<td>1701.09</td>
</tr>
<tr>
<td>Methyl group</td>
<td>1459.53</td>
<td>------</td>
<td>1485.82</td>
<td>1478.07</td>
<td>1494.47</td>
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<tr>
<td>C-N stretching</td>
<td>1370.94</td>
<td>1398</td>
<td>1372.60</td>
<td>1322.55</td>
<td>1326.33</td>
</tr>
<tr>
<td>N-H Stretching</td>
<td>------</td>
<td>3366,3170</td>
<td>3129,3034</td>
<td>3148,3037(weak band)</td>
<td>3137,3047</td>
</tr>
</tbody>
</table>
Figure 4(a)- IR spectrum of cucurbit[6]uril, Figure 4(b)- IR spectrum of benzamide Figure. 4(c)- IR spectrum of cucurbit[6]uril and benzamide.

Figure 5- IR spectrum of mixed ligand complex of lanthanum with cucurbit[6]uril and benzamide.

Figure 6- IR spectrum of mixed ligand complex of gadolinium with cucurbit[6]uril and benzamide.

**Powder x-ray diffraction studies**

Powder XRD studies were done for CB[6] (i), host guest molecule of CB[6] and benzamide (ii), mixed ligand complex of lanthanum with CB[6] and benzamide (iii) and gadolinium with CB[6] and benzamide (iv).

The XRD pattern of inclusion complex and mixed ligand complexes (Figure- 8, 9 and 10) are different from parent compound (Figure 7) and this confirms the formation of inclusion complexes and mixed ligand complexes\textsuperscript{14-16}.

Two peaks are observed at $\theta = 14^\circ$ and $23^\circ$ for the XRD of CB[6] (Figure-7) and the XRD of the host-guest molecule (Figure-8) shows sharp peaks are at $\theta = 24^\circ$ and $34^\circ$. Powder XRD of mixed ligand complex iii shows sharp peaks at $\theta = 16^\circ$, $24^\circ$ and $34^\circ$ (Figure. 9). The powder XRD of mixed ligand complex iv exemplify a sharp peak at $\theta = 35^\circ$ (Figure. 10).
X-ray powder diffraction pattern illustrates many reflections from low to high angle regions envisaging crystalline phase. The sharp peaks in the graph for intensity vs. 2θ values indicate the crystalline structure in the samples.

Fig. 7- Powder XRD of cucurbit[6]uril.

Fig. 8- Powder XRD of host guest molecule of cucurbit[6]uril and benzamide.

Fig. 9- Powder XRD of mixed ligand complex of lanthanum with cucurbit[6]uril and benzamide.
The region between 20-120°C is broad and corresponds to dehydration of cucurbit[6]uril. The corresponding current flow and loss of mass depend on the initial water content of samples.

At temperature 250°C, the values of current flow and loss of mass are respectively 80μV and 20%. So we can conclude that the thermal degradation of cucurbituril starts at 250°C.

The rapid mass loss observed from room temperature up to 120°C is likely due to water and acid removal. A small plateau is reached for CB[6] and may start to slightly decompose before clear macrocycle destruction after 300°C.

The TG analysis of benzamide and cucurbit[6]uril (Figure-12) host-guest molecule shows that decomposition starts at 300°C. The TG analysis of the mixed ligand complexes of gadolinium with cucurbituril and benzamide starts decomposition near 380°C (Figure-13). The TG analysis of the mixed ligand complexes of lanthanum with cucurbituril and benzamide starts decomposition near 400°C (Figure-14). Change in weight % and the temperature shows the formation of complexes and earlier work also confirms from TG/DTA studies that the metal ions coordinate to the carbonyl oxygen atoms at its portals.
The CB[6]’s mass spectroscopic result gives a peak at 996.00 and its molecular weight is 996.824 very close to theoretical simulation (Figure -15). Formation of inclusion and mixed ligand complexes of CB[6] was confirmed with the mass spectroscopic results shown in Figures 16, 17 and 18. The experimental isotopic peak distribution of the mixed ligand complex
iii (1256.8662), and mixed ligand complex iv (1275.2110) is close to the theoretic simulation with molecular weight of 1256.865 for lanthanum and 1275.2111 for gadolinium complexes.

Formation of inclusion complexes is confirmed directly by using the mass spectroscopy. All the experimental results for the m/z values and the isotopic peak distributions of the complexes are the same as those simulated from the molecular formulae.

Figure 15- Mass spectrum of cucurbit[6]uril.

Cucurbit[6]uril is a heavier particle and so its deflection is small and is at 996.00.

Figure 16- Mass spectrum of cucurbit[6]uril and benzamide.

Cucurbit[6]uril and benzamide inclusion complex is a heavier particle and so its deflection at 1117.9610.
Mixed ligand complex of **iii** is a heavier particle and so its deflection is at 1256.8662.

Mixed ligand complex of **iv** is a heavier particle and so its deflection is at 1275.2110.

**CONCLUSION**

The present work restates the uniqueness of CB[6] as a host macromolecule. The following important aspects emerge from the studies.

The large modulation in physical characteristics of cucurbit[6]uril 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 of host-guest complexes. The host CB[6] which was insoluble in common solvents, was found to be soluble in most of the common solvents, after forming stable host-guest complexes. IR, TG–DTA, XRD and mass spectroscopic studies reveal the formation of stable host-guest complexes. The stability is largely accredited
to the strong interaction of carbonyl oxygen donor atoms of CB[6] with the cations and from the results we conclude that CB[6] forms stable complexes with lanthanum and gadolinium, and IR spectroscopic studies reveal the presence of such polar oxygen portals.

The TG and DTA analysis show the loss of water which is followed by the decomposition of cucurbit[6]uril. The studies also reveal that change in weight% and the temperature show the formation of complexes and also confirm the decomposition temperature of the samples. Powder x-ray diffraction pattern denote maintenance of the crystalline structure in the complex. Formation of inclusion complexes is further confirmed using mass spectroscopy. All the experimental results for the m/z values and the isotopic peak distributions of the complexes are the same as those simulated from the molecular formulae.

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