

## Cucurbituril as a host molecule for the complexation of cations and acetamide in aqueous solution

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### ABSTRACT

Mixed ligand complexes of Cobalt and Nickel with acetamide and cucurbituril as host molecule were prepared and characterized using UV-Visible, IR and XRD techniques. These mixed ligand complexes are quite stable and this stability was largely attributed to the strong interaction of carbonyl oxygen donor atoms of cucurbituril with the cations. From the increase in absorbance in UV-Visible region the interaction between metal and host molecule was proved. The IR spectra showed significant variations, especially in  $3500\text{cm}^{-1}$  region and between  $1700$  and  $1200\text{cm}^{-1}$  indicating prevalence of enhanced hydrogen bonding. Cucurbituril cobalt benzamide complex showed two sharp peaks at  $2\theta = 31.7$  and  $25.89$ . This indicates that crystalline structure is still maintained in some complexes.

**Key words :** Cucurbituril, Host-guest complex, Supramolecular chemistry, Macrocyclic molecule

The area of supramolecular chemistry has established itself as an emerging field in chemistry (Lehn, 1995; Vogtle, 1989; Balzani and De.Cola, 1992). Cucurbiturils (Fig. 1) are macrocyclic molecules consisting of glycouril repeat units. These compounds are particularly interesting to chemists because they are molecular containers that are capable of binding other molecules within their cavity. The name cucurbituril is derived from the resemblance of this molecule with the pumpkin of the family *Cucurbitaceae*. The cavity of Cucurbit[6]uril has nanoscale dimensions (Jason Lagona *et al.*, 2005) with an approximate height of 9.1pm, outer diameter 5.8pm and inner diameter 3.9 pm.

Cucurbituril is a rigid molecule and possesses a hydrophobic cavity. At each entrance to the cavity, six polar carbonyl groups are located. These conditions are ideal for complexation of positively charged organic molecules with hydrophobic groups. So, the complexation of a large number of different ammonium ions by cucurbituril were studied first (Mock and Shih, 1983; Behrend *et al.*, 1905; Mock and Shih, 1988; Meschke *et al.*, 1997; Buschmann *et al.*, 1998a). Cucurbituril is also able to bind alkali and alkaline earth cations (Buschmann *et al.*, 1992; Hoffmann *et al.*, 1994; Buschmann *et al.*, 1998b). Cucurbituril is not soluble in many common solvents but it is found to be soluble in ionic and acidic solutions (Mock and Shih, 1986).

Host guest chemistry (Fig. 2) 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. As a general rule, a host is chosen to be complementary to a particular guest such that in solution, a complex is formed spontaneously.

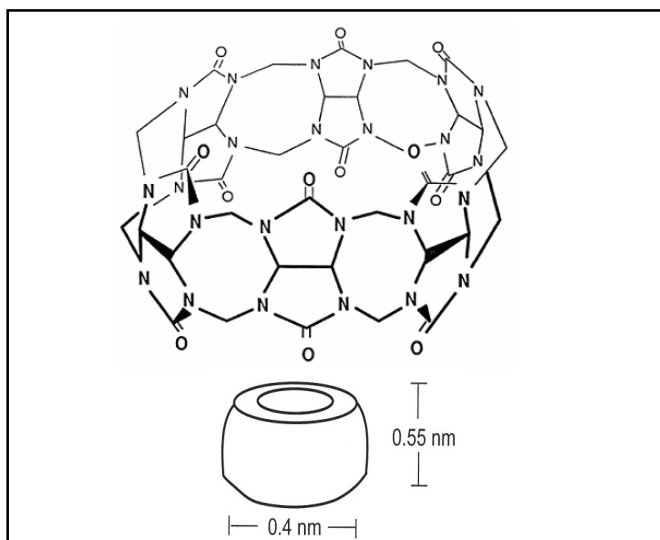


Fig. 1 : Structure of Cucurbituril

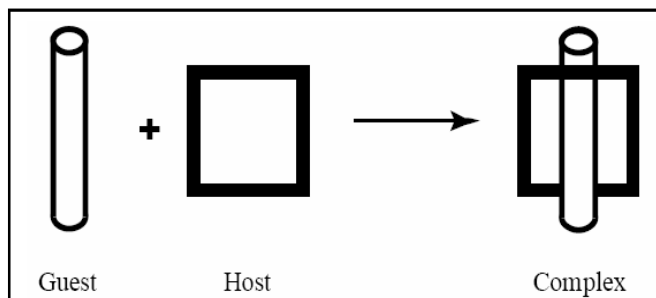


Fig. 2 : Host guest chemistry

The extent of host guest complex formation depends on various factors like the affinity of the host for the guest, the affinity of both the host and the guest for the solvent and the rate of complex dissociation.

The present work aims at the complexation of metal cations Nickel, Cobalt and an organic moiety acetamide with cucurbituril as a host molecule.

## MATERIALS AND METHODS

Cucurbituril is synthesized following the standard method found in the literature (Kim *et al.*, 2001).

### Synthesis of complex of Cobalt with cucurbituril:

10mL solution of cucurbituril in aqueous HCl was added with 5mL of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  dissolved in water. The amount of the ligand was taken in excess. The final blue solution was mixed thoroughly and allowed to stand at room temperature. Slow evaporation was carried out by keeping the mixture on a water bath. After two days, shiny blue crystals separated out. The crystals obtained were filtered off and dried.

### Synthesis of complex of Nickel with cucurbituril:

Similar steps as given in (i) were followed, using  $\text{NiSO}_4$  instead of Cobalt chloride. After two days, yellowish crystals separated out. The crystals obtained were filtered off and dried.

### Synthesis of mixed ligand complex of Cobalt with acetamide and cucurbituril:

10mL solution of cucurbituril in aqueous HCl solution was added to a mixture of 5mL of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and 5 mL of acetamide in water. The final blue solution was mixed thoroughly and allowed to stand at room temperature. Slow evaporation was carried out by keeping the mixture on a water bath. After two days, blue crystals separated out. The crystals obtained were filtered off, dried and the yield of the complex was found to be 70%.

### Synthesis of mixed ligand complex of Nickel with acetamide and cucurbituril:

Similar steps as in (iii) were followed using Nickel sulphate solution. After two days, yellowish green crystals separated out. The crystals obtained were filtered off and dried and the yield of the complex was 48.8%.

UV-visible absorption spectra of the samples were recorded keeping the concentration of metal and acetamide constant and varying the concentration of cucurbituril. All UV-visible spectrophotometric measurements were carried out using Perkin Elmer, Lambda 35, UV-Vis spectrophotometer. IR Spectroscopy

was used to substantiate the formation of the product. IR measurements were carried out using Perkin Elmer, FT-IR Spectrometer, Spec RX1. For X-ray diffraction study, powder specimens were prepared by placing a powder in a non-reflective diffractive plate. The instrument used is Philips Xpert diffractometer (Netherlands).

## RESULTS AND DISCUSSION

Cucurbituril was obtained as a white solid in 30% yield. The sample was found to be soluble only in aqueous solutions of HCl and was insoluble in common solvents like water, acetone, chloroform, 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 Q(n) and the hydronium ions in the acid solution (Kim *et al.*, 2001). Cucurbituril as well as the complexes did not have a sharp melting point but underwent decomposition.

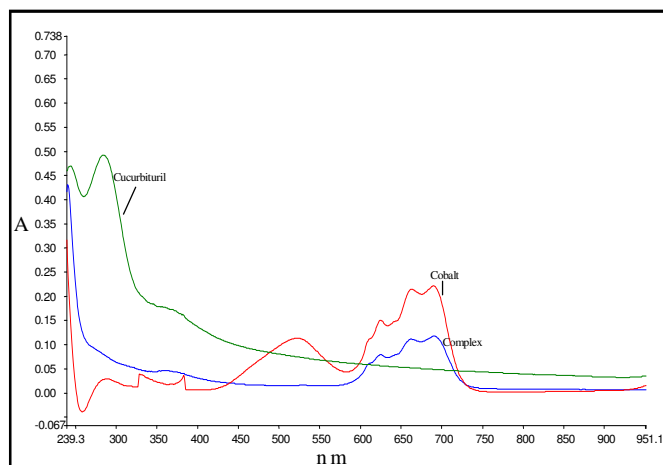
**Table 1 : Decomposition temperature of cucurbituril and its complexes**

Sr. No.	Sample	Decomposition temperature (°C)
1.	Cucurbituril	247
2.	Mixed Nickel complex with cucurbituril	200
3.	Mixed complex of Cobalt with cucurbituril and acetamide	260
4.	Mixed complex of Nickel with cucurbituril and acetamide	140

### Characterisation of cucurbituril:

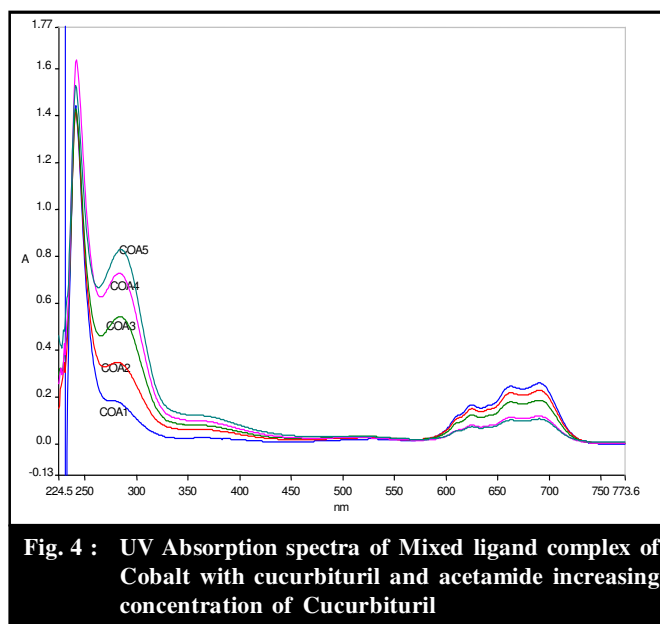
#### UV-Visible spectroscopy:

The UV-Visible spectrum of cucurbituril showed a characteristic absorption peak at 280 nm (Fig. 3). The



**Fig. 3 : uv-visible spectra of Mixed ligand complex of Cobalt with cucurbituril and acetamide**

mixed ligand complex of cucurbituril and acetamide with Cobalt is obtained as intense blue crystals. The yield of the complex is 70%. The substance however does not show a sharp melting point. It undergoes decomposition at 260°C. The UV visible spectrum indicated an absorption peak around 680nm and a reduction in absorption around 280nm was observed when compared with the spectrum of free cucurbituril. The variation in UV-Visible spectra of free cucurbituril and complexed cucurbituril are shown in Fig. 4. It is clear that the wavelength of absorption increased upon complexing with transition metal ions.



**Fig. 4 :** UV Absorption spectra of Mixed ligand complex of Cobalt with cucurbituril and acetamide increasing concentration of Cucurbituril

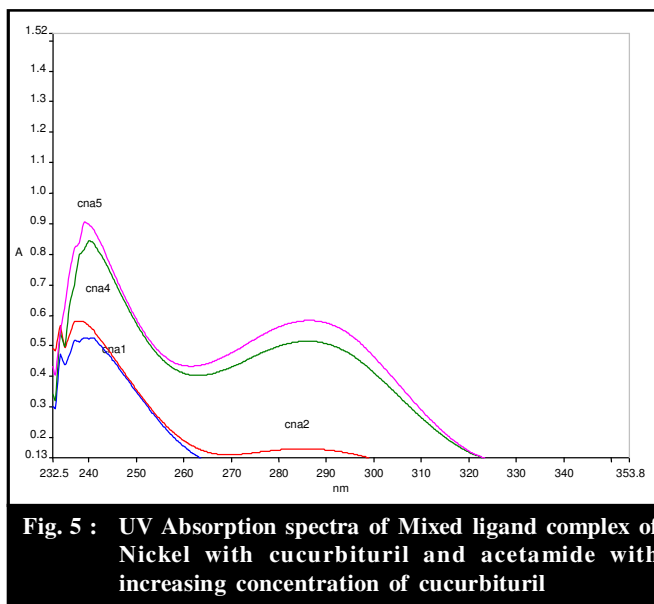
The UV-Visible spectra were also obtained by changing the composition ratio of cucurbituril to cobalt and acetamide from 1:1:1 to 1:6:1 (Metal:Q:A). There was an enhancement in the absorbance from CoA1 to CoA5 (Cobalt:Cucurbituril:Acetamide) Similar trends were observed in earlier studies with other cucurbituril complexes (Xuyang *et al.*, 2002).

This absorption change was used to calculate the equilibrium constants for these complexes. In the present study, we used the spectra to identify the interaction between metal and host molecule.

Fluorescent green crystals of the Nickel complex with cucurbituril and acetamide were obtained in 48.8% yield. Sharp melting point was not obtained and the substance decomposed at 200°C. The UV-visible spectrum indicated an absorption peak around 410 nm and there was a reduction in absorption around 240nm when compared with the spectrum of free cucurbituril. The variation in UV-visible spectra of free cucurbituril

and complexed cucurbituril are shown in Fig. 5. It is clear that UV-visible absorbance increased upon complexing with transition metal ions.

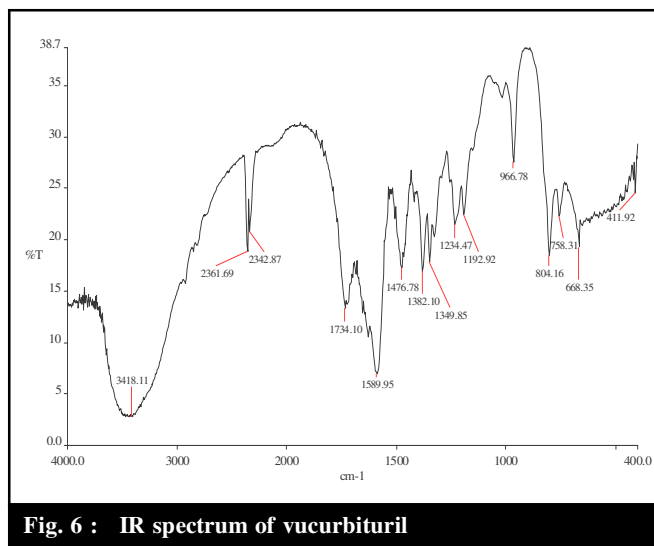
The UV-visible spectra were also obtained by changing the composition ratio of cucurbituril to nickel and acetamide from 1:1:1 to 1:5:1 (Metal:Q:A). There was an enhancement in the absorbance from CNA1 to CNA5. (C-Cucurbituril,N-Nickel,A-Acetamide)



**Fig. 5 :** UV Absorption spectra of Mixed ligand complex of Nickel with cucurbituril and acetamide with increasing concentration of cucurbituril

### IR Spectroscopy:

The IR spectrum of the cucurbituril sample is given in Fig. 6. It shows an absorption peak, which is not very broad, at 3418.11 cm<sup>-1</sup>. Earlier reports have also indicated the O-H, stretching bands at 3500-3200 cm<sup>-1</sup>. The appearance of band at such lower frequencies indicates



**Fig. 6 :** IR spectrum of cucurbituril

the involvement of hydrogen bonding. The non bonded free O-H stretching frequencies appear near  $3600\text{cm}^{-1}$  as a sharp peak.

The sharp peak at  $1589.95$  is indicative of  $\nu_{\text{C=O}}$ . The shift to lower frequency is indicative of more single bond character to  $\text{C-O}$  bond. Thus, cucurbituril has higher negative charges on the oxygen atoms of portals making it earlier for cucurbiturils to form stable adduct with positively charged ions. The IR spectra showed significant variations, especially in  $3500\text{cm}^{-1}$  region and between  $1700$  and  $1200\text{cm}^{-1}$  indicating prevalence of enhanced hydrogen bonding (Fig. 7). Though earlier studies indicate that hydrogen bonding was less important to complex formation than ion-dipole interactions, their role in complex formation cannot be completely neglected in the present

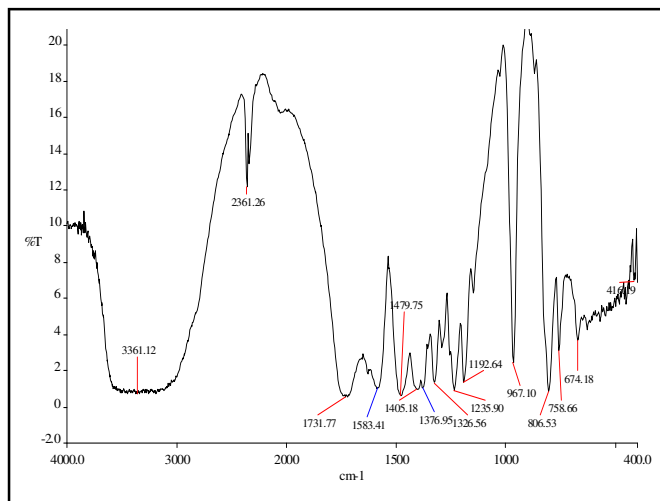


Fig. 7 : IR Spectrum of mixed complex of Cobalt with cucurbituril and acetamide

study. Previous studies support this proposition and have suggested the formation of coordination of transition and post 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. (Fig. 8 and Fig. 9).

The more electropositive and large ions of alkali metals form bonds with the macrocyclic ligand through ion dipole interactions. Transition metals form smaller ions and they prefer covalent bonding. Higher charge and smaller size of transition metal cations enhance the acidity of coordinated water in the aqua ions. This acidity allows the formation of strong hydrogen bonds between the polar  $\text{C=O}$  groups of cucurbituril and coordinated water molecules

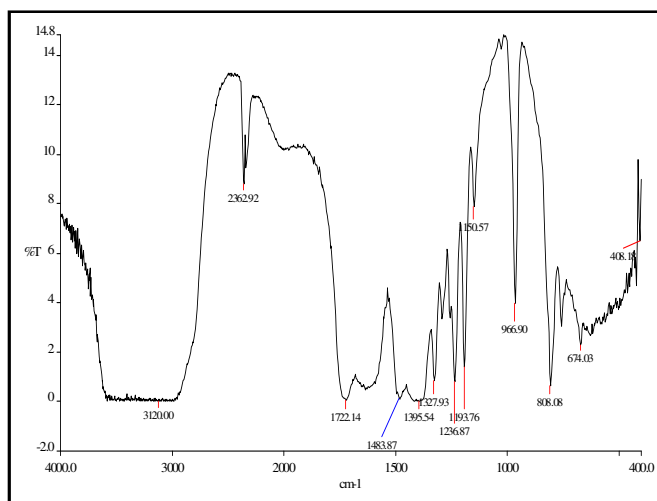


Fig. 8 : IR Spectrum of mixed ligand complex of nickel with cucurbituril and acetamide

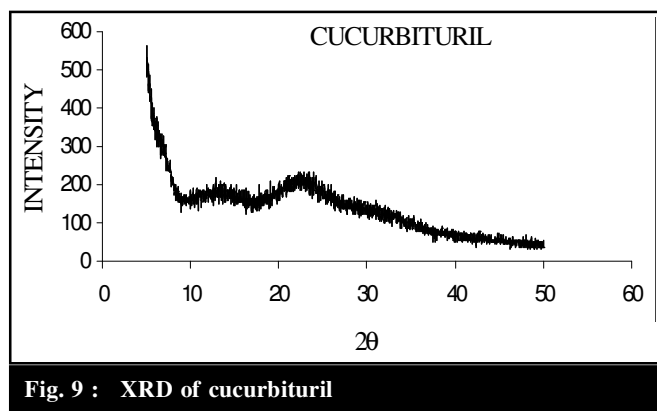


Fig. 9 : XRD of cucurbituril

#### X-ray Powder diffraction (XRD):

Fig. 10 and 11 show the XRD pattern of mixed ligand complex of Cobalt with cucurbituril and mixed ligand complex of Nickel with cucurbituril and acetamide. No Sharp peaks are reflected in the pattern of complexes and probably the complexes are non-crystalline in nature. CB[6] has crystal composition as indicating two sharp

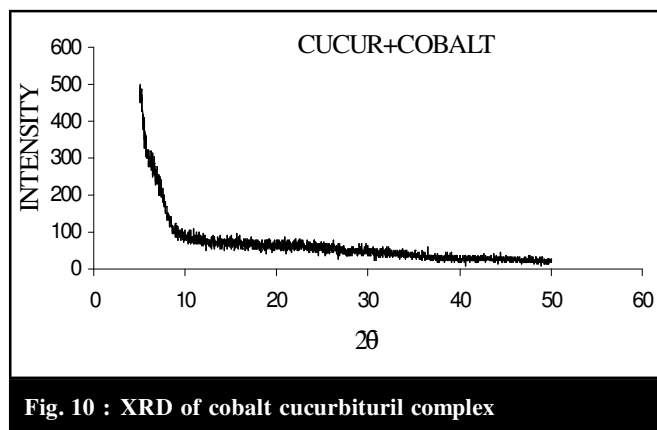
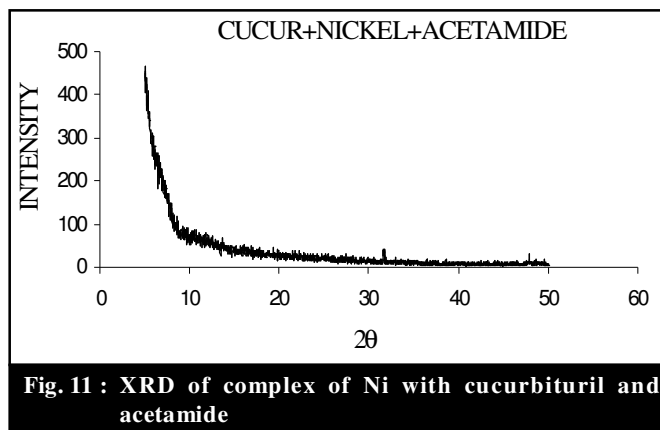
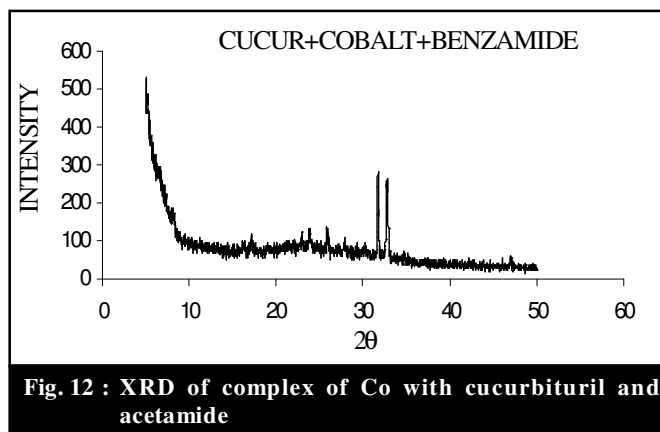


Fig. 10 : XRD of cobalt cucurbituril complex



peaks at  $2\theta=23.2$  and  $31.2^\circ$ . On the other hand, cucurbituril-cobalt- benzamide complex showed two sharp peaks at  $2\theta =31.7, 25.89$  (Fig. 12). This indicates that crystalline structure is still maintained in some complexes.



### Conclusion:

The present studies reiterate the versatility of cucurbituril as a host macromolecule. The following important aspects emerge from the studies:

Cobalt and Nickel cations form stable complexes with cucurbituril and acetamide 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. The synthesis of complexes is made possible through the geometric and functional complementarity of portal oxygen atoms cucurbituril and water molecules of metal salts ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NiCO}_3 \cdot 6\text{H}_2\text{O}$ ).

Host and guest molecules should possess complementary sizes to form stable complexes. The

binding forces in such complexes could be either hydrogen bonds or ion dipole interactions with the oxygen in carbonyl portals of cucurbituril. The guest molecule has affinity to the hydrophobic cavity of cucurbituril. Amides were chosen as guests because they have the capability to bind, as they are relatively small. UV-Visible absorption, IR and XRD techniques are employed to determine these interactions.

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