

Good afternoon, ladies and gentlemen. I would like to present you the recent advances of our laboratory in the field of inclusion chemistry of macrocyclic host cucurbit[8]uril.

Cucurbit[8]urils (further we'll say CB[8]) is a barrel-shaped molecule comprising 8 glycoluril units connected via 16 methylene moieties. CB[8] has a highly symmetrical rigid structure (oppositely to cyclodextrins and calixarenes) with two identical hydrophilic carbonyl-fringed portals and hydrophobic inner cavity of approximately 9 angstroms diameter. This cavity displays strong affinity towards neutral and cationic guests such as organic molecules or metal-organic complexes.

We have used transition metal complexes as guests, containing aliphatic amines as ligands. Three approaches to synthesis of such inclusion compounds were developed.

The first method, proposed by prof. Kim (S. Korea), represents the reaction between excess of metal aquo-complex and desired ligand, which is already encapsulated in the host cavity. This approach was successful for obtaining the CB[8] inclusion compound of cationic square-planar nickel(II) complex with such well-known cyclic tetradentate ligand, called cyclam. The compound has this chemical composition.

The X-ray crystal structure of the substance revealed CB[8] molecules occupied by the nickel complex as a guest. Interestingly, the plane based on four nitrogen atoms of the guest complex is significantly inclined towards the equatorial plane of the host (round 70 degrees). The possible explanation is that the cyclam complex has large size and remarkable structural rigidity. So it prefer such orientation within the cavity, as to be less sterically constrained.

Electrospray mass spectrum of this compound shows unequivocally, that the metal complex remains encapsulated into CB[8] in aqueous solution. The initial Ni-cyclam complex in a form of perchlorate salt and its inclusion compound exhibit identical absorption spectra, which means that the electronic structure of the guest remains intact upon inclusion.

It is remarkable, that inside the CB[8] cavity the abovementioned complex of **divalent** nickel may undergo one-electron chemical oxidation with the use of acidic cerium 4 solution. This leads to precipitation of stable inclusion compound with **trivalent** Ni-cyclam guest complex. According to X-ray structural data, oxidation didn't cause any significant changes to configuration and dimensions of the first and second coordination spheres of nickel atom, so was for packing mode.

Electron spin resonance studies confirmed undoubtedly the presence of low-spin trivalent nickel with  $d^7$  configuration in the inclusion compound. The ESR spectrum revealed hyperfine structure, which is consistent with square-planar nitrogens environment of nickel atom. This environment is exceptionally unusual for this oxidation state of nickel, because commonly free Ni(III)-cyclam complexes are octahedral with axial positions occupied by solvent molecules or counterions. So inclusion into CB[8] may function as a novel way to obtain and stabilize metal complexes with unique oxidation states and unusual coordination environments. This is due to steric constraints, imposed by size and shape of CB[8] cavity.

The second approach to synthesize metal complex inclusion compounds implies a conventional direct method "host + guest". This method failed to give the Ni(II)(cyclam) inclusion compound, because the complex is quite rigid to penetrate through more narrow portals into the cavity of barrel. But the direct reaction is convenient for obtaining the series of CB[8] inclusion compounds with less bulky trans-bis-ethylenediamine complexes of nickel(II), copper(II) and cobalt(III), as guests.

We should mention the well-known fact, that the original trans-complex tends to isomerise rapidly into cis-form when heated in solution. It is accompanied by the color change from green to dark-purple. However, upon the dissolution of CB[8] in this mixture of isomers followed by 2hours refluxing **the unprecedented selective encapsulation of only trans-complex** was observed. This resulted in precipitation of only green crystals, containing trans-isomer included into CB[8] cavity with quantitative yield. This remarkable selectivity may be due to excellent matching between geometries of the host cavity and trans-guest rather than for cis-complex.

When comparing guests orientations in the CB[8] cavity, some differences should be mentioned between those of copper, nickel and cobalt complexes. In the case of copper and nickel compounds the plane, based on four nitrogen atoms of the guest, almost coincides the equatorial plane of CB[8]. Their axial aquo-ligands lay at portals. On the contrary, **in the cobalt compound** the nitrogens plane is tilted **orthogonally** to CB[8]. So its axial chloro-ligands are also situated within the cavity. This orientational

diversity may be explained implying that the guests have different sizes and coordinated water molecules display weaker affinity towards hydrophobic CB[8] cavity than chloro-ligands.

In the case of small copper complex its inclusion compound is stable only in solid state and dissociates upon dissolution in water. When more sizeable nickel complex is encapsulated, its solution is stable, which is in correspondence with ESI-MS data. However, it can be substituted by other guest molecules, for example, 4-cyanopyridine, leading to inclusion compound with stoichiometry guest to host 2 to 1.

And, finally, the most stable among the series both in solution and in solid state is the cobalt compound. In fact, while isomerization reaction is favourable for free trans-complex upon slight heating, it requires severe conditions for the encapsulated one and results in dissociation into free CB[8] and free cis-complex. The reasons for it seem to be originated from the structure of the inclusion compound. The distances cobalt-ligand become shorter upon inclusion. This was evidenced in solid state by X-ray crystallography and in aqueous solution by significant hypsochromic shifts of absorption bands belonging to guest complex.

The solution proton NMR spectroscopy revealed that the resonances of ethylenediamine were remarkably upfield-shifted upon inclusion, which means a considerable host-guest interaction.

Thermogravimetric data comparison for inclusion compound, free cobalt complex and pristine CB[8] hydrate showed that the decomposition temperature for encapsulated guest **is for almost 140 degrees higher** than for free cobalt complex. It means undoubtedly, that inclusion into the cavity dramatically stabilizes the guest cobalt complex towards thermolysis in solid state.

And, finally, the third approach to synthesis of metal complex inclusion compounds refers to the guest substitution within the host cavity. The possible driving force for the substitution is different affinity of various guest molecules towards the interior of the host.

This method was successfully applied to obtain the inclusion compound of such multi-ligands copper complex with host-guest stoichiometry 2 to 1. We treated continually the solution of Ni-cyclam complex, encapsulated in the CB[8], with excess of copper complex. It resulted in extrusion of cyclam complex followed by inclusion of copper complex into CB[8] cavity. The crystal structure of the compound is particularly interesting. Copper atoms with their closest environment of diethylenetriamine molecule and aqua-ligand are situated at the exterior of CB[8] molecule, above carbonyl portals. Meanwhile, the cavity of macrocycle is occupied by two dipyridyl ligands, which are oriented to each other in a parallel mode, allowing pi-pi interactions. These interactions may stabilize the structure and serve as one of driving forces responsible for the formation of this inclusion compound. The additional stabilizing factor is a hydrogen bonding between apical aqua-ligand of one guest complex and pyridine nitrogen atom of another complex, leading to the formation of such a dimer in the CB[8] cavity. Solid state ESR-studies gives the g parallel value, which is slightly higher than for free guest complex. This is consistent with slight elongation of the bond between copper and apical aqua ligand upon inclusion.





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Tatiana:

Vot nazvanie:  
V.P. Fedin, T.V. Mitkina, O.A. Gerasko, Cucurbit[n]urils and metal complexes: supramolecular adducts, complexes and inclusion compounds

Posilaju tezisi, chto bili v Moskve, vozmite po vkljucheniju, dobavte po portalam.

Posilaju pravila.  
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Spasibo,

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