# Synthesis and guest exchange reactions of inclusion compounds of cucurbit[8]uril with nickel(II) and copper(II) complexes

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Inclusion compounds of the macrocyclic cavitand cucurbit[8]uril (CB[8]) with the nickel(II) complex, {*trans*-[Ni(en)$_2$(H$_2$O)$_2$]@CB[8]}Cl$_2$·23.5H$_2$O, the copper(II) complex, {2[Cu(dien)(bipy)(H$_2$O)]@CB[8]}(ClO$_4$)$_4$·11H$_2$O, and the organic molecules, 2(pyCN)@CB[8]}·16H$_2$O and {2(bpe)@CB[8]}·17H$_2$O, where bipy is 4,4´-bipyridyl, pyCN is 4-cyanopyridine, and bpe is *trans*-1,2-bis(4-pyridyl)ethylene, were synthesized. The inclusion compounds with organic molecules were synthesized starting from inclusion compounds of cucurbit[8]uril with cyclam and ethylenediamine complexes of copper(II) and nickel(II) by the guest exchange method, which is based on the replacement of one guest with another in the cavity of the cavitand The resulting compounds were characterized by X-ray diffraction, ESR, $^1$H NMR, IR, and electronic absorption spectroscopy, and electrospray mass spectrometry. Photochemically induced [2+2]-cycloaddition of two 1,2-bis(4-pyridyl)ethylene molecules included in cucurbit[8]uril was studied.

**Key words:** nickel, copper, cucurbituril, complexes, supramolecular compound, X-ray diffraction study.

Inclusion compounds of organic macrocyclic cavitands with metal complexes is a new rapidly developing field of supramolecular chemistry. Inclusion of transition metal complexes in organic cavitands gives rise to a unique microenvironment of the metal ion similar to that observed in metalloenzymes. Hence, these compounds hold promise as model systems in studies of small molecule activation and metal ion transport in biological systems. Inclusion compounds of metal complexes can find use in the design of a new generation of prolonged-action pharmaceuticals based on biologically active metal compounds encapsulated within the cavity of a host, which prevents the guest complex from rapid decomposition and performs transport of the active component in organisms.[1—6]

Studies of inclusion compounds of cucurbit[*n*]urils with metal complexes have been started in the last few years,[1—3,7,8] although encapsulation of neutral organic molecules and organic cations in these cavitands has been investigated in depth.[9—13] Cucurbit[*n*]urils (CB[*n*]) belong to a family of macrocyclic molecules of composition $C_{6n}H_{6n}N_{4n}O_{2n}$ ($n$ = 5—10) consisting of *n* glycoluril fragments linked to each other by 2*n* methylene bridges.[14,15] Cucurbit[*n*]urils have a rigid (unlike such molecular containers as calixarenes and cyclodextrins) hydrophobic inner cavity, which is of importance for selective inclusion of guests of particular size. Guests can enter the cavity through two hydrophilic portals formed by *n* carbonyl groups.

Several inclusion compounds of cucurbit[*n*]urils with metal complexes have been structurally characterized. These are copper(II) and zinc(II) complexes with cyclam (1,4,8,11-tetraazacyclotetradecane) and cyclene (1,4,7,10-tetraazacyclododecane) encapsulated in the cavity of cucurbit[8]uril (CB[8]), [1] the inclusion compound of CB[7] with the [*cis*-SnCl$_4$(H$_2$O)$_2$] complex,[8] and inclusion compounds of CB[8] with the [Ni(cyclam)]$^{2+}$ and [*trans*-Cu(en)$_2$(H$_2$O)$_2$]$^{2+}$ complexes, whose synthesis has been described in our recent publication.[16] Studies of aqueous solutions by $^1$H NMR spectroscopy showed that the ferrocenium and cobalticenium cations form stable inclusion compounds with cucurbit[7]uril, which exhibit unusual electrochemical properties. However, these compounds were not isolated in the solid state.[7] The inclusion compound of cucurbit[7]uril with oxaliplatinum (oxalato-1,2-diaminohexaneplatinum(II), [Pt(1,2-(NH$_2$)$_2$C$_6$H$_{10}$(C$_2$O$_4$)]) has antitumor activity and is covered by patents.[2,3]

Hence, it is of interest to synthesize new inclusion compounds of macrocyclic hosts with metal complexes and examine the influence of the microenvironment of the cavitand on the reactivity of encapsulated guests.

In the present study, we synthesized a new inclusion compound of the macrocyclic cavitand cucurbit[8]uril with the nickel(II) complex {*trans*-[Ni(en)$_2$(H$_2$O)$_2$]@@CB[8]}Cl$_2$·23.5H$_2$O (**1**) and performed the guest exchange reactions starting from CB[8] inclusion com-

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pounds of copper(II) and nickel(II) complexes to prepare the {2(pyCN)@CB[8]} • $16H_2O$ (**2**), {2(bpe)@CB[8]} • $17H_2O$ (**3**) and {2[Cu(dien)(bipy)($H_2O$)]@@CB[8]}$(ClO_4)_4$ • $11H_2O$ (**4**) complexes (pyCN is 4-cyanopyridine, bpe is *trans*-1,2-bis(4-pyridyl)ethylene, dien is diethylenetriamine, and bipy is 4,4´-bipyridyl).

## Results and Discussion

**Inclusion compound {*trans*-[Ni(en)$_2$($H_2O$)$_2$]@@CB[8]}$Cl_2$ • 23.5$H_2O$ (1).** The inclusion compound of cucurbit[8]uril with the *trans*-diaqua-bis-ethylenediaminenickel(II) cation of composition {*trans*-[Ni(en)$_2$($H_2O$)$_2$]@CB[8]}$Cl_2$ • 23.5$H_2O$ (**1**) was prepared according to the "guest + host" scheme by refluxing cucurbit[8]uril in an aqueous solution of an eightfold molar excess [Ni(en)$_2$$Cl_2$]. The analogous synthesis of the copper(II) compound {*trans*-[Cu(en)$_2$($H_2O$)$_2$]@@CB[8]}$Cl_2$ • $17H_2O$ has been described in our earlier publication.[16] This compound was obtained as pale-lilac prismatic crystals soluble in hot water.

X-ray diffraction study demonstrated that the crystal structure of **1** consists of cucurbit[8]uril molecules containing the *trans*-$[Ni(en)_2(H_2O)_2]^{2+}$ cations in the inner cavities (Fig. 1, *a*). The first coordination sphere of the nickel atom can be described as an octahedron formed by four nitrogen atoms of two ethylenediamine molecules, which lie in a single plane with the central atom and form a rectangle, and two axial $H_2O$ ligands located virtually perpendicular to the $NiN_4$ plane (85°). In molecule **1**, the Ni—N distances are 2.100(4) and 2.101(5) Å and the Ni—O distance is 2.129(3) Å. The $NiN_4$ plane does not coincide with the equatorial plane of cucurbit[8]uril and is inclined to the latter at an angle of ~28° (see Fig. 1, *b*). In the structure of **1**, a substantial ellipsoidal distortion of the CB[8] molecule is observed. The difference between the largest and smallest diameters (distance between the opposite carbon atoms of the CH groups) $\Delta_{CH}$ is 2.92 Å. For comparison, the $CuN_4$ plane in the inclusion compound of the analogous copper(II) complex coincides with the equatorial plane of CB[8], $\Delta_{CH}$ = 0.49 Å.[16] These structural features of molecule **1** are attributed to a poorer size matching between the nickel complex and the cavity of the host molecule compared to the copper complex (Ni—N distances are 0.1 Å longer than Cu—N distances). The cavitand molecule in complex **1** is the most deformed of all known inclusion compounds of CB[8] with both other metal complexes and organic molecules available in the Cambridge Structural Database (October 2004 release).[17]

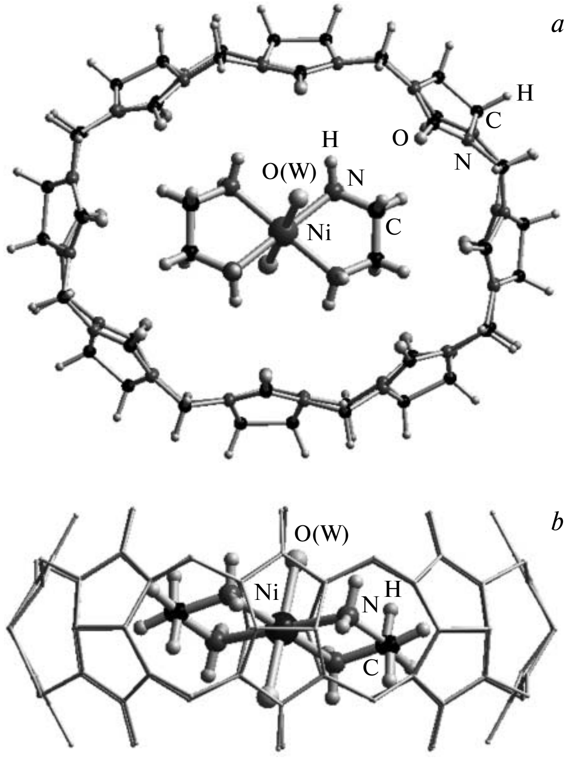


**Fig. 1.** Structure of the inclusion compound {*trans*-$[Ni(en)_2(H_2O)_2]$@CB[8]}$^{2+}$ (**1**): *a*, the top view; *b*, the side view (hydrogen atoms of cucurbit[8]uril are omitted).

The crystal packing of compound **1** has an island motif. The cucurbit[8]uril molecules are packed (Fig. 2) so that one-dimensional channels are formed along the *c* axis. The channels are filled with water molecules of crystallization and chloride anions. The channel diameter is ~5.8 Å. Removal of water of crystallization is accompanied by decomposition of crystals of **1**.

The electrospray mass spectrum of an aqueous solution of **1** unambiguously proves encapsulation of the metal complex in cucurbit[8]uril in solution because the spectrum has an intense peak of the $[CB[8] + Ni(en)_2]^{2+}$ ion.

Solutions of [Ni(en)$_2$$Cl_2$] and compound **1** in $D_2O$ were studied by $^1H$ NMR spectroscopy. The $^1H$ NMR spectrum of the starting diamagnetic [Ni(en)$_2$$Cl_2$] complex shows only one sharp resonance for the protons of the $CH_2$ group of ethylenediamine, whereas the spectrum of inclusion compound **1** has signals for the protons of the CH and $CH_2$ groups of cucurbit[8]uril, which are strongly broadened up to a loss of the fine structure, along with a very broad signal at $\delta \approx 3.2$, which is assigned to the methylene protons of the encapsulated nickel complex. A broadening of the signals of cucurbit[8]uril is indicative of symmetry distortion of the host molecule upon encapsulation (which was observed in the solid phase as well) and the presence of a strong interaction between the host and guest molecules in solution. A broadening of the signals of the host can be attributed to paramagnetism of the octahedral *trans*-$[Ni(en)_2(H_2O)_2]^{2+}$ complex.[18]

Earlier, it has been noted[19—21] that encapsulation of complexes in such macrocyclic cavitands as cyclodextrins enhances the thermal stability of guests. We performed

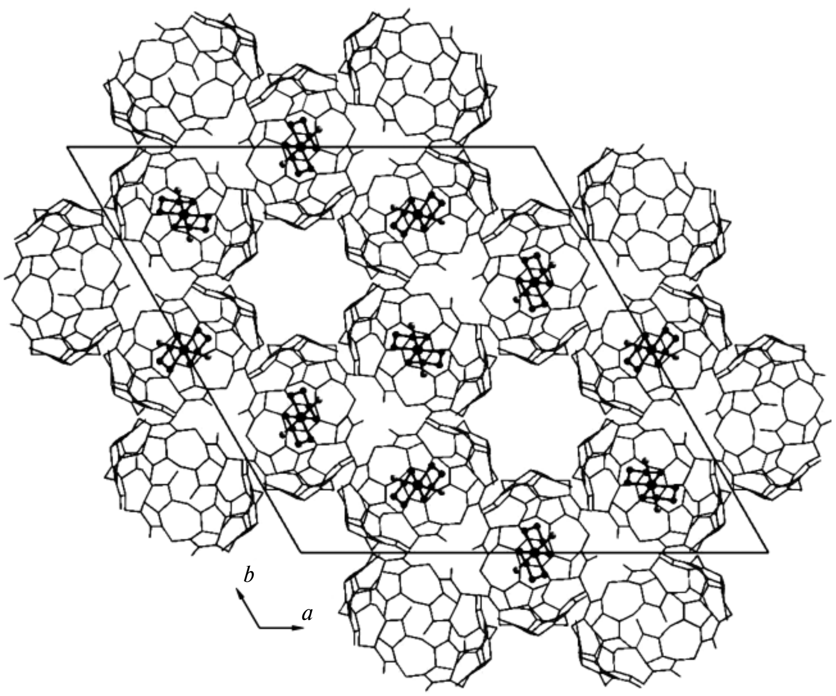


**Fig. 2.** Crystal packing of compound **1** projected onto the *ab* plane. The guest complexes are represented by black spheres. The hydrogen atoms, water molecules of crystallization, and chloride anions are omitted.

thermogravimetric analysis (in air) of solid samples of compound **1** and cucurbit[8]uril hydrate (Fig. 3). In the first step of decomposition (heating to 150 °C), these compounds lost all water molecules of crystallization. Decomposition of inclusion compound **1** in the second step of thermolysis started at the same temperature as decomposition of free cucurbit[8]uril (~350 °C). For comparison, Fig. 3 shows data on thermolysis of the free *trans*-[Ni(en)$_2$Cl$_2$] complex under the same conditions, whose decomposition started at a temperature 70 °C lower than compound **1**.

Compounds prepared by encapsulation of the *trans*-[Ni(en)$_2$(H$_2$O)$_2$]$^{2+}$ complex and the copper(II) and nickel(II) complexes with cyclam, which have been synthesized earlier,[1,16] in the cavity of cucurbit[8]uril are readily soluble in water. Hence, these compounds can be used for the preparation of new inclusion compounds containing organic molecules as guests. In an aqueous solution, inclusion compounds with metal complexes are involved in guest exchange reactions, in which the complex (G1) is displaced from the cavity of the cavitand and is replaced with two other guest molecules (G2). This makes it possible to prepare the inclusion compounds {2G2@CB[8]} in homogeneous conditions. The latter compounds cannot be synthesized by the direct "guest + host" method because of poor solubility of CB[8] in water.

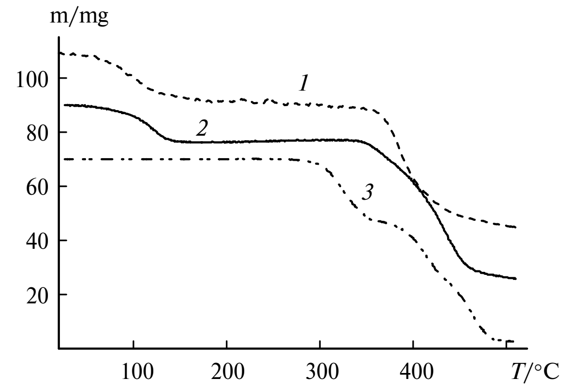
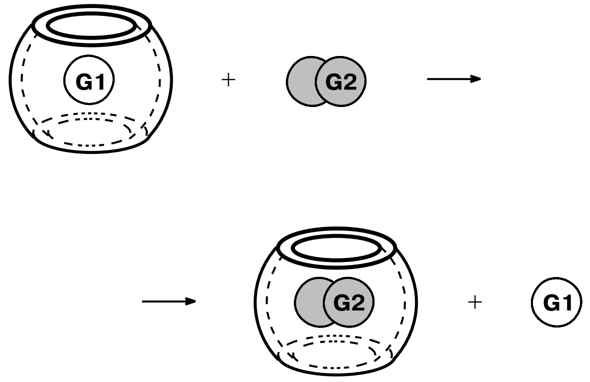


**Fig. 3.** Thermogravimetric analysis data for CB[8]·20H$_2$O (*1*), {*trans*-[Ni(en)$_2$(H$_2$O)$_2$]@CB[8]}Cl$_2$·23.5H$_2$O (*2*), and *trans*-[Ni(en)$_2$Cl$_2$] (*3*).



**Inclusion compound {2(pyCN)@CB[8]}·16H$_2$O (2).** Aqueous solutions of inclusion compound **1** and 4-cyanopyridine were mixed in a ratio of 1 : 2 at high temperature. After one day, colorless crystals were obtained as truncated square pyramids from the colored solution. X-ray diffraction study showed that these crystals have the composition {2(pyCN)@CB[8]} • $16H_2O$ (**2**), and the reaction product is an inclusion compound of cucurbit[8]uril with two 4-cyanopyridine molecules.

$$\{[\mathrm{Ni(en)_2(H_2O)_2}]@\mathrm{CB[8]}\}^{2+} + 2\ (\mathrm{pyCN}) \longrightarrow$$

$$\longrightarrow \{2(\mathrm{pyCN})@\mathrm{CB[8]}\} + [\mathrm{Ni(en)_2(H_2O)_2}]^{2+}$$

In the starting compound **1**, the axial positions of the guest complex are occupied by easily replaceable $H_2O$ ligands. Hence, the reaction with an N-donor ligand, such as 4-cyanopyridine, would be expected to give {*trans*-$[\mathrm{Ni(en)_2(pyCN)_2}]$@CB[8]$\}^{2+}$. However, under these conditions, the guest exchange reaction occurs instead of the ligand exchange, which is indicative of higher stability of the {2(pyCN)@CB[8]} compound compared to **1** and {*trans*-$[\mathrm{Ni(en)_2(pyCN)_2}]$@CB[8]$\}^{2+}$. It should be noted that attempts to synthesize compound **2** by the direct "guest + host" reaction failed because CB[8] is insoluble in an aqueous solution of 4-cyanopyridine.

X-ray diffraction study of compound **2** demonstrated that the pyridyl rings of the guest molecules are located in the cavity of the cavitand (Fig. 4) and the CN groups are located above the opposite portals of the cucurbit[8]uril molecule and are slightly inclined to the planes of the rings (by ~5°). The pyridyl rings are parallel to each other, and the distance between the planes is ~3.74 Å. The rings are shifted with respect to each other in such a way that the angle ($\alpha$) between the perpendicular to the plane of the ring and the vector between the centers of the opposite rings is ~22°, and the distance between these centers is $l = 4.03$ Å. Analysis of the structures of the complexes with aromatic nitrogen-containing heterocycles shows that this shift is typical of structures with $\pi$—$\pi$ stacking interactions between the aromatic rings; the average values of $\alpha$ and $l$ are 20° and 3.8 Å, respectively.[22] The data for compound **2** are indicative of the presence of a weak $\pi$—$\pi$ stacking interaction between the guest molecules. The distortion of the cucurbit[8]uril molecule ($\Delta_{\mathrm{CH}}$) in **2** is substantially smaller (1.79 Å) than that observed in the inclusion compound with the nickel complex, which is associated with a better size matching between two 4-cyanopyridine molecules and the cavity of the cavitand.

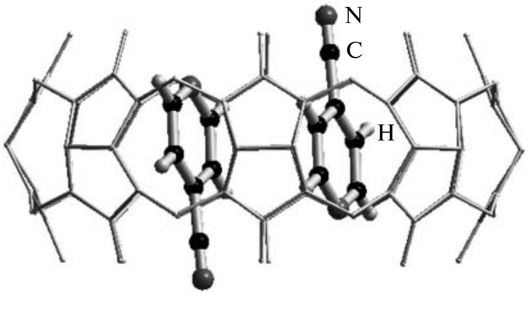


**Fig. 4.** Structure of the {2(pyCN)@CB[8]} fragment in the crystal structure of **2**.

In the crystal structure of **2**, the cucurbit[8]uril molecules containing encapsulated 4-cyanopyridine guest molecules are arranged in a herringbone fashion. In this case, the cavitands are packed so that no channels are formed, and the cavities are filled by water molecules of crystallization involved in a network of hydrogen bonds with each other and with the oxygen atoms at the portals of cucurbit[8]uril.

**Inclusion compound {2(bpe)@CB[8]} • $17H_2O$ (3).** The inclusion compound of CB[8] with *trans*-1,2-bis(4-pyridyl)ethylene (bpe) was synthesized by the guest exchange reaction. The reaction of {[Cu(cyclam)]@ @CB[8]}$(NO_3)_2$ • $14H_2O$ [1] with bpe afforded pale-orange crystals of composition {2(bpe)@CB[8]} • $17H_2O$ (**3**). In this case, the direct scheme of the synthesis is also inefficient because bpe is insoluble in water.

$$\{[\mathrm{Cu(cyclam)}]@\mathrm{CB[8]}\}^{2+} + 2\ (\mathrm{bpe}) \longrightarrow$$

$$\longrightarrow \{2(\mathrm{bpe})@\mathrm{CB[8]}\} + [\mathrm{Cu(cyclam)}]^{2+}$$

In the structure of **3**, the guest molecules are located in the cavity of the host so that only one pyridyl ring and the —CH=CH— double bond of each bpe molecule are completely encapsulated within the macrocycle, whereas two other rings are above the opposite portals of the cucurbit[8]uril molecule (Fig. 5). The planes of the $\pi$ systems of two encapsulated pyridyl rings of the bpe molecules are parallel to each other and are ~3.75 Å apart. The rings are substantially shifted with respect to each other ($\alpha$ = 39°, $l$ = 4.8 Å) so that the —CH=CH—

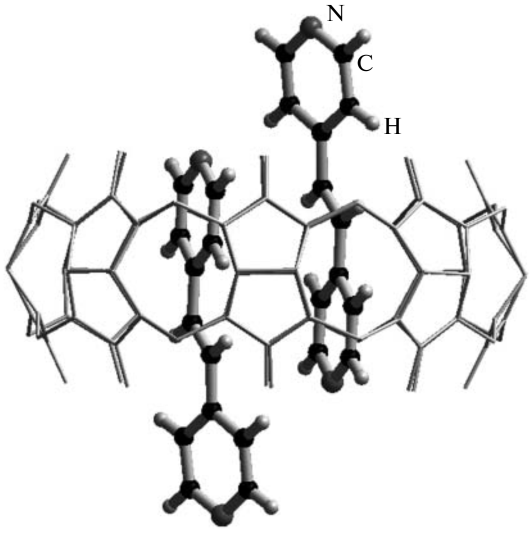


**Fig. 5.** Structure of the {2(bpe)@CB[8]} fragment in the crystal structure of **3**.

double bond of one bpe molecule is virtually above the pyridyl ring of another molecule. The close contacts between the plane of the pyridyl ring and the carbon atoms of the double bond of the opposite molecule (3.56 and 3.73 Å) indicate that the π orbitals of the double bonds are involved in weak π-stacking interactions between the guests. The deformation of the cucurbit[8]uril molecule ($\Delta_{CH}$) in the structure of **3** is 1.47 Å. Encapsulation also causes slight distortion of the guest molecules. The pyridyl rings of each *trans*-1,2-bis(4-pyridyl)ethylene molecule are twisted with respect to one another by ~22°, unlike free bpe in which all atoms are in a single plane.**[23]**

The crystal packing of **3** has an island motif. The molecular packing of cucurbit[8]uril, like that of compound **2**, does not give rise to channels. The cavities in the crystal lattice formed by the cavitand molecules are occupied by water molecules of crystallization, which are involved in a network of hydrogen bonds with each other, the oxygen atoms at the portals of cucurbit[8]uril, and the nitrogen atoms of the pyridyl rings.

The IR spectrum of compound **3** has, along with characteristics bands of cucurbit[8]uril, bands of *trans*-1,2-bis(4-pyridyl)ethylene at 1597 (s) and 1558 $cm^{-1}$ (w) (ν(C—C) and ν(C—N) of the pyridyl rings) and at 552 (m) and 536 $cm^{-1}$ (m) (skeletal vibrations of the pyridine ring). Since absorption bands of structural fragments other than cucurbit[*n*]uril are rather rarely observed in IR spectra, IR spectroscopy has insufficient information to confirm the existence of inclusion compounds of this class of cavitands.

Study by $^1$H NMR spectroscopy demonstrated that encapsulation of *trans*-1,2-bis(4-pyridyl)ethylene in cucurbit[8]uril is accompanied by noticeable upfield shifts of the signals for the protons of the guest ($\Delta_\delta = -0.12$, $-0.24$, and $-0.36$ for the α- and β-protons of the pyridine ring and the olefinic protons, respectively), which unambiguously proves encapsulation of the bpe molecule in the cavitand in solution (Fig. 6, *c*, *d*). The largest shift $\Delta_\delta$ is observed for the resonance of the hydrogen atom at the double bond. This indicates that the strongest interactions occur between these atoms and the cavity of the host.

The electrospray mass spectrum of an aqueous solution of compound **3** has an intense peak of $[CB[8] + 2\ bpe + 2\ H + Na]^{3+}$, which also confirms the presence of the inclusion compound in solution.

**Inclusion compound $\{2[Cu(dien)(bipy)(H_2O)]@CB[8]\}(ClO_4)_4 \cdot 11H_2O$ (4).** Refluxing of an aqueous solution containing $\{[Ni(cyclam)]@CB[8]\}Cl_2 \cdot 16H_2O$ [16] and a tenfold excess of the copper(II) complex $[Cu(dien)(bipy)(H_2O)](ClO_4)_2$ (see Ref. 24) leads to the replacement the nickel complex from the cavity of the cavitand with the copper complex. Upon cooling of the reaction solution, a blue-violet crystalline product of composition $\{2[Cu(dien)(bipy)(H_2O)]@CB[8]\}(ClO_4)_4 \cdot 11H_2O$ (**4**) was obtained.

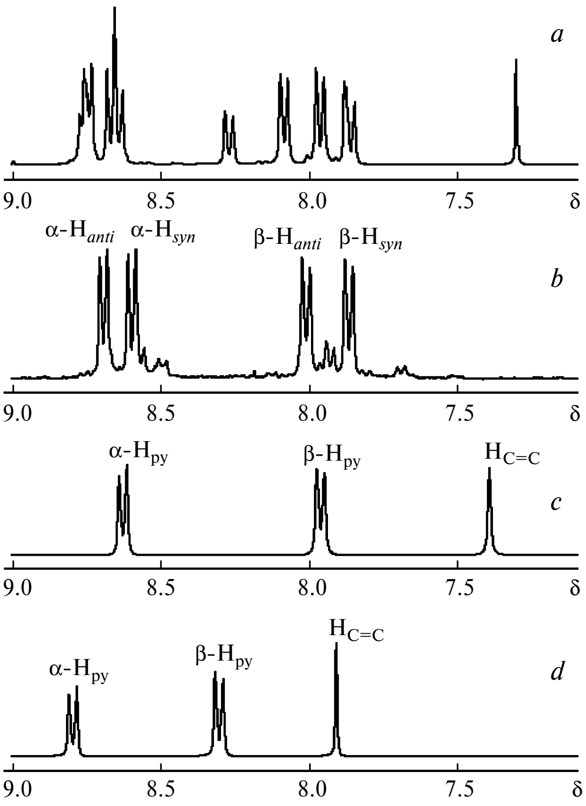


**Fig. 6.** $^1$H NMR spectra of solutions of *trans*-1,2-bis(4-pyridyl)ethylene (*a*, *d*) and compound **3** (*b*, *c*) after irradiation (*a*, *b*) and before irradiation (*c*, *d*).

$$[Ni(cyclam)]@CB[8]\}^{2+} + 2\,[Cu(dien)(bipy)(H_2O)]^{2+} \longrightarrow$$

$$\longrightarrow \{2[Cu(dien)(bipy)(H_2O)]@CB[8]\}^{4+} + [Ni(cyclam)]^{2+}$$

In the structure of **4**, the cavities of cucurbit[8]uril are occupied by two 4,4′-bipyridyl molecules coordinated by two $Cu^{II}$ atoms, whereas the metal atoms with the aqua and diethylenetriamine ligands are outside the cavity of the macrocycle (Fig. 7). The first coordination sphere of copper(II) in molecule **4** can be described as a square pyramid, whose basal plane is formed by three nitrogen atoms of dien and one of two nitrogen atoms of bipy, and the apical position is occupied by the oxygen atom of the coordinated water molecule. Two crystallographically independent water molecules with occupancies of 1/2 are at equal distances from the $CuN_4$ plane at the opposite sides, and, consequently, two opposite directions of the axis of the pyramid can exist in the crystal.

Two guest molecules in the cavity of cucurbit[8]uril form a dimer, in which the parallel π systems of the 4,4′-bipyridyl molecules are ~3.57 Å apart and are shifted with respect to each other ($\alpha = 17°$, $l = 3.70$ Å), which is indicative of the presence of a π—π-stacking

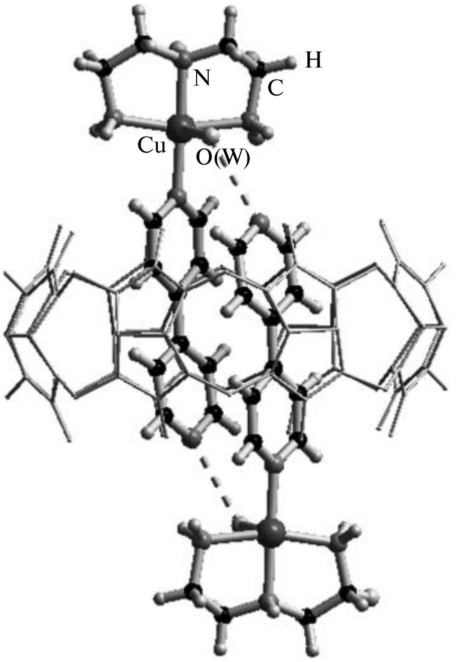


**Fig. 7.** Structure of the $\{2[Cu(dien)(bipy)(H_2O)]@CB[8]\}^{4+}$ fragment in the crystal structure of **4** (O...H...N hydrogen bonds are indicated by dashed lines).

interaction between these systems. Analogous dimers are also observed in the crystal structure of the free (which is not encapsulated in cucurbit[8]uril) $[Cu(dien)(bipy)(H_2O)](ClO_4)_2$ complex,[24] in which the distance between the π systems of the bipy molecules is 3.34 Å (α = 25°, $l$ = 3.67 Å). The dimer in compound **4**, like that in the free complex, is additionally stabilized by a hydrogen bond between the $H_2O$ ligand of one guest molecule and the uncoordinated nitrogen atom of 4,4´-bipyridyl of the second guest molecule (O...N, 2.923 Å). The Cu—N distances are virtually equal to those observed in the free complex, whereas the Cu—O bond in molecule **4** is 0.19 Å longer. The $CuN_4$ plane is inclined to the plane of the vicinal ring of 4,4´-bipyridyl by 40°, whereas this angle in $[Cu(dien)(bipy)(H_2O)](ClO_4)_2$ is 43.9°. The distortion of the cucurbit[8]uril molecule ($\Delta_{CH}$) in the structure of **4** is insignificant (0.22 Å).

The crystal packing of **4** has an island motif. This packing is composed of two types of alternating layers parallel to the *ab* plane (Fig. 8). Layers of one type (hydrophilic) consist of water molecules of crystallization, perchlorate anions, and copper(II) atoms coordinated by $H_2O$ and diethylenetriamine molecules. Layers of another type (hydrophobic) are composed of cucurbit[8]uril molecules with encapsulated 4,4´-bipyridyl molecules.

The electrospray mass spectrum of an aqueous solution of compound **4** shows an intense peak of the $[CB[8] + Cu(dien)(bipy)]^{2+}$ ion, which is evidence for the presence of inclusion compounds with a guest : host ratio of 1 : 1 in solution.

The electronic absorption spectrum of an aqueous solution of **4** is identical to the spectrum of the free $[Cu(dien)(bipy)(H_2O)](ClO_4)_2$ complex, which indicates that the electronic structure of the complex remains unchanged upon encapsulation in the cavity of cucur-

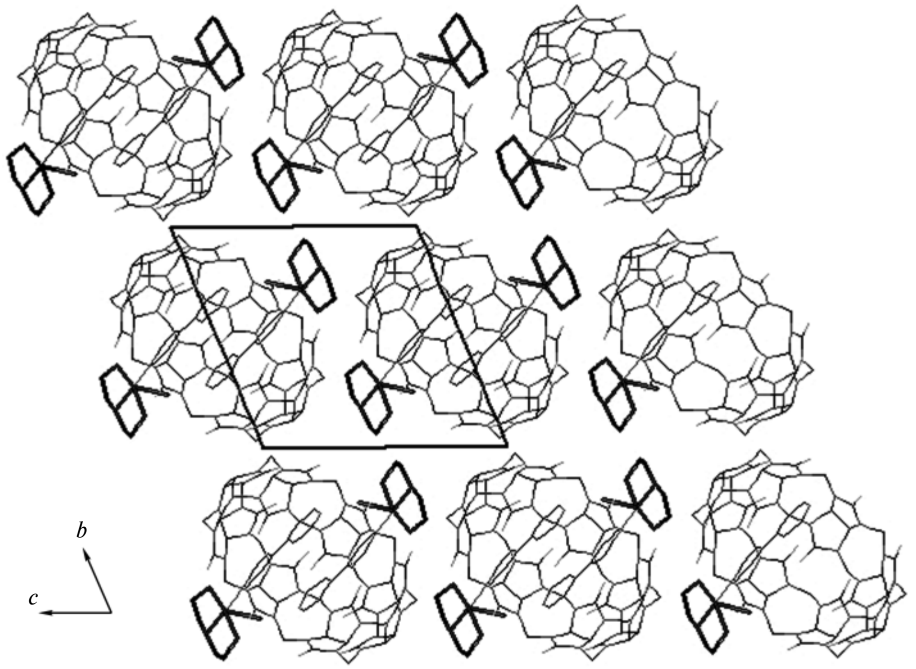


**Fig. 8.** Crystal packing of compound **4** projected onto the *bc* plane. The $[Cu(dien)(H_2O)]^{2+}$ fragments are indicated by thick lines. The hydrogen atoms, water molecules of crystallization, and chloride anions are omitted.

bit[8]uril in solution. The first coordination sphere of the metal atom is outside the cavity of the cavitand and remains undistorted.

The ESR spectrum of a single-crystalline sample of **4** has axial symmetry and is characterized by $g_x = g_y = 2.045$, which are virtually equal to $g_\perp = 2.06$ for the free complex and are even slightly larger than $g_z = 2.312$ ($g_\parallel = 2.24$ for $[Cu(dien)(bipy)(H_2O)](ClO_4)_2$). This correlates with the bond lengths in the first coordination sphere of the metal atom determined by X-ray diffraction. The Cu—N distances in the basal plane remain unchanged, whereas the Cu—O bond with the apical ligand in **4** is elongated.

The IR spectrum of **4** shows, along with characteristic bands of cucurbit[8]uril, bands of the perchlorate anion at 1109 and 624 $cm^{-1}$, bands of the guest molecule at 1616 and 1589 $cm^{-1}$ (ν(C—C) and ν(C—N) of the pyridyl rings, respectively) and 1537 (δ($R_2N$—H) of the coordinated dien ligand[24]), and bands at 1288, 1088, 1038, and 544 $cm^{-1}$.

An attempt to perform the direct reaction of cucurbit[8]uril with an aqueous solution of $[Cu(dien)(bipy)(H_2O)](ClO_4)_2$ even with prolonged heating led only to the partial transfer of CB[8] to a solution. This gives rise to a problem of separation of the solid phases of the product and the unconsumed host.

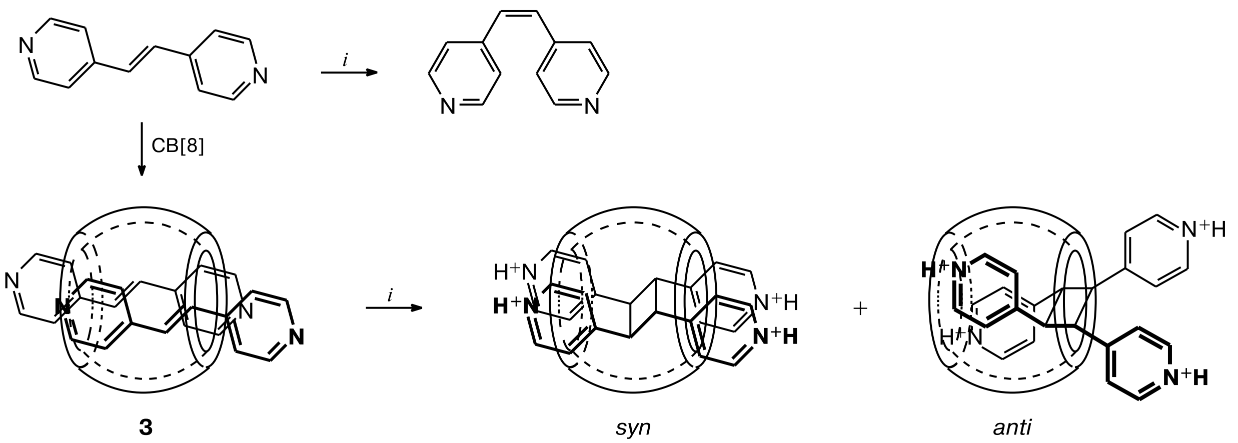
Therefore, inclusion compounds of cucurbit[8]uril with metal complexes are rather unstable and are involved in guest exchange reactions in aqueous solutions, resulting in the displacement of the metal complex from the cavity of the cavitand with organic molecules to form guest : host inclusion compounds of 2 : 1 composition. The formation of inclusion compounds essentially depends on the presence of van der Waals interactions, which held organic molecules in the hydrophobic cavity of cucurbit[8]uril. Under the reaction conditions (prolonged refluxing and the presence of an excess of the ligand), neither the replacement of the $H_2O$ ligands of the encapsulated metal complex with the N-donor ligands, *viz.*, cyanopyridine or 1,2-bis(4-pyridyl)ethylene, nor coordination of the latter at the vacant axial positions of nickel(II) and copper(II) complexes with cyclam occur.

**Photolysis of the inclusion compound {2(bpe)@CB[8]} · · $17H_2O$.** Due to ability to encapsulate two closely-spaced guest molecules in particular positions, cucurbit[8]uril can be used as a synthetic molecular container in which bimolecular reactions between the specially chosen guests can proceed with high regio- and stereoselectivity. For example, two *trans*-4,4′-diaminostilbene molecules included in the cavity of CB[8] are involved in the photochemically initiated stereoselective [2+2]-cycloaddition to form the *syn* isomer of a cyclobutane derivative,[25] whereas photodimerization does not occur in the absence of CB[8].[26]

We performed an analogous [2+2]-cycloaddition reaction for *trans*-1,2-bis(4-pyridyl)ethylene encapsulated in cucurbit[8]uril (**3**) (Scheme 1). In the UV spectrum of a solution of **3** in 2 *M* $H_2SO_4$, the intense absorption bands at 302, 313, and 327 nm are assigned to π → π* transitions in the conjugated aromatic system of the guest. The reaction was initiated with the use of a mercury lamp.

Under irradiation of a solution of compound **3** in 2 *M* $D_2SO_4$, the colorless solution turned yellow. The reaction was monitored by $^1H$ NMR spectroscopy using sample withdrawing. It was found that the NMR spectrum of the solution ceased to change after irradiation for 3 h. After completion of the reaction, the singlet corresponding to the hydrogen atom at the —CH=CH— double bond in the bpe molecule completely disappeared, and four doublets belonging to the α- and β-protons of the pyridyl rings of the *syn* and *anti* isomers of the guest appeared, which indicates that the [2+2]-cycloaddition reaction occurs with quantitative yield (see Scheme 1). Based on the

**Scheme 1**



*i.* $H^+$, *h*ν, 3 h.

integrated intensities of the signals, the ratio of the *syn* and *anti* isomers is 1 : 1, *i.e.*, this photochemical reaction is nonstereoselective, unlike the above-described reaction of *trans*-4,4´-diaminostilbene.[25] The resulting mixture of the inclusion compounds of cucurbit[8]uril with isomers of 1,2,3,4-tetrakis(4-pyridyl)cyclobutane was treated with a NaOH solution and then with an excess of methanol to isolate cucurbit[8]uril as a complex with a sodium cation. The solution was concentrated to dryness on a rotary evaporator. The $^1$H NMR spectrum of a solution of the resulting solid product in $CDCl_3$ confirmed the formation of two isomers of 1,2,3,4-tetrakis(4-pyridyl)cyclobutane in a ratio of 1 : 1. It should be noted that irradiation of *trans*-1,2-bis(4-pyridyl)ethylene, which is not encapsulated in CB[8], under analogous conditions led only to its transformation into the *cis* isomer, whereas photodimerization did not occur.

## Experimental

The starting compounds $NiCl_2 \cdot 6H_2O$ (analytical grade), $CuCl_2 \cdot 2H_2O$ (analytical grade), cyclam (1,4,8,11-tetraazacyclotetradecane) (reagent grade), *trans*-1,2-bis(4-pyridyl)ethylene (reagent grade), ethylenediamine (99% purity), diethylenetriamine (99%), 4,4´-bipyridyl dihydrate (98%), 4-cyanopyridine (99%), $D_2O$ (99.9%), and $D_2SO_4$ (98%) were used without additional purification. Cucurbit[8]uril,[14] $[Ni(en)_2Cl_2]$,[27] $\{[Ni(cyclam)]@CB[8]\}Cl_2 \cdot 16H_2O$,[16] $\{[Cu(cyclam)(H_2O)]@@CB[8]\}(NO_3)_2 \cdot 14H_2O$,[1] and $[Cu(dien)(bipy)(H_2O)](ClO_4)_2$ (see Ref. 24) were synthesized according to procedures published earlier.

The IR spectra were recorded on Bruker IFS-85 and Scimitar FTS 2000 spectrophotometers in KBr pellets. The electronic absorption spectra were measured on Ultrospec 3300pro and Shimadzu UV-3101PC spectrophotometers in 200—1100 and 190—1100 nm ranges, respectively. The $^1$H NMR spectra were recorded on a Bruker DPX/250 spectrometer at room temperature with $Me_3Si(CD_2)_2CO_2Na$ as the internal standard. Analyses for C, H, N, and Cl were carried out in the Laboratory of Microanalysis of the Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. X-ray diffraction studies were performed on Bruker SMART CCD and Bruker Nonius X8Apex single-crystal diffractometers equipped with a 4K CCD detector.[28] The ESR spectra were recorded on a Varian E-109 spectrometer with the use of diphenylpicrylhydrazyl as the external standard. The photochemical reaction was performed under irradiation with a DRT-250 mercury lamp. The mass spectra (ESI-MS) were obtained on Quattro LC and QTOF I mass spectrometers (Micromass, Manchester, UK).

**Cucurbit[8]uril (*trans*-diaqua-bis-ethylenediaminenickel(II)) dichloride clathrate 23.5-hydrate, $\{trans\text{-}[Ni(en)_2(H_2O)_2]@@CB[8]\}Cl_2 \cdot 23.5H_2O$ (1).** Cucurbit[8]uril ($C_{48}H_{48}N_{32}O_{16} \cdot \cdot 20H_2O$) (0.100 g, 0.059 mmol) was dissolved with slight heating in a solution of $[Ni(en)_2Cl_2]$ (0.118 g, 0.472 mmol) in water (15 mL). The reaction solution was refluxed on a sand bath for 2 h and then slowly cooled. After 7 days, pale-lilac crystals of **1** that precipitated were filtered off on a green ribbon paper filter, washed with a small amount of cold water, and dried in air. Compound **1** is soluble in hot water and rapidly loses water of crystallization in air. The yield was 0.098 g (81% based on consumed cucurbit[8]uril). Found (%): C, 33.81; H, 4.88; N, 27.39; Cl, 3.44. $C_{52}H_{93}NiN_{36}O_{30.5}Cl_2$ (with a loss of 11 $H_2O$ molecules). Calculated (%): C, 33.94; H, 5.09; N, 27.40; Cl, 3.85. ESI-MS, *m/z* (*I* (%)): 503.7 $[CB[8] + Ni(en) + H]^{3+}$ (100), 510 $[CB[8] + Ni(en)_2 + Na]^{3+}$ (97), 516 $[CB[8] + Ni(en)_2 + H]^{3+}$ (63), 695 $[CB[8] + (en) + 2 H]^{2+}$ (10), 725 $[CB[8] + 2 (en) + 2 H]^{2+}$ (12), 753.5 $[CB[8] + Ni(en)_2]^{2+}$ (20). $^1$H NMR ($D_2O$, 250 MHz), δ: 5.79, 5.61, and 4.31 (all br.s, 16 H each). IR (KBr), $\nu/cm^{-1}$: 3430 s, 3006 w, 2935 w, 2885 w, 1718 s, 1641 sh, 1472 s, 1421 m, 1375 s, 1322 s, 1294 m, 1231 s, 1191 s, 1154 m, 1027 w, 994 w, 968 s, 830 m, 809 s, 758 m, 675 m, 631 w, 505 w, 450 w.

**Cucurbit[8]uril (bis-4-cyanopyridine) clathrate hexadecahydrate, $\{2(pyCN)@CB[8]\} \cdot 16H_2O$ (2).** A solution of compound **1** (0.010 g, 0.005 mmol) in water (3 mL) was mixed with an aqueous solution of 4-cyanopyridine (0.43 mL, 2.37 mg $mL^{-1}$, 0.010 mmol). The resulting solution was heated almost to boiling and then slowly cooled in the closed vessel. After 1 day, large colorless crystals of **2** were obtained as truncated square pyramids. The yield was 0.007 g (70%). Found (%): C, 38.85; H, 4.07; N, 28.04. $C_{60}H_{88}N_{36}O_{32}$. Calculated (%): C, 39.48; H, 4.86; N, 27.62. IR (KBr), $\nu/cm^{-1}$: 3441 s, 3004 w, 2924 w, 1726 s, 1645 sh, 1596.5 s, 1473 s, 1426 m, 1375 s, 1319 s, 1295 w, 1232 s, 1191 s, 1156 m, 1028 w, 994 w, 970 s, 808 s, 758 m, 673 m, 630 w, 561 m, 443 w.

**Cucurbit[8]uril [bis-(*trans*-1,2-bis(4-pyridyl)ethylene)] clathrate heptadecahydrate, $\{2(bpe)@CB[8]\} \cdot 17H_2O$ (3).** The $\{[Cu(cyclam)(H_2O)]@CB[8]\}(NO_3)_2 \cdot 14H_2O$ compound (0.050 g, 0.025 mmol) was dissolved in water (21 mL) at high temperature. Then *trans*-1,2-bis(4-pyridyl)ethylene (bpe) (0.0154 g, 0.213 mmol) was added, and the solution was refluxed on a sand bath for 2 h. After cooling of the solution, a precipitate of unconsumed bpe was filtered off on a paper filter. After 1 day, pale-orange crystalline compound **3** was obtained. The latter was filtered off on a green ribbon paper filter and dried in air. Compound **3** is insoluble in water, soluble in 2 *M* $H_2SO_4$, and rapidly loses water of crystallization in air. The yield was 0.022 g (47% based on consumed $\{[Cu(cyclam)(H_2O)]@CB[8]\}(NO_3)_2 \cdot \cdot 14H_2O$). Found (%): C, 46.21; H, 4.51; N, 26.74. $C_{72}H_{88}N_{36}O_{26}$ (with a loss of seven $H_2O$ molecules). Calculated (%): C, 46.15; H, 4.73; N, 26.91. EAS (2 *M* $H_2SO_4$, 190—400 nm), λ/nm: 220 sh, 302 sh, 313, 327 sh. $^1$H NMR (2 *M* $D_2SO_4$ solution in $D_2O$, 250 MHz), δ: 8.40 and 7.79 (both d, 8 H each); 7.27 (s, 4 H); 5.45 (d, 16 H); 5.27 (s, 16 H); 3.98 (d, 16 H). $^1$H NMR spectrum of free bpe (2 *M* $D_2SO_4$ solution in $D_2O$, 250 MHz), δ: 8.52 and 8.03 (both d, 8 H each); 7.63 (s, 4 H). ESI-MS, *m/z* (*I* (%)): 573.5 $[CB[8] + 2 bpe + 2 H + Na]^{3+}$ (65), 578.4 $[CB[8] + 2 dpe + 3 H]^{3+}$ (100). IR (KBr), $\nu/cm^{-1}$: 3427 s, 3026 w, 2920 w, 1733 s, 1596.5 s, 1558 w, 1468 s, 1374 s, 1317 s, 1229 s, 1189 s, 1154 m, 993 w, 970 s, 825 m, 806 s, 757 m, 668 m, 627 w, 552 m, 537 w.

**Photochemical [2+2]-cycloaddition.** A solution of compound **3** (0.010 g, 0.005 mmol, $2.5 \cdot 10^{-3}$ mol $L^{-1}$) in 2 *M* $D_2SO_4$ (2 mL) was placed in a quartz tube and irradiated for 3 h using a mercury lamp. Samples for $^1$H NMR spectroscopy were withdrawn after irradiation for 0.5, 1, 1.5, and 3 h. In the course of the reaction, the colorless solution gradually turned lemon-yellow. After completion of the reaction, the solution was neutralized with 1 *M* NaOH (9 mL) and then methanol (70 mL) was added. The reaction mixture was stirred for 1 h, after which a white precipitate was obtained. The precipitate was filtered off on a porous glass filter, and the filtrate was concentrated to dryness on a rotary evaporator. The $^1$H NMR spectrum of the crude dry beige residue (1 : 1 mixture of *syn* and *anti* isomers, $CDCl_3$, 250 MHz), δ: 8.54, 8.47, 7.34, and 7.20 (all d, 8 H each); 4.97 (s, 4 H).

**Cucurbit[8]uril (bis-diethylenetriamine-4,4′-dipyridylethyleneaquacopper(II)) tetraperchlorate clathrate endecahydrate, {2[Cu(dien)(bipy)($H_2O$)]@CB[8]}($ClO_4$)$_4$ · 11$H_2O$ (4).** A hot solution of [Cu(dien)(bipy)($H_2O$)]($ClO_4$)$_2$ (0.028 g) in water (3.5 mL) was added to a hot solution of {[Ni(cyclam)]@@CB[8]}$Cl_2$ · 16$H_2O$ (0.010 g) in water (3.5 mL). The resulting suspension was refluxed for 3 h and then slowly cooled. After one day, violet-blue elongated crystals of **4** were obtained. The crystals are poorly soluble in hot water and slowly lose water of crystallization in air. The yield was 0.008 g (60% based on consumed {[Ni(cyclam)]@CB[8]}$Cl_2$ · 16$H_2O$). Found (%): C, 35.36; H, 4.16; N, 22.78; Cl, 5.53. $Cu_2C_{76}H_{116}N_{42}O_{45}Cl_4$. Calculated (%): C, 35.02; H, 4.49; N, 22.57; Cl, 5.44. ESR: $A_{zz}$ = 91 Gs, $A_{xx} = A_{yy}$ = 20 Gs; $g_z$ = 2.312, $g_x = g_y$ = 2.045. ESI-MS, *m/z* (*I* (%): 717 [CB[8] + dien + 2 H]$^{2+}$ (28), 745 [CB[8] + Cu(dien)]$^{2+}$ (15), 825.8 [CB[8] + Cu(dien)(bipy)]$^{2+}$ (33). EAS ($H_2O$, 190—1100 nm), λ/nm (ε/L mol$^{-1}$ cm$^{-1}$): 600 (185), 270 sh, 240 (46200). IR (KBr), ν/cm$^{-1}$: 3441 w, br, 3285 m, 3262 m, 3175 w, 2936 w, 2893 w, 1734 s, 1616 m, 1589 w, 1537 w, 1462 s, 1410 w, 1373 s, 1319 s, 1288 m, 1231 s, 1192 s, 1157 m, 1088 s, 1038 m, 989 w, 968 s, 829 m, 808 s, 756 m, 673 m, 625 w, 544 w, 447 w.

**X-ray diffraction study.** The crystallographic characteristics and details of X-ray diffraction study for single crystals of **1—4** are given in Table 1. X-ray data sets were collected according to a standard procedure at 150 K. In all experiments, Mo-Kα radiation (λ = 0.71073 Å) and a graphite monochromator were used. Semiempirical absorption corrections were applied based on the intensities of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares method against $F^2$ with anisotropic displacement parameters for nonhydrogen atoms using the SHELX97 program

**Table 1.** Crystallographic data and details of X-ray diffraction study

| Compound | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| Molecular formula | $C_{52}H_{115}N_{36}O_{41.5}Cl_2Ni_1$ | $C_{60}H_{88}N_{36}O_{32}$ | $C_{72}H_{102}N_{36}O_{33}$ | $C_{76}H_{116}Cl_4Cu_2N_{42}O_{45}$ |
| Molecular weight/g mol$^{-1}$ | 2038.30 | 1825.66 | 1999.90 | 2606.99 |
| *T*/K | 150(2) | 150(2) | 150(2) K | 150(2) K |
| Crystal system | Trigonal | Monoclinic | Monoclinic | Triclinic |
| Space group | $R\bar{3}$ | $P2_1/c$ | $P2_1/c$ | $P\bar{1}$ |
| *a*/Å | 36.3444(3) | 22.491(6) | 23.4417(9) | 14.6313(10) |
| *b*/Å | 36.3444(3) | 21.443(6) | 16.8384(7) | 14.6540(7) |
| *c*/Å | 16.4567(3) | 16.775(4) | 23.7316(12) | 15.4606(11) |
| α/deg | 90 | 90 | 90 | 64.683(2) |
| β/deg | 90 | 90.170(4) | 109.239(2) | 68.719(2) |
| γ/deg | 120 | 90 | 90 | 74.992(2) |
| *Z* | 9 | 4 | 4 | 1 |
| *V*/Å$^3$ | 18825.6(4) | 8090(4) | 8844.2(7) | 2770.9(3) |
| *d*/g cm$^{-3}$ | 1.618 | 1.499 | 1.502 | 1.562 |
| μ/mm$^{-1}$ | 0.380 | 0.123 | 0.121 | 0.588 |
| Transmission, max/min | 0.886/0.833 | 0.9617/0.9467 | 0.9763/0.9647 | 0.9169/0.8864 |
| *F*(000) | 7812 | 3824 | 4200 | 1352 |
| Crystal dimensions/mm | 0.62×0.40×0.32 | 0.45×0.40×0.32 | 0.30×0.30×0.20 | 0.21×0.18×0.15 |
| Scan range, θ/deg | 1.94—25.35 | 1.31—25.35 | 1.75—28.28 | 1.51—25.35 |
| Ranges of *h, k, l* indices | $-41 \le h \le 43$ | $-27 \le h \le 27$ | $-30 \le h \le 31$ | $-16 \le h \le 17$ |
|  | $-43 \le k \le 33$ | $-25 \le k \le 25$ | $-22 \le k \le 19$ | $-15 \le k \le 17$ |
|  | $-16 \le l \le 19$ | $-8 \le l \le 19$ | $-31 \le l \le 31$ | $-17 \le l \le 18$ |
| Number of measured reflections | 33718 | 43874 | 69064 | 17004 |
| Number of independent reflections ($R_{int}$) | 7548 (0.0528) | 14488 (0.0443) | 20285 (0.0292) | 9934 (0.0378) |
| Number of reflections with $I > 2\sigma(I)$, | 4571 | 11271 | 14468 | 6258 |
| Completeness of the data set | 0.985 | 0.978 | 0.964 | 0.979 |
| *S* factor based on $F^2$ | 0.934 | 1.575 | 1.088 | 1.244 |
| *R* factor ($I > 2\sigma(I)$) |  |  |  |  |
| $R_1$ | 0.0717 | 0.0564 | 0.0664 | 0.0623 |
| $wR_2$ | 0.2051 | 0.0731 | 0.2147 | 0.0870 |
| *R* factor (for all reflections) |  |  |  |  |
| $R_1$ | 0.1036 | 0.0727 | 0.0906 | 0.1113 |
| $wR_2$ | 0.2212 | 0.0770 | 0.2327 | 0.0995 |
| Residual electron density (max/min)/e Å$^{-3}$ | 1.173/−1.067 | 0.431/−0.465 | 0.853/−0.814 | 0.555/−0.425 |

package.[29] The hydrogen atoms of cucurbit[8]uril and organic ligands were calculated geometrically and refined using a riding model. The hydrogen atoms of the water molecules were not revealed.

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