Inclusion of nickel(II) and copper(II) complexes with aliphatic polyamines in cucurbit[8]uril

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The inclusion compound of macrocyclic cavitand cucurbit[8]uril (CB[8]) with the nickel(II) complex containing the tetraazamacrocyclic ligand cyclam, $\{[Ni(cyclam)]@CB[8]\}Cl_2 \cdot 16H_2O$ (**1**), and the inclusion compounds of CB[8] with the copper(II) bis-ethylenediamine complex, $\{trans\text{-}[Cu(en)_2(H_2O)_2]@CB[8]\}Cl_2 \cdot \{CB[8]\} \cdot 42H_2O$ (**2a**) and $\{trans\text{-}[Cu(en)_2(H_2O)_2]@CB[8]\}Cl_2 \cdot 17H_2O$ (**2b**), were synthesized and characterized by X-ray diffraction analysis, IR and ESR spectroscopy, and electrospray mass spectrometry. Guest—host inclusion compounds can be directly synthesized starting from a metal complex and cucurbit[8]uril, as was exemplified by the preparation of compounds **2a** and **2b**.

Key words: guest—host complexes, nickel(II), copper(II), cucurbit[8]uril, supramolecular compounds, X-ray diffraction analysis.

Transition metal complexes with polyamines are used as model compounds in studies of metal ion transport in biological systems,[1] for metal regeneration,[2] as NMR contrast agents,[3] for radioactive diagnostics,[4] *etc*. Metal complexes with tetraazamacrocyclic ligands are of interest as highly promising materials for use in medicine[5] and as catalysts for various reactions, such as epoxidation or DNA hydrolysis.[6]

Inclusion of metal complexes in large organic macrocycles is a rather rare phenomenon. Nevertheless, such compounds, particularly, those with transition metals, are of considerable interest because of a unique environment of the metal ions, which is similar to that observed in metalloenzymes. The first inclusion compounds of macrocycles with metal complexes were synthesized in the late 1980s.[7] In these compounds, alkali metal complexes with crown ethers and cryptands are included in the γ-cyclodextrin cavity. For transition metals, an example of inclusion compounds is the zinc pyridylporphyrin complex included in a macrocycle formed by four other porphyrin complexes.[8] Earlier, inclusion compounds of transition metal complexes with polyamines have been synthesized in the only study,[9] where the inclusion of copper(II) and zinc(II) complexes with the tetraazamacrocyclic ligands cyclam (cyclam is 1,4,8,11-tetraazacyclotetradecane) and cyclen (cyclen is 1,4,7,10-tetraazacyclododecane) in the cavity of the organic macrocyclic cavitand cucurbit[8]uril (CB[8]) was described.

Cucurbit[*n*]urils (CB[*n*]) belong to a family of organic compounds with the composition $C_{6n}H_{6n}N_{4n}O_{2n}$. These compounds have a rigid macrocyclic structure consisting of *n* glycoluril fragments linked *via* 2*n* methylene bridges, where $n = 5—10$.[10,11] Since cucurbiturils have a large intramolecular cavity, they can serve as hosts and form inclusion compounds with guest molecules or ions of appropriate size (methylpyridinium cations,[12] tetrahydrofuran molecules,[13] $PhP(O)_2(OH)$[14]). Inclusion of two or more guest molecules in the cavity of large cucurbit[*n*]urils offers a unique possibility to study new forms of stereoisomerism, bimolecular reactions, and the molecular behavior in the microenvironment.[15,16]

Cucurbit[*n*]urils differ from other molecular containers with cavities of similar size, such as cyclodextrins and calixarenes, in the shape of these macrocyclic cavitands. The cavity in cucurbit[*n*]urils has a barrel shape, whereas cyclodextrins and calixarenes have bowl-shaped cavities. The diameter of the portals of cucurbit[*n*]urils is smaller

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than the diameter of the inner cavity. However, the portals can be slightly deformed, thus allowing the guest molecule to be included inside the macrocycle. The fixed diameters of the cavities in cucurbit[*n*]urils is an important factor for the selective inclusion of guests of particular size.

In the present study, we synthesized new inclusion compounds of the macrocyclic cavitand cucurbit[8]uril with the nickel(II) complex containing the tetraazamacrocyclic ligand cyclam, $\{[Ni(cyclam)]@CB[8]\}Cl_2 \cdot 16H_2O$ (**1**), and with the copper(II) bis-ethylenediamine complex, $\{trans\text{-}[Cu(en)_2(H_2O)_2]@CB[8]\}Cl_2 \cdot \{CB[8]\} \cdot 42H_2O$ (**2a**) and $\{trans\text{-}[Cu(en)_2(H_2O)_2]@CB[8]\}Cl_2 \cdot 17H_2O$ (**2b**), and investigated the properties of these compounds.

Results and Discussion

The inclusion compound of cucurbit[8]uril with the nickel cyclam complex $\{[Ni(cyclam)]@CB[8]\}Cl_2 \cdot 16H_2O$ (**1**) was prepared as yellow crystals in 89% yield by refluxing an aqueous solution containing an adduct of the cucurbit[8]uril inclusion compound of cyclam with the composition cyclam@CB[8]·4HCl·$18H_2O$ and an excess of nickel chloride. Cyclam can be coordinated (as a tetradentate ligand) to metal atoms through the nitrogen atoms even inside the cucurbit[8]uril cavity giving rise to a tetrakis-chelate. This ability has been successfully employed for the first time in the synthesis of the copper complex $\{[Cu(cyclam)(H_2O)]@CB[8]\}(NO_3)_2 \cdot 14H_2O$.[9]

The IR spectrum of complex **1** confirms the presence of cucurbit[8]uril in the crystals. The structure of complex **1** was established by X-ray diffraction analysis. In molecule **1**, the inner cavities of cucurbit[8]uril (host) are occupied by the cationic square-planar nickel cyclam complexes (guest) (Fig. 1, *a*). All nitrogen atoms of the tetraazamacrocyclic moiety are coordinated to the metal atom (Ni—N, 1.913(4) and 1.927(4) Å). Therefore, the nickel atom has a coordination number of four. The plane of the Ni^{II} complex is strongly inclined (by ~70°) to the equatorial plane of cucurbit[8]uril (see Fig. 1, *b*). An inclination of the plane of the inner macrocycle relative to the outer macrocycle is observed also in the inclusion compounds of cucurbit[8]uril with cyclen and cyclam, *viz.*, (cyclen)@CB[8]·4HCl·$13H_2O$ and cyclam@CB[8]·4HCl·$18H_2O$ (angles of inclination are 38° and 59°, respectively).[9] However, coordination of cyclen to the copper(II) atom in the $\{[Cu(cyclen)(H_2O)]@CB[8]\}(NO_3)_2 \cdot 16H_2O$ compound results in a virtually parallel arrangement of the planes of the macrocycles (angle of inclination is ~4°).[9] A substantial inclination of the plane of the metal complex in compound **1** is apparently attributable to a larger size of the cyclam complex compared to the cyclen complex, which tends to be located in the host cavity in such a way as to minimize steric strain.

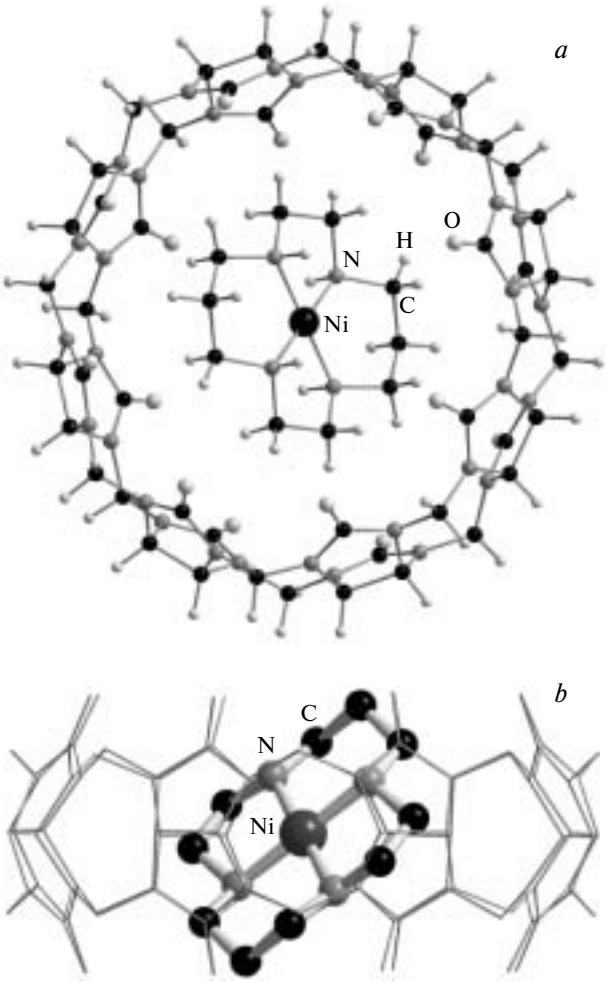

Fig. 1. Inclusion of the $[Ni(cyclam)]^{2+}$ complex in the cavity of the cucurbit[8]uril molecule in structure **1**: *a*, a top view; *b*, a side view.

The plane of each portal of the macrocyclic cavitand is occupied by two water molecules, which form hydrogen bonds with each other (O...O, 2.74 Å), with the amino groups of the ligand (O...N, 2.84 and 2.88 Å), and with the oxygen atoms of two carbonyl groups at each portal of cucurbit[8]uril (O...O, 2.84 and 2.88 Å). The presence of these water molecules is an additional factor preventing the complex from leaving the cavitand cavity.

The crystal packing of compound **1** contains one-dimensional channels along the *c* axis occupied by crystallization water molecules and Cl^- anions; the diameter of the channels is ~4.5 Å (Fig. 2). A loss of crystallization water leads to destruction of the crystals.

Compound **1** is soluble in water. The UV-Vis spectrum of this compound shows a characteristic band at 446 nm and is identical to the UV-Vis spectrum of the free nickel(II) perchlorate complex with cyclam.[17] This is evidence that in solution the nickel atom is in a square-planar environment formed by the nitrogen atoms of

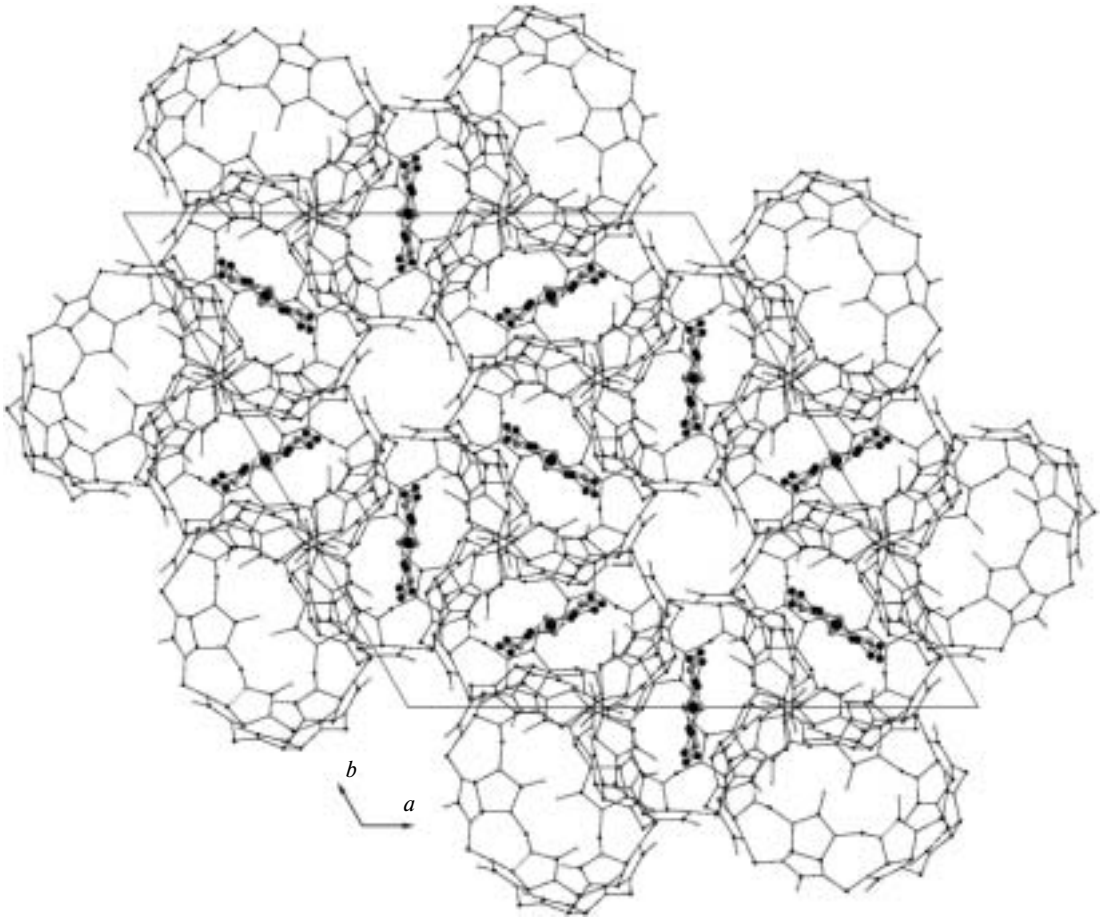

Fig. 2. Crystal packing of inclusion compound **1** projected along the *c* axis. The water solvate molecules and the chloride anions are omitted.

cyclam inside the cucurbit[8]uril cavity.[18] Investigation of an aqueous solution of **1** by electrospray mass spectrometry demonstrated that the supramolecular compound of the "a complex in a macrocycle" type observed in the solid state is retained in solution, because the most intense signal in the mass spectrum corresponds to the $[CB[8] + Ni(cyclam)]^{2+}$ ion.

Since the NiN_4 plane in molecule **1** is substantially inclined to the equatorial plane of cucurbit[8]uril, additional coordination to the nickel(II) atoms is impossible. This coordination is of interest for the construction of chain coordination polymers, in which various N-donor ligands can serve as linking units. Hence, it was of interest to examine the possibility of including the smaller copper bis-ethylenediamine complex *trans*-$[Cu(en)_2(H_2O)_2]^{2+}$ in cucurbit[8]uril. The largest van der Waals size of the copper(II) bis-ethylenediamine complex (9.2 Å) is ~1 Å smaller than that of the nickel(II) cyclam complex (10.1 Å), whereas the van der Waals size of the inner cavity of CB[8] is 8.8 Å.[11] The presence of the hydrophobic $CH_2—CH_2$ groups in the ethylenediamine molecule would be favorable for the inclusion of the complex in the hydrophobic cavity of cucurbit[8]uril, and the possible replacement of the weakly coordinated axial H_2O ligands with N-donor ligands is a prerequisite for the formation of coordination polymers. The $\{[Cu(en)_2(H_2O)_2]@CB[8]\}^{2+}$ compound is the first example of the successful synthesis of inclusion compounds of a macrocyclic cavitand with a complex using cucurbit[8]uril (host) and the metal ethylenediamine complex (guest) as the starting reagents. Earlier,[9] inclusion compounds of cyclen and cyclam complexes have been prepared by the reactions of the inclusion compound (cyclen)@CB[8] or (cyclam)@CB[8] with an excess of a metal salt. The $[M(cyclen)]^{2+}$ and $[M(cyclam)]^{2+}$ complexes cannot be directly inserted into the inner cavity of cucurbit[8]uril (van der Waals diameter of the portal is ~6.9 Å)[11] because of the larger sizes of these complexes and their rather high conformational rigidity.

Lilac-colored crystals of the $\{trans\text{-}[Cu(en)_2(H_2O)_2]@CB[8]\}Cl_2 \cdot \{CB[8]\} \cdot 42H_2O$ compound (**2a**) were prepared by refluxing an aqueous solution of cucurbit[8]uril and a sixfold excess of $[Cu(en)_2]Cl_2 \cdot 0.5H_2O$. According to the results of elemen-

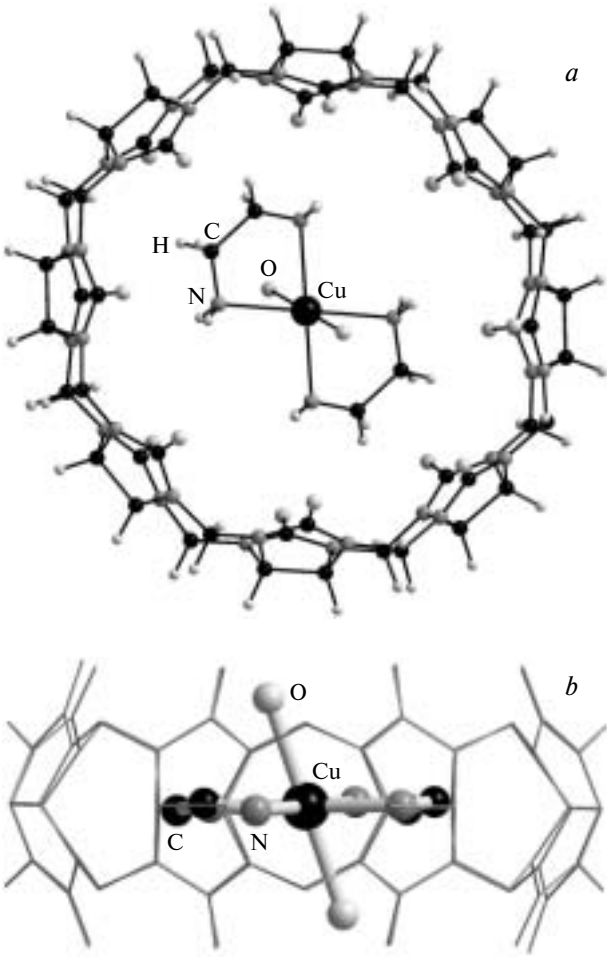

Fig. 3. Inclusion of the *trans*-$[Cu(en)_2(H_2O)_2]^{2+}$ complex in the cavity of the cucurbit[8]uril molecule in structure **2a**: *a*, a top view; *b*, a side view.

tal analysis and X-ray diffraction study, the cavities of only half of the cucurbit[8]uril molecules in the crystal lattice of **2a** contain the guest molecules, *viz.*, the cationic complex $[Cu(en)_2(H_2O)_2]^{2+}$ (Fig. 3, *a*). The fact that only half of the hosts molecules are occupied (recall that a sixfold excess of the metal complex with respect to the macrocycle was used) is indicative of instability of this inclusion compound. An even higher excess of the starting copper complex is required to fill all CB[8] cavities with the guests molecules. The reaction with the use of a 30-fold excess of the copper complex afforded the {*trans*-$[Cu(en)_2(H_2O)_2]$@CB[8]}$Cl_2 \cdot 17H_2O$ compound (**2b**) with a guest : host ratio of 1 : 1.

The *trans*-$[Cu(en)_2(H_2O)_2]^{2+}$ complex is smaller than the nickel(II) cyclam complex (**1**), and the plane through the four nitrogen atoms of two en ligands in compounds **2a** and **2b** coincides with the equatorial plane of the cucurbit[8]uril molecule (see Fig. 3, *b*). The inclusion of the guest is accompanied by a slight distortion of the cavitand molecule; the difference in the distances between the opposite carbon atoms of the CH groups of cucurbit[8]uril is 0.49 Å. This deformation associated with the inclusion of guests molecules is typical of cucurbit[*n*]urils, particularly, if the van der Waals size of the guest is comparable with that of the host cavity. In the inclusion compounds of CB[8] with two bulky organic molecules, this difference is 1.31 Å.[19]

In compound **2a**, the Cu—N distances are 2.000(11) and 2.004(10) Å. The coordination environment of the copper(II) atom involves also two H_2O ligands, which are rather far removed from the central atom (Cu—O, 2.547(9) Å). The Cu—O axis is virtually perpendicular to the CuN_4 plane (80°). The copper atom has a coordination number of six, and the coordination polyhedron is a distorted octahedron. The plane of each portal of cucurbit[8]uril is occupied by two water molecules, which are linked to the H_2O water molecule of the copper complex (O...O, 2.71 and 2.72 Å), the amino groups of ethylenediamine (O...N, 2.75 and 2.85 Å), and the oxygen atoms of four carbonyl groups of the CB[8] portal (O...O, 2.92—2.96 Å) *via* hydrogen bonds.

Compounds **2a** and **2b** are isostructural. The crystal packing has an island motif, and the cucurbit[8]uril molecules are arranged in a herringbone fashion.

Heating of compounds **2a** and **2b** in water leads to their decomposition. The $[Cu(en)_2(H_2O)_2]^{2+}$ complex goes into solution (pale-violet color), and water-insoluble cucurbit[8]uril precipitates.

$$\{trans\text{-}[Cu(en)_2(H_2O)_2]@CB[8]\}Cl_2 \rightarrow$$
$$\rightarrow trans\text{-}[Cu(en)_2(H_2O)_2]^{2+} + 2\ Cl^- + CB[8]$$

The results of the present study demonstrate that compounds **2a** and **2b** are less stable than the inclusion compound of cyclam complex **1**. Heating of the latter in water over a long period of time did not lead to decomposition of this compound and precipitation of cucurbit[8]uril.

The electrospray mass spectrum of an aqueous solution of compound **2a** shows two intense peaks of the $[CB[8] + Cu(en)_2]^{2+}$ supramolecular adduct, which confirm the existence of the inclusion compound and free cucurbit[8]uril ($[CB[8] + 2\ H]^{2+}$ cation) in solution.

The ESR spectrum of a solid sample of **2a** is characteristic of the axial environment of the central Cu^{II} atom (square is formed by the nitrogen atoms of ethylenediamine, and the oxygen atoms of the H_2O ligands are in the axial positions). The hyperfine coupling constant $a_{\parallel}$ = 175.6 Gs is typical of the square-planar environment of Cu^{2+} formed by the nitrogen atoms. The $g_{\perp}$ factor is equal to the corresponding value for the $[Cu(en)_2]Cl_2 \cdot 0.5H_2O$ complex in the solid state ($g_{\perp}$ = 2.049).[20] Consequently, the electronic structure of the guest remains virtually unchanged upon inclusion in the cucurbit[8]uril cavity.

To summarize, we demonstrated using the copper(II) ethylenediamine complex as an example that guest—host inclusion compounds can be directly synthesized starting from a metal complex and cucurbit[8]uril. In the *trans* form of the copper complex included in cucurbit[8]uril, the easily replaceable H_2O ligands are in the axial positions. Hence, such inclusion compounds can be considered as convenient starting reagents for the synthesis of coordination polymers. Experiments on the construction of such chain coordination polymers with various N-donor ligands, for example, with *trans*-4,4′-dipyridylethylene, are currently underway in our laboratory.

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), ethylenediamine (99% purity), and HCl (reagent grade) were used without additional purification. Cucurbit[8]uril,[21] cyclam@CB[8]·4HCl·$18H_2O$,[9] and $[Cu(en)_2]Cl_2 \cdot 0.5H_2O$ [22] were synthesized according to procedures published earlier.

The IR spectra were recorded on a Bruker IFS-85 spectrophotometer in KBr pellets. The UV-Vis spectra were measured on an Ultrospec 3300pro spectrophotometer. Elemental analysis was carried out at the Laboratory of Microanalysis of the Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. X-ray diffraction study was performed on Bruker SMART CCD and Bruker Nonius X8Apex single-crystal diffractometers equipped with a 4K-CCD detector.[23] The ESR spectra were recorded on a Varian E-109 spectrometer. The mass spectra (ESI-MS) were obtained on Quattro LC and QTOF I mass spectrometers (Micromass, Manchester, UK).

Cucurbit[8]uril (1,4,8,11-tetraazacyclotetradecanickel(II) clathrate dichloride hexahydrate, {[Ni(cyclam)]@CB[8]}$Cl_2 \cdot 16H_2O$ (1). A hot solution of $NiCl_2 \cdot 6H_2O$ (0.048 g 0.202 mmol) in water (5 mL) was mixed with a hot solution of cyclam@CB[8]·4HCl·$18H_2O$ (0.030 g, 0.016 mmol) in water (5 mL). The reaction mixture was refluxed for 2 h. In the course of the synthesis, the pale-green solution turned yellow. Then the reaction mixture was slowly cooled and concentrated in air at room temperature, after which the product precipitated as yellow large crystals. The crystals were filtered off, washed with a small amount of cold water, and dried in air. The yield was 0.026 g (89% with respect to cyclam@CB[8]·4HCl·$18H_2O$). The product is soluble in hot water and rapidly loses crystallization water in air. Found (%): C, 35.51; H, 5.28; N, 26.05; Cl, 3.64. $C_{58}H_{104}Cl_2N_{36}O_{32}Ni$. Calculated (%): C, 35.76; H, 5.38; N, 25.89; Cl, 3.64. UV-Vis (200—1100 nm), λ/nm (ε): 446 (74). MS (ESI-MS), m/z (I_{rel} (%)): 536.511 [CB[8] +

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

Compound	**1**	**2a**	**2b**
Molecular weight	1953.39	3705.72	1890.10
T/K	120(2)	150(2)	150(2)
Space group	$R\bar{3}$	$I4_1/a$	$I4_1/a$
a/Å	28.9600(13)	28.0962(3)	28.0382(4)
b/Å	28.9600(13)	28.0962(3)	28.0382(4)
c/Å	26.2096(17)	21.9381(5)	21.9038(5)
V/Å^3	19036.5(17)	17317.9(5)	17219.5(5)
Z	9	4	8
d/g cm^{-3}	1.534	1.421	1.458
μ/mm^{-1}	0.398	0.268	0.417
F(000)	9228	7788	7912
Crystal dimensions/mm	0.15×0.10×0.05	0.25×0.22×0.15	0.60×0.35×0.22
θ Scan range/deg	1.80—28.05	1.45—25.03	1.18—25.03
Ranges of h, k, l indices	$-38 \le h \le 36$	$-23 \le h \le 23$	$-22 \le h \le 22$
	$-38 \le k \le 37$	$-33 \le k \le 33$	$-33 \le k \le 33$
	$-34 \le l \le 34$	$-25 \le l \le 25$	$-26 \le l \le 26$
Number of measured reflections	45524	48748	24813
Number of independent reflections	10026	7364	6827
(R_{int})	(0.1111)	(0.0541)	(0.0450)
Number of parameters in refinement*	598	670	670
S factor on F^2	0.858	1.090	1.187
R factor ($I > 2\sigma(I)$)			
R_1	0.0768	0.0658	0.0646
wR_2	0.1747	0.2240	0.2310
R factor (all reflections)			
R_1	0.1679	0.0868	0.0837
wR_2	0.2116	0.2635	0.2759

* The refinement was carried out without restrictions on the parameters to be refined.

+ Ni(cyclam) + Na]$^{3+}$ (5), 542.513 [CB[8] + Ni(cyclam) + + Na + H_2O]$^{3+}$ (5), 793.245 [CB[8] + Ni(cyclam)]$^{2+}$ (100). IR (KBr), ν/cm^{-1}: 3448 s, 3002 w, 2919 w, 1722 s, 1471 s, 1425 m, 1372 s, 1316 s, 1289 m, 1229 s, 1188 s, 1153 m, 1026 w, 992 w, 969 s, 829 m, 806 s, 758 m, 672 m, 629 w.

[Cucurbit[8]uril *trans*-bisethylenediaminediaquacopper(II) clathrate] dichloride [cucurbit[8]uril solvate] 42-crystal hydrate, {*trans*-[Cu(en)$_2$(H$_2$O)$_2$]@CB[8]}Cl$_2$·{CB[8]}·42H$_2$O (2a). Cucurbit[8]uril ($C_{48}H_{48}N_{32}O_{16}\cdot 20H_2O$) (0.0315 g, 0.019 mmol) was added with slight heating to a solution of $[Cu(en)_2]Cl_2\cdot 0.5H_2O$ (0.030 g, 0.114 mmol) in water (8 mL). The reaction mixture was refluxed for 2 h and then slowly cooled. After 4 days, lilac-colored octahedral crystals that precipitated were filtered off, washed with a small amount of cold water, and dried in air. The yield was 0.033 g (96% with respect to cucurbit[8]uril). Found (%): C, 32.30; H, 4.70; N, 25.94; Cl, 2.21. $C_{100}H_{200}Cl_2CuN_{68}O_{76}$. Calculated (%): C, 32.41; H, 5.44; N, 25.70; Cl, 1.91. MS (ESI-MS), m/z (I_{rel} (%)): 512 [CB[8] + Cu(en)$_2$ + Na]$^{3+}$ (60), 518 [CB[8] + Cu(en)$_2$ + Na + + H_2O]$^{3+}$ (37), 666 [CB[8] + 2 H]$^{2+}$ (65), 676 [CB[8] + H + + Na]$^{2+}$ (77), 684 [CB[8] + H + Na + H_2O]$^{2+}$ (35), 688 [CB[8] + 2 Na]$^{2+}$ (27), 695 [CB[8] + en + 2 H]$^{2+}$ (100), 704 [CB[8] + en + 2 H + H_2O]$^{2+}$ (43), 756 [CB[8] + Cu(en)$_2$]$^{2+}$ (44). ESR: $a_{\parallel}$ = 175.6 Gs, $g_{\parallel}$ = 2.212, $g_{\perp}$ = 2.049. IR (KBr), ν/cm^{-1}: 3435 s, 3004 w, 2922 w, 1727 s, 1472 s, 1426 m, 1375 s, 1319 s, 1293 m, 1230 s, 1191 s, 1155 m, 1027 w, 993 w, 970 s, 829 m, 808 s, 759 m, 674 m, 631 w.

Cucurbit[8]uril *trans*-bis(ethylenediamine)diaquacopper(II) clathrate dichloride heptahydrate, {*trans*-[Cu(en)$_2$(H$_2$O)$_2$]@CB[8]}Cl$_2$·17H$_2$O (2b). Cucurbit[8]uril ($C_{48}H_{48}N_{32}O_{16}\cdot 20H_2O$) (0.0315 g, 0.019 mmol) was added with slight heating to a solution of $[Cu(en)_2]Cl_2\cdot 0.5H_2O$ (0.150 g, 0.569 mmol) in water (8 mL). The reaction mixture was refluxed for 2 h and then slowly cooled. After one day, violet octahedral crystals that precipitated were filtered off, washed with a small amount of cold water, and dried in air. The yield was 0.024 g (66% with respect to cucurbit[8]uril). Found (%): C, 33.36; H, 4.85; N, 26.72; Cl, 3.75. $C_{52}H_{98}Cl_2CuN_{36}O_{33}$. Calculated (%): C, 33.05; H, 5.23; N, 26.68; Cl, 3.75. IR (KBr), ν/cm^{-1}: 3440 s, 3006 w, 2921 w, 2855(w), 1721 s, 1631(m), 1471 s, 1421 m, 1375 s, 1323 s, 1294 m, 1231 s, 1192 s, 1154 m, 1028 w, 994 w, 970 s, 810 s, 757 m, 675 m, 632 w.

X-ray diffraction study. The structures of compounds **1**, **2a**, and **2b** were established by X-ray diffraction analysis. X-ray data were collected according to a standard procedure at 120 K for **1** and at 150 K for **2a** and **2b**. In all experiments, Mo-Kα radiation (λ = 0.71073 Å) and a graphite monochromator were used. The crystallographic data and details of X-ray diffraction study are given in Table 1. The semiempirical absorption correction was applied based on 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 package.[24] 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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