Inclusion compounds of cucurbit[8]uril with noble metal polyamine complexes

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Inclusion compounds of the macrocyclic cavitand cucurbit[8]uril (CB[8]) with the ruthenium(III) bis(ethylenediamine) complex {*trans*-$[Ru(en)_2Cl_2]$@CB[8]}$Cl \cdot 27.5H_2O$ (**1**), the gold(III) diethylenetriamine complex {[Au(dien)Cl]@CB[8]}$Cl_2 \cdot 11H_2O$ (**2**), and the gold(III) and platinum(II) cyclam complexes $(H_3O)_5${[Au(cyclam)]@CB[8]}$Cl_8 \cdot 18H_2O$ (**3**) and {$[Pt(cyclam)]_{0.11}(H_2cyclam)_{0.89}$@CB[8]}$Cl_2 \cdot 16H_2O$ (**4**), respectively, where cyclam is the tetraazamacrocyclic ligand, were synthesized. The inclusion compounds were synthesized both directly starting from CB[8] and the metal complexes with polyamines (en or dien) and by the two-step method with the use of the cyclic polyamine ligand (cyclam) pre-included into the cavity of the macrocycle. The inclusion compounds were characterized by X-ray diffraction (**1**, **2**, and **4**), IR spectroscopy, electrospray ionization mass spectrometry, UV—Vis spectroscopy, and thermogravimetric analysis.

Key words: ruthenium, gold, platinum, cucurbit[8]uril, inclusion compounds, X-ray diffraction analysis.

Cucurbit[*n*]urils ($C_{6n}H_{6n}N_{4n}O_{2n}$, CB[*n*]; n = 5—10) comprise a family of macrocyclic molecules containing an open hydrophobic intramolecular cavity accessible through two hydrophilic portals formed by *n* carbonyl groups.[1—4] This structure determines the behavior of cucurbit[*n*]urils as cavitands, *viz.*, host molecules capable of encapsulating guest molecules of suitable size into the inner cavity. A high negative electrostatic potential on the portals[3] is responsible for the formation of stable inclusion compounds of CB[*n*] with positively charged guests, for example, with alkylammonium cations.[2,3] The cavity sizes in cucurbit[*n*]urils with $n > 6$ are sufficient for the inclusion of metal complexes with small organic ligands. The spectroscopic (NMR), calorimetric, and electrochemical studies showed that highly stable host—guest compounds are formed.[5—9] However, only a few inclusion compounds of CB[*n*] with metal complexes were structurally characterized.[6,10—12] Complexes included into the barrel-shaped cavity of CB[*n*] can be fully embedded in the cavitand, as opposed to most of inclusion compounds of such receptors as calixarenes and cyclodextrins where complexes are only partially encapsulated in the bowl-shaped cavities.[13]

In recent years, this class of compounds has attracted considerable interest because of the possibility of the inclusion of biologically active metal complexes into cavitands. This opens wide opportunities for the design of new generation prolonged-action pharmaceuticals in which the host molecules prevents the guest molecules from rapid decomposition, decrease their toxicity, and have the transport function of the active component in the organism.[14] Recent studies[14—16] have shown that the inclusion of platinum polyamine complexes having antitumor activity into cucurbit[*n*]urils leads to a substantial decrease in the toxicity of these complexes. Antitumor drugs containing inclusion compounds of CB[7] and CB[8] with platinum, palladium, and gold complexes were covered by patents.[17—20]

Previously,[21—25] we have shown that CB[8] forms inclusion compounds with cobalt(III), nickel(III), and copper(II) complexes containing cyclic and acyclic aliphatic polyamines, such as cyclam, ethylenediamine, 1,3-diaminopropane, and 1,3-diaminopropan-2-ol. The presence of hydrophobic —$(CH_2)_n$— groups in these compounds is favorable for the inclusion of complexes into the hydrophobic cavity of the macrocycle. The inclusion leads to a change in the geometric and spectroscopic characteristics of the complexes and to their stabilization against the thermolysis, isomerization, and aquation. As a continuation of this research, it was of interest to synthesize inclusion compounds of noble metal polyamine complexes, which are promising in terms of bioinorganic chemistry. Thus gold(III) complexes with polydentate amines (ethylenediamine, diethylenetriamine, *etc.*) are known to have antitumor and cytotoxic properties and, unlike other Au^{III} complexes, are more stable under physiological conditions.[26,27] Complexes with the cyclic tetradentate cyclam ligand (1,4,8,11-tetraazacyclotetradecane,

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$C_{10}N_4H_{24}$) and its derivatives are widely used in medicine, for example, as antiviral agents.[28—30]

In the present study, we synthesized and characterized the inclusion compounds of CB[8] with the ruthenium(III) ethylenediamine complex {*trans*-$[Ru(en)_2Cl_2]$@CB[8]}Cl • $27.5H_2O$ (**1**), the gold(III) diethylenetriamine complex {[Au(dien)Cl]@CB[8]}Cl_2 • $11H_2O$ (**2**), and the gold(III) and platinum(II) complexes containing the tetraazamacrocyclic cyclam ligand, $(H_3O)_5${[Au(cyclam)]@CB[8]}Cl_8 • $18H_2O$ (**3**) and {$[Pt(cyclam)]_{0.11}[H_2cyclam]_{0.89}$@CB[8]}$Cl_2$ • $16H_2O$ (**4**), respectively.

Results and Discussion

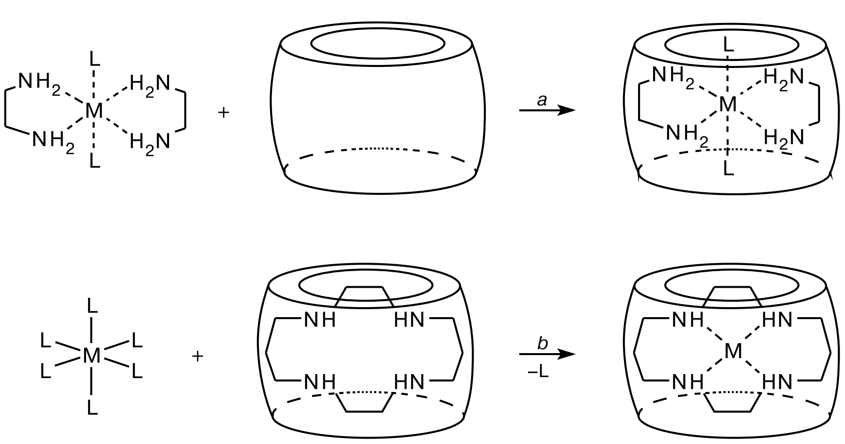
The inclusion compounds of ruthenium(III) and gold(III) complexes with ethylenediamine and diethylenetriamine ligands were synthesized by the direct host + guest scheme where CB[8] (host) and metal complexes with polyamine ligands (guests) were used as the starting compounds (Scheme 1, path *a*). We have suggested this method earlier[21—24] for the synthesis of inclusion compounds of cobalt(III), nickel(II), and copper(II) complexes with polyamine ligands. Inclusion compounds of gold(III) and platinum(II) with the tetraazamacrocyclic cyclam ligand were synthesized by the two-step method starting from the corresponding metal complexes with monodentate ligands and the inclusion compound of CB[8] with cyclam (Scheme 1, path *b*). Since the complexes with cyclam are larger in size than ethylenediamine complexes and are conformationally more rigid than the free cyclam, they cannot pass through the portals of CB[8], and it is impossible to use the direct host + guest method. This two-step approach has been used for the first time for the synthesis of inclusion compounds of copper(II) and zinc(II) complexes[10] and successfully employed for the preparation of inclusion compounds of the nickel(II) complex.[21]

The inclusion compound of the ruthenium(III) complex {*trans*-$[Ru(en)_2Cl_2]$@CB[8]}Cl • $27.5H_2O$ (**1**) was synthesized in high yield as pale-yellow crystals by refluxing cucurbit[8]uril with a tenfold molar excess of the complex *trans*-$[Ru(en)_2Cl_2]$Cl in 0.1 *M* HCl followed by cooling of the solution. It is necessary to use the solution in hydrochloric acid as the reaction medium to prevent hydrolysis of the ruthenium complex.[31] Crystals of **1** are readily soluble in water and 0.1 *M* HCl.

The single-crystal X-ray diffraction study showed that the *trans*-$[Ru(en)_2Cl_2]^+$ complex in inclusion compound **1** is located in the cavity of each cavitand molecule. The metal atom is surrounded by four coplanar nitrogen atoms of two ethylenediamine ligands. Two chlorine atoms are in the *trans* position (Fig. 1). Compound **1** is isostructural with the inclusion compound of the cobalt(III) ethylenediamine complex, {*trans*-$[Co(en)_2Cl_2]$@CB[8]}Cl • $17H_2O$, which we have synthesized earlier.[23]

In the structure of **1**, there are two (**1A** and **1B**) crystallographically independent cations {*trans*-$[Ru(en)_2Cl_2]$@CB[8]}$^+$, which differ in the dihedral angle between the RuN_4 plane of the guest and the equatorial plane of the cavitand (75° and 90° for **1A** and **1B**, respectively) and in some geometric parameters of the guest and host molecules. The axial chloride ligands in **1A** and **1B** are embedded in the cavity of CB[8]. This arrangement of the complexes with chloride ligands differs from the orientation of the aqua complexes in the cavity of CB[8], in which the *trans* positions in the coordination environment of the metal atoms are occupied by water molecules, {*trans*-$[Cu(en)_2(H_2O)_2]$@CB[8]}$^{2+}$ and {*trans*-$[Ni(en)_2(H_2O)_2]$@CB[8]}$^{2+}$.[21,22] The aqua complexes are arranged so that the MN_4 plane almost coincides with the equatorial plane of CB[8], and the aqua ligands are located at the portals of the cavitand rather than inside the cavity. The fact that the aqua and chloro complexes as the guests are in different orientations in the cavities of CB[8]

Scheme 1



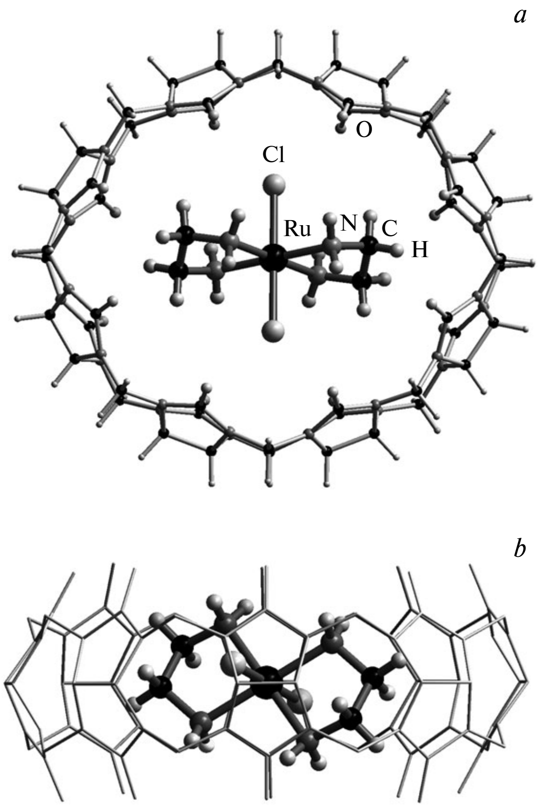


Fig. 1. Molecular structure of the inclusion compound {*trans*-$[Ru(en)_2Cl_2]@CB[8]\}^+$ in the crystal structure of **1**: *a*, top view; *b*, side view. The hydrogen atoms of cucurbit[8]uril are not shown.

is apparently attributed to the difference in the nature of the axial ligands. Thus, the arrangement near the negatively charged portals is less favorable for the coordinated chloride anion than for water.

The *trans*-$[Ru(en)_2Cl_2]^+$ cation was not characterized by X-ray diffraction. Hence, it is impossible to estimate the influence of the inclusion of the complex into CB[8] on the geometric parameters of the guest in structure **1**. The Ru—N (2.089(5)—2.112(4) Å) and Ru—Cl (2.332(1), 2.334(1) Å) distances in **1** are in the range characteristic of "free" ruthenium(III) polyamine complexes. For example, the Ru—N and Ru—Cl bond lengths in the complex *trans*-$[Ru(cyclam)Cl_2]Br$ are 2.083 and 2.344 Å, respectively,[32] and the Ru—N bond lengths in the complex $[Ru(en)_3]Cl_3$ are in the range of 2.102—2.117 Å.[33]

The CB[8] molecules in the structure of **1** show an ellipsoidal distortion (Δ_{CH}, the largest difference in the distances between the opposite carbon atoms of CH groups) typical of inclusion compounds of this cavitand. For two crystallographically independent molecules (**1A** and **1B**), the distortions are different (1.87 and 0.89 Å, respectively). Similar distortions of the CB[8] molecules (Δ_{CH} 1.43 and 0.78 Å) were observed[23] for the inclusion compounds of the cobalt(III) complex. In the inclusion compound of the nickel(II) complex, the distortion (2.92 Å) is the largest of all the values known[22] for CB[8]. Apparently, the distortion of CB[8] molecules is influenced by the crystal packing effect of these compounds.

The crystal structure of **1** consists of alternating layers composed of molecules **1A** and **1B** (Fig. 2). In each layer, the equatorial planes of the CB[8] molecules are parallel to each other. The angle between the planes of the CB[8] molecules of the adjacent layers is 54°. Crystallization water molecules and chloride anions are located between the layers.

The IR spectrum of compound **1** shows characteristic bands of CB[8] (1800—400 cm^{-1}) and water, as well as narrow medium-intensity bands at 2924 and 2855 cm^{-1}, which can be assigned to N—H stretching vibrations of the coordinated ethylenediamine ligand.

The thermogravimetric analysis of inclusion compound **1** and, for the comparison, of the "free" (not encapsulated into the cavity of the cavitand) ruthenium complex *trans*-$[Ru(en)_2Cl_2]Cl$ was carried out (Fig. 3). The storage of inclusion compound **1** in air leads to the rather rapid loss of the crystallization water molecules. According to the data from elemental analysis, compound **1** dried over P_2O_5 contains 19 water molecules less compared to the crystal freshly isolated from the solution (X-ray diffraction data). In the first decomposition step for inclusion compound **1** (heating to 130 °C), the weight loss is 8 wt.%, which corresponds to the removal of eight water molecules. Therefore, a total of 27 molecules are eliminated after drying over P_2O_5 and thermal decomposition, which is consistent with the formula determined by X-ray diffraction. The decomposition of inclusion compound **1** in the second step of the thermolysis begins at 350—360 °C, *i.e.*, at the decomposition temperature of CB[8],[22,23]

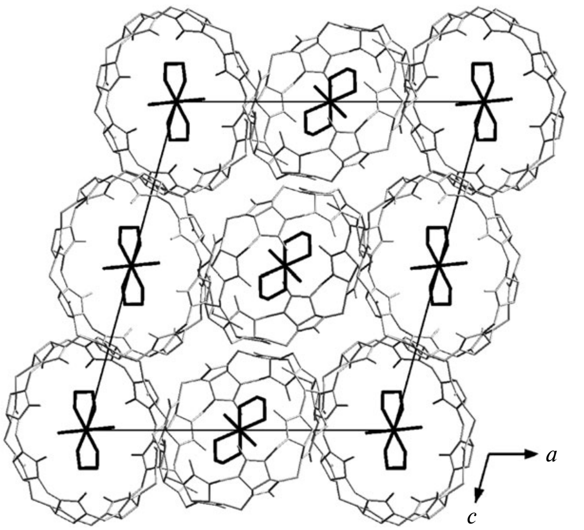


Fig. 2. Crystal packing of **1** (projection along the *b* axis). The guest complexes are drawn by black lines. The hydrogen atoms, solvent water molecules, and chloride anions are not presented.

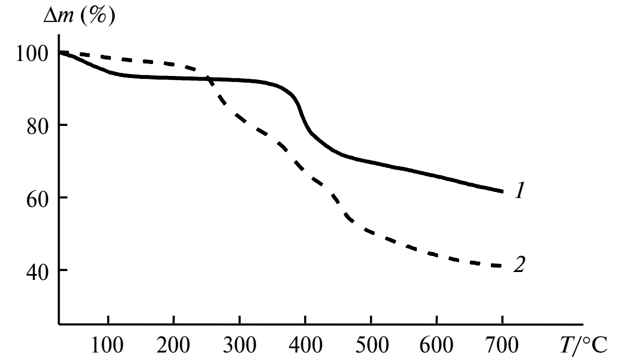


Fig. 3. Thermogravimetric analysis data for {*trans*-$[Ru(en)_2Cl_2]$@CB[8]}Cl • $14H_2O$ (*1*) and *trans*-$[Ru(en)_2Cl_2]Cl$ (*2*).

whereas the thermal decomposition of the "free" ruthenium complex begins at a substantially lower temperature (~220 °C). An increase in the thermal stability of metal complexes included into cavitands, for example, into cyclodextrins,[34,35] occurs rather frequently. As in the case of the inclusion compound of CB[8] with the cobalt complex,[23] the maximum increase in the thermal stability is observed at ~140 °C.

The electrospray ionization mass spectrum (ESI-MS) of an aqueous solution of **1** consists of a large number of different-intensity peaks, the most abundant peaks belonging to the $\{[Ru(en)_2Cl_2] + 2\ Na + CB[8]\}^{3+}$ and $\{[Ru(en)_2Cl_2] + Na + CB[8]\}^{2+}$ ions. This is evidence for the presence of host—guest complexes in an aqueous solution. However, the spectrum shows rather abundant peaks of the "free" $[Ru(en)_2Cl_2]^+$ ion, whose origin can be assigned to both the decomposition of the inclusion compound in the gas phase under experimental conditions and the partial dissociation of the inclusion compound in the aqueous solution. It should be noted that the oxidation state +3 of ruthenium in compound **1** is retained under the conditions of ESI-MS, whereas the metal atom in the cobalt analog is reduced to Co^{II}.[23]

The UV—Vis spectrum of an aqueous solution of inclusion compound **1** is, on the whole, similar to the spectrum of the "free" complex *trans*-$[Ru(en)_2Cl_2]Cl$.[36—38] In the UV—Vis spectra, the charge-transfer bands $e_g^* \leftarrow e_u$ from the occupied p—π orbital of the chloride ligand to the unoccupied d orbital of ruthenium are the major bands. The inclusion of the *trans*-$[Ru(en)_2Cl_2]^+$ cation into CB[8] leads to a substantial bathochromic shift of the most intense absorption band of the complex at 343 nm (to 352 nm for **1**) and an increase in the extinction coefficient of this band. The charge-transfer bands determining the spectral behavior of the ruthenium complexes are related to the changes in the outer-sphere environment of the metal atoms in a different way compared to the d—d transition bands of metals. The spectrum of the inclusion compound of the cobalt complex {*trans*-$[Co(en)_2Cl_2]$@CB[8]}Cl • $17H_2O$ shows the opposite effect, where a decrease in the extinction is observed. This fact is attributed to the less polarizable (compared to water) environment of the cavity of CB[8].[23] The bands of the "free" ruthenium complex *trans*-$[Ru(en)_2Cl_2]^+$ at 292 and 272 nm coalesce into one broad band, whose extinction decreases by a factor of 2 after the inclusion of the complex into CB[8].

The inclusion compound of the gold(III) diethylenetriamine complex with the composition {[Au(dien)Cl]@CB[8]}Cl_2 • $11H_2O$ (**2**) was synthesized in 67% yield as bright-yellow crystals by the slow diffusion of methanol into a solution of CB[8] and $[Au(dien)Cl]Cl_2$ (a threefold molar excess) in 0.01 *M* HCl. The solution in hydrochloric acid was used to prevent hydrolysis of the complex and deprotonation of diethylenetriamine coordinated to Au^{III} (the complex $[Au(dien)Cl]Cl_2$ is a weak acid (NH group of the ligand) with $pK_a = 4$).[39] Crystals of **2** are readily soluble in water.

In the crystal structure of compound **2**, the cavity of each cavitand molecule is occupied by the $[Au(dien)Cl]^{2+}$ cation disordered over two positions about the center of inversion (Fig. 4). The Au^{III} atom is in a weakly distorted square coordination environment formed by three nitrogen atoms of diethylenetriamine and the chloride ligand.

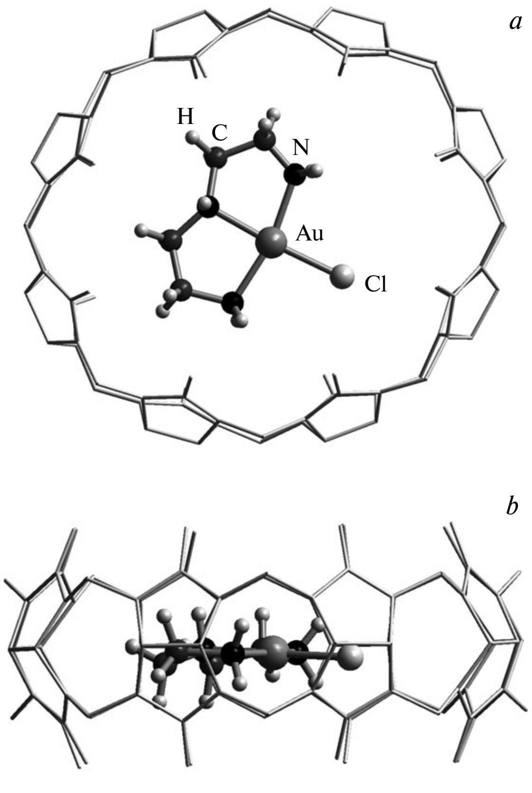


Fig. 4. Molecular structure of the inclusion compound $\{[Au(dien)Cl]@CB[8]\}^{2+}$ in the crystal structure of **2**: *a*, top view; *b*, side view. One position of the disordered guest molecule is presented. The hydrogen atoms of cucurbit[8]uril are not shown.

Due to the disorder, it is impossible to compare the geometry of the gold complex included into CB[8] and the "free" complex. The plane passing through the nitrogen and chlorine atoms (MN_3Cl) almost coincides with the equatorial plane of the CB[8] molecule; the dihedral angle between these planes is ~3°. The inclusion of $[Au(dien)Cl]^{2+}$ leads to a substantial ellipsoidal distortion of the cucurbit[8]uril molecule (Δ_{CH} = 1.41 Å). In the crystal structure of **2**, the CB[8] molecules are packed to form one-dimensional channels 4.9 Å in diameter (Fig. 5), which are extended along the *c* axis and are occupied by crystallization water molecules and the chloride ions.

The IR spectrum confirms the presence of cucurbit[8]uril in compound **2**. The bands at 2925 and 2855 cm^{-1} can be assigned to N—H stretching vibrations of diethylenetriamine.

According to the results of thermogravimetric analysis, the inclusion of the gold diethylenetriamine complex into CB[8] does not lead to its stabilization. After heating of inclusion compound **2** to 130 °C, the weight loss was 4.5 wt.%, which corresponds to the removal of five water molecules. The further decomposition of compound **2**, like that of the "free" complex, occurs upon heating above 180 °C.

The fact that the $[Au(dien)Cl]^+$ cation remains included into CB[8] in an aqueous solution is confirmed by the electrospray ionization mass spectrum of an aqueous solution of compound **2**. Thus the spectrum has abundant peaks belonging to the $\{CB[8] + [Au(dien)]\}^{3+}$, $\{CB[8] + [Au(dien)Cl] + H\}^{3+}$, $\{CB[8] + [Au(dien)Cl] + Na\}^{3+}$, $\{CB[8] + [Au(dien)Cl] + K\}^{3+}$, and $\{CB[8] + [Au(dien)Cl]\}^{2+}$ ions.

The inclusion compound of the gold(III) cyclam complex with the composition $(H_3O)_5\{[Au(cyclam)]@CB[8]\}Cl_8 \cdot 18H_2O$ (**3**) was synthesized in 82% yield as a yellow fine-crystalline precipitate from an aqueous solution of the inclusion compound of CB[8] with cyclam $\{cyclam@CB[8]\} \cdot 4HCl \cdot 18H_2O$ and the acid $HAuCl_4$ taken in a sixfold molar excess. Compound **3** is very poorly soluble in water. Attempts to obtain crystals suitable for X-ray diffraction by the recrystallization from solutions of mineral acids failed.

The composition of compound **3** was determined by elemental analysis. The number of H_3O^+ cations was estimated based on the principle of electroneutrality according to the number of chloride anions determined by elemental analysis. The IR spectrum confirms the presence of cucurbit[8]uril in compound **3**.

According to the results of thermogravimetric analysis, the weight loss after heating of compound **3** to 130 °C is 5 wt.%, which corresponds to the removal of six water

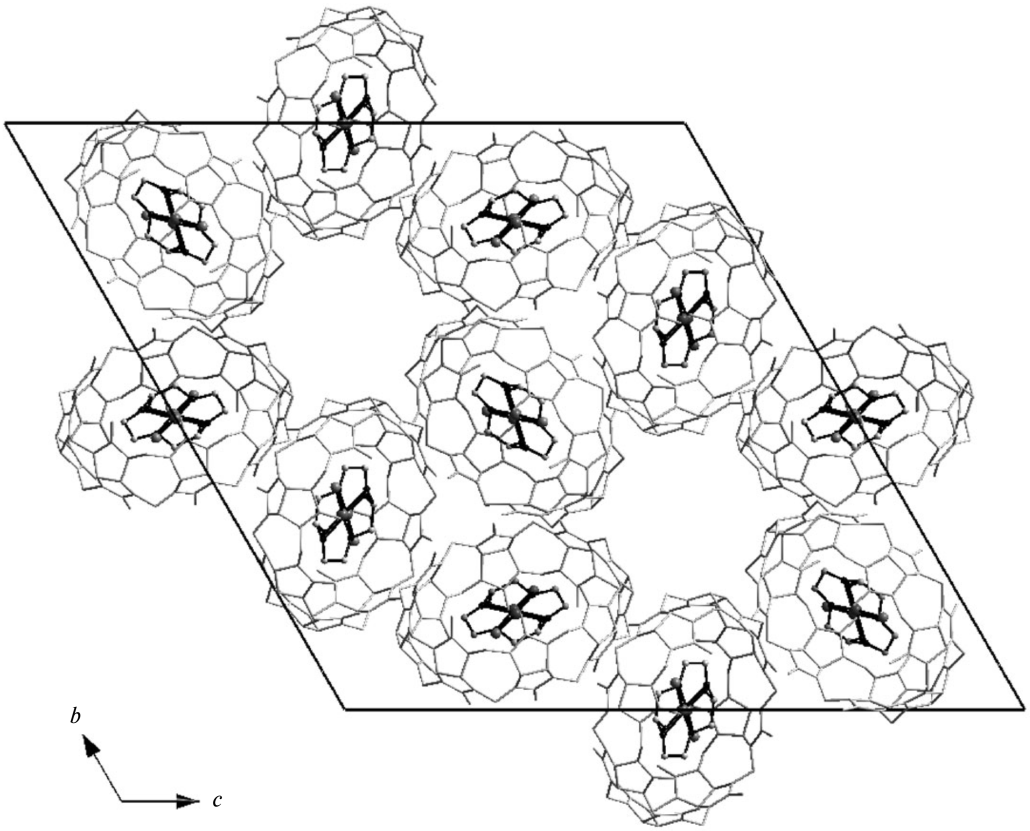


Fig. 5. Crystal packing of $\{[Au(dien)Cl]@CB[8]\}^{2+}$ in the structure of **2** (projection along the *c* axis). Both positions of the disordered guest molecule are presented. The hydrogen atoms, solvent water molecules, and chloride anions are not shown.

molecules. The heating above 180 °C leads to the further decomposition of compound **3**. The temperature of the onset of decomposition of the "free" gold(III) complex with cyclam is 160 °C. Therefore, as opposed to nickel(II),[22] cobalt(III),[23] and ruthenium(III) polyamine complexes **1**, the inclusion of thermally unstable gold(III) polyamine complexes **2** and **3** into CB[8] does not lead to an increase in the thermal stability.

In spite of the poor solubility of compound **3**, its concentration in an aqueous solution appeared to be sufficient for mass spectrometry. The mass spectrum has a set of different-intensity peaks. The most abundant peaks belong to the ions of the inclusion compound [Au(cyclam) + + CB[8] – H]$^{2+}$, and the appearance of these peaks is indicative of the presence of supramolecular host—guest adducts in an aqueous solution of **3** (Fig. 6).

The inclusion compound of the platinum complex with the composition {[Pt(cyclam)]$_{0.11}$[H$_2$cyclam]$_{0.89}$@-CB[8]}Cl$_2$ · 16H$_2$O (**4**) was synthesized as colorless crystals by refluxing an aqueous solution of {cyclam@CB[8]} · · 4HCl · 18H$_2$O with a fivefold molar excess of K$_2$PtCl$_4$ followed by cooling of the solution. Crystals of **4** are very poorly soluble in water and blacken upon storage in air for one day. The IR spectrum confirms the presence of cucurbit[8]uril in compound **4**.

The X-ray diffraction study of the crystal structure of **4** showed that the cavity of each cavitand molecule is occupied by the cyclam molecule. The platinum atom is disordered and is coordinated by the nitrogen atoms of the encapsulated cyclam molecule to form the [Pt(cyclam)]$^{2+}$ complex with an occupancy of 11%.

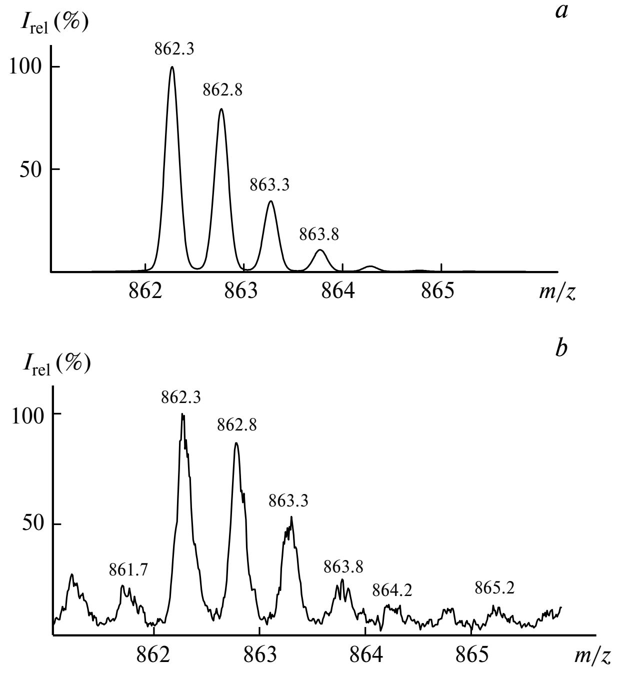


Fig. 6. Fragment of an electrospray ionization mass spectrum of compound **3**: the calculated (*a*) and experimental (*b*) isotopic distribution for [Au(cyclam) + CB[8] – H]$^{2+}$.

In spite of the fact that K$_2$PtCl$_4$ was used in a fivefold molar excess with respect to the cavitand, only partial complexation occurred. In the inclusion compounds of nickel(II) (see Ref. 21) and palladium(II) complexes,[25] which we have synthesized earlier according to the similar scheme (see Scheme 1, path *b*) with the use of a 10—12-fold excess of the metal salts, all cyclam molecules in the cavities of CB[8] are coordinated to the metal atoms. An increase in the excess of K$_2$PtCl$_4$ (to a 20-fold excess) and the storage of the reaction solution under reflux during a longer period of time did not lead to the formation of a crystalline precipitate.

In the structure of **4**, the metal atom of the [Pt(cyclam)]$^{2+}$ complex included into the cavity of the cavitand is in a weakly distorted square coordination environment formed by four N atoms of the cyclam (Fig. 7). The Pt—N distances are 1.948(4) and 2.069(4) Å and are similar to those in the "free" complex [Pt(cyclam)]Cl$_2$ · HCl · H$_2$O (2.039—2.045 Å).[40]

Cyclam in the structure of **4** adopts the most stable *trans*-III configuration (*S*,*S*,*R*,*R*) characteristic of both

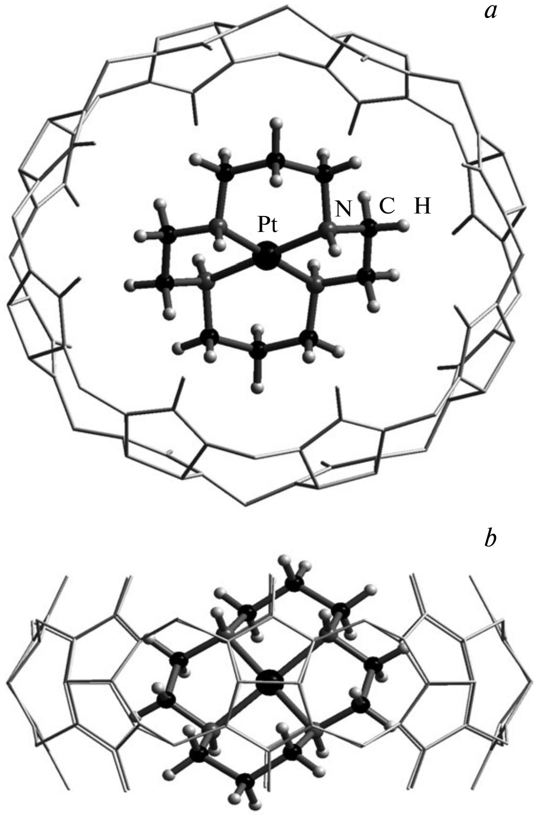


Fig. 7. Molecular structure of the inclusion compound {[Pt(cyclam)]@CB[8]}$^{2+}$ in the crystal structure of **4**: *a*, top view; *b*, side view. The hydrogen atoms of cucurbit[8]uril are not shown.

the free ligand and its complexes with metals.[41] In the inclusion compounds of nickel(ii),[21] palladium(ii), and palladium(iv) complexes,[25] which we have synthesized earlier, cyclam also adopts the *trans*-III configuration. Quite recently, it has been reported for the first time that copper(ii) complexes with unusual isomers of cyclam, *trans*-I (*R*,*S*,*R*,*S*) and *trans*-II (*R*,*S*,*R*,*R*), are stabilized in the inclusion compound $\{[Cu(cyclam)(H_2O)_{1.3}]@CB[8]\}(CB[8])_{0.5}(NO_3)_2 \cdot 17H_2O$.[12] The authors attributed the stabilization to the inclusion of the complexes into CB[8].

In the structure of **4**, the PtN_4 plane is inclined to the equatorial plane of CB[8] (the corresponding dihedral angle is ~77°), which is characteristic of inclusion compounds of CB[8] with both cyclam and its complexes.[10,12,21,25] The ellipsoidal distortion of the cavitand molecule Δ_{CH} in the structure of **4** is 0.88 Å, which is somewhat smaller than those found in the inclusion compounds of the nickel(ii) and palladium(ii) cyclam complexes (1.12 and 1.10 Å, respectively).[21,25]

In compound **4**, the protonation of 0.89% of the cyclam molecules, which are not coordinated to the platinum atoms, was estimated taking into account the principle of electroneutrality in accordance with the amount of the chloride anions determined by X-ray diffraction.

In the crystal structure of **4**, the cucurbit[8]uril molecules form one-dimensional channels 2.0 Å in diameter, which are extended along the *c* axis and are occupied by crystallization water molecules and chloride anions.

In summary, we synthesized and structurally characterized inclusion compounds of the macrocyclic cavitand CB[8] with noble metal (Au^{III}, Ru^{III}, and Pt^{II}) polyamine complexes. The inclusion compounds were synthesized both directly (from CB[8] and metal complexes with polyamines (en and dien)) and by the two-step method with the use of the polyamine ligand (cyclam) pre-included into the cavity of the cavitand. The resulting supramolecular compounds are quite stable and retain the host—guest structure in aqueous solutions. The inclusion of the guest molecules leads to a substantial ellipsoidal distortion of the CB[8] molecule. It was found that the thermal stability of the ruthenium(iii) ethylenediamine complex is essentially increased after the inclusion of this complex into the cavity of CB[8], whereas the thermal stabilization of the guest complex is not observed for the gold(iii) complexes with diethylenetriamine and cyclam.

Experimental

The starting reagents $HAuCl_4$ (analytical grade), K_2PtCl_4 (analytical grade), ethylenediamine (99%), diethylenetriamine (99%), cyclam (1,4,8,11-tetraazacyclotetradecane) (reagent grade), and HCl (reagent grade) were used without additional purification. Cucurbit[8]uril ($C_{48}H_{48}N_{32}O_{16} \cdot 20H_2O$)[4], $[Au(dien)Cl]Cl_2$,[42] *trans*-$[Ru(en)_2Cl_2]Cl$,[36] and $\{cyclam@CB[8]\} \cdot 4HCl \cdot 18H_2O$ (see Ref. 10) were synthesized according to procedures reported previously.

The IR spectra were recorded on a Scimitar FTS 2000 spectrophotometer in KBr pellets. The thermogravimetric analysis was carried out on a Q-1000 (MOM, Hungary) derivatograph with the use of a TG 209 F1 Iris® thermobalance (NETZSCH) under helium (~40 mL min^{-1}); the heating rate was 10 deg min^{-1}. The mass spectra (ESI-MS) were obtained on a Q-TOF I mass spectrometer (Micromass, Manchester, UK). The UV—Vis spectra were recorded on an Ultrospec 3300proљ spectrofluorimeter in the 190—1100 nm range. The elemental analysis for C, H, N, Cl was carried out in the Analytical Laboratory of the A. V. Nikolaev Institute of Inorganic Chemistry of the Siberian Branch of the Russian Academy of Sciences. The X-ray diffraction study was performed on a Bruker Nonius X8Apex single-crystal diffractometer equipped with a 4K-CCD detector.[43]

Cucurbit[8]uril(*trans*-dichloro-bis-ethylenediamine-ruthenium(iii)) chloride clathrate crystal 27.5-hydrate {*trans*-$[Ru(en)_2Cl_2]@CB[8]\}Cl \cdot 27.5H_2O$ (1). Cucurbit[8]uril (0.129 g, 0.076 mmol) was dissolved with gentle heating in a solution of *trans*-$[Ru(en)_2Cl_2]Cl$ (0.252 g, 0.769 mmol) in 0.1 *M* HCl (35 mL). The reaction solution was refluxed for 2 h and then slowly cooled. Pale-yellow crystals that precipitated after 9 days were filtered off, washed with a small amount of cold water, and dried in air. The yield was 0.129 g (79% based on cucurbit[8]uril). Found (%): C, 34.55; H, 4.6; N, 27.9. $C_{52}H_{81}Cl_3N_{36}O_{24.5}Ru$ (with a loss of 19 H_2O molecules). Calculated (%): C, 34.50; H, 4.51; N, 27.88. ESI-MS, *m/z* (*I* (%)): 292.0 $[Ru(en)_2Cl_2]^+$ (100), 547.8 $\{[Ru(en)_2Cl_2] + H + Na + CB[8]\}^{3+}$ (13), 555.4 $\{[Ru(en)_2Cl_2] + 2 Na + CB[8]\}^{3+}$ (100), 810.8 $\{[Ru(en)_2Cl_2] + H + CB[8]\}^{2+}$ (30), 821.8 $\{[Ru(en)_2Cl_2] + Na + CB[8]\}^{2+}$ (30). UV—Vis (aqueous solution), λ/nm (ε/L mol^{-1} cm^{-1}): 352 (5336), 292 br (475). IR, ν/cm^{-1}: 3429 s, 3003 w, 2924 m, 2855 w, 1726 s, 1638 m, 1472 s, 1425 m, 1373 m, 1292 m, 1231 s, 1190 s, 1155 m, 1124 m, 1055 w, 1026 w, 993 m, 968 s, 829 m, 808 s, 758 m, 671 m, 627 w, 544 m, 474 w, 446 w.

Cucurbit[8]uril(chloro-bis-diethylenetriaminegold(iii)) dichloride clathrate crystal undecahydrate $\{[Au(dien)Cl]@CB[8]\}Cl_2 \cdot 11H_2O$ (2). Since Au^{III} salts are light sensitive, all synthetic operations were carried out in vessels covered with an aluminum foil. Cucurbit[8]uril (0.026 g, 0.015 mmol) was dissolved with stirring in a solution of $[Au(dien)Cl]Cl_2$ (0.020 g, 0.049 mmol) in 0.01 *M* HCl (7 mL). The slow diffusion of methanol vapor into the reaction solution during 10 days afforded bright-yellow crystals. The crystals were filtered off and dried over P_2O_5 for one day. The yield was 0.020 g (67% based on cucurbit[8]uril). Found (%): C, 32.01; H, 3.56; N, 24.93. $C_{52}H_{83}AuCl_3N_{35}O_{27}$. Calculated (%): C, 32.30; H, 4.33; N, 25.37. ESI-MS, *m/z* (*I* (%)): 543.9 $[CB[8] + Au(dien)]^{3+}$ (20), 555 $[CB[8] + Au(dien)Cl + H]^{3+}$ (40), 562.5 $[CB[8] + Au(dien)Cl + Na]^{3+}$ (91), 568 $[CB[8] + Au(dien)Cl + K]^{3+}$ (100), 832 $[CB[8] + Au(dien)Cl]^{2+}$ (18). IR, ν/cm^{-1}: 3441 s, 2999 w, 2954 w, 2925 m, 2855 w, 1730 s, 1594 w, 1645 sh, 1470 s, 1424 m, 1375 s, 1318 s, 1294 m, 1230 s, 1188 s, 1155 m, 1026 w, 993 w, 968 s, 906 w, 830 m, 807 s, 757 m, 671 m, 629 w, 442 w.

Pentahydroxoniumcucurbit[8]uril(1,4,8,11-tetraazacyclotetradecanegold(iii)) octachloride clathrate crystal octadecahydrate $(H_3O)_5\{[Au(cyclam)]@CB[8]\}Cl_8 \cdot 18H_2O$ (3). The compound $\{cyclam@CB[8]\} \cdot 4HCl \cdot 18H_2O$ (0.052 g, (0.026 mmol) was dissolved with gentle heating in a solution of $HAuCl_4$ (0.057 g, 0.168 mmol) in H_2O (5 mL). The reaction solution was refluxed for 1—2 min, during which the pale-yellow substance immediately began to precipitate. Then the reaction mixture was refluxed for 10—15 min and slowly cooled. The precipitate was filtered off, washed with a small amount of cold water, ethanol, and diethyl ether, and dried in air. The yield was 0.052 g (82% based on {cyclam@CB[8]}$\cdot$4HCl$\cdot$18H_2O). Found (%): C, 28.7; H, 5.2; Cl, 11.9; N, 20.65. $C_{58}H_{123}AuCl_8N_{36}O_{39}$. Calculated (%): C, 28.71; H, 5.11; Cl, 11.54; N, 20.79. ESI-MS, *m/z* (*I* (%)): 862.3 [Au(cyclam) + CB[8] – H]$^{2+}$ (15), 765.1 [CB[8] + (cyclam) + 2 H)]$^{2+}$ (100). IR, ν/cm^{-1}: 3455 s, 1729 s, 1595 sh, 1469 s, 1425 m, 1374 s, 1316 s, 1292 m, 1229 s, 1188 s, 1154 m, 1026 w, 993 w, 970 s, 902 w, 829 m, 807 s, 756 m, 672 m, 630 w, 444 w.

Cucurbit[8]uril(1,4,8,11-tetraazacyclotetradecaneplatinum(III)) dichloride clathrate crystal hexadecahydrate {[Pt(cyclam)]$_{0.11}$-(H_2cyclam)$_{0.89}$@CB[8]}$Cl_2\cdot16H_2O$ (4). The compound {cyclam@CB[8]}$\cdot$4HCl$\cdot$18H_2O (0.022 g, 0.011 mmol) was dissolved with gentle heating in a solution of K_2PtCl_4 (0.022 g, 0.053 mmol) in H_2O (5 mL). The reaction solution was refluxed for 2 h and then slowly cooled. After two weeks, colorless crystals precipitated. The crystals were filtered off, washed with a small amount of cold water, and dried in air. The yield was 0.007 g (33% based on {cyclam@CB[8]}$\cdot$4HCl$\cdot$18H_2O). The composition and the structure of compound **4** were determined by single-crystal X-ray diffraction. IR, ν/cm^{-1}: 3453 s, 1730 s, 1593 sh, 1471 s, 1424 m, 1372 s, 1317 s, 1292 m, 1229 s, 1187 s, 1153 m, 1028 w, 995 w, 968 s, 904 w, 830 m, 806 s, 757 m, 673 m, 629 w, 442 w.

X-ray diffraction study. The X-ray diffraction data sets for compounds **1**, **2**, and **4** were collected according to a standard procedure at 150 K using a graphite-monochromated Mo-Kα radiation source (λ = 0.71073 Å). The crystallographic characteristics and the X-ray data collection and refinement statistics are given in Table 1. Semiempirical absorption corrections were applied based on the intensities of equivalent reflections with the use of the SADABS program.[43] The structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for non-hydrogen atoms using the SHELX97 program package.[44] The hydrogen atoms of cucurbit[8]uril and organic ligands were positioned geometrically and refined using a riding model. The positions of the hydrogen atoms of the water molecules were not refined. The atomic coordinates of compounds **1**, **2**, and **4** were deposited with the Cambridge Structural Database (CCDC 768843, 723481, and 768844, respectively) and can be obtained from the authors.

Table 1. Crystallographic data and the X-ray diffraction data collection and refinement statistics for compounds **1**, **2**, and **4**

Parameter	1	2	4
Molecular formula	$C_{52}H_{119}Cl_3N_{36}O_{43.5}Ru$	$C_{52}H_{83}AuCl_3N_{35}O_{27}$	$C_{58}H_{105.78}Cl_2N_{36}O_{32}Pt_{0.11}$
Molecular weight/g mol^{-1}	2152.16	1933.85	1911.84
T/K	150(2)	100(2)	150(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$P2_1/c$	$P\bar{3}$	$P\bar{3}$
a/Å	22.8349(15)	39.0680(5)	29.1580(5)
b/Å	16.0865(11)	—	—
c/Å	25.2605(16)	13.5204(4)	26.4561(11)
β/deg	105.395(2)	—	—
Z	4	9	9
V/Å^3	8946.1(10)	17871.6(6)	19479.2(9)
d/g cm^{-3}	1.5979	1.617	1.467
μ/mm^{-1}	0.3784	2.052	0.354
T_{min}/T_{max}	0.847/0.916	0.578/0.709	0.878/0.933
F(000)	8812	8874	9029
Crystal dimensions/mm	0.42×0.31×0.22	0.30×0.24×0.18	0.38×0.25×0.20
θ-Scan range, deg	2.49—31.80	1.81—27.11	1.11—24.99
Ranges of h, k, l indices	$-27 \le h \le 24$,	$-40 \le h \le 50$,	$-34 \le h \le 34$,
	$-19 \le k \le 19$,	$-50 \le k \le 49$,	$-34 \le k \le 26$,
	$-30 \le l \le 24$	$-14 \le l \le 17$	$-31 \le l \le 31$
Number of measured reflections	51297	43863	40316
Number of independent reflections (R_{int})	16727 (0.0339)	8766 (0.0529)	7622(0.0390)
Number of reflections with $I > 2\sigma_I$	13409	7148	5363
S factor based on F^2	1.040	1.782	1.126
R factor ($I > 2\sigma_I$)			
R_1	0.0663	0.1181	0.0668
wR_2	0.1720	0.3909	0.1998
R factor (all reflections)			
R_1	0.0825	0.1333	0.0869
wR_2	0.1811	0.4007	0.2128
Residual electron density (max/min)/e$\cdot$Å^{-3}	1.941/–1.991	1.891/–4.941	1.040/–0.405

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