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Inclusion compounds of the copper(II) and zinc(II) complexes with cyclam in cucurbit[8]uril: synthesis and structure*

E. A. Kovalenko,[a] D. A. Mainichev,[a] O. A. Gerasko,[a] D. Yu. Naumov,[a] and V. P. Fedin[a,b]*

[a]A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation
[b]Novosibirsk State University, Novosibirsk, Russian Federation.
Fax: +7 (383) 330 9489. E-mail: cluster@niic.nsc.ru

Inclusion compounds of the macrocyclic cavitand cucurbit[8]uril (CB[8], $C_{48}H_{48}N_{32}O_{16}$) with the copper(II) and zinc(II) complexes with the tetraazamacrocyclic ligand cyclam, $\{[Cu(cyclam)(H_2O)_2]@CB[8]\}Cl_2 \cdot 18H_2O$ (**1**) and $\{[Zn(cyclam)]@CB[8]\}Cl_2 \cdot 13H_2O$ (**2**), were synthesized. The compounds were characterized by X-ray diffraction analysis, electrospray mass spectrometry, IR spectroscopy, and elemental analysis. The ^{1}H and ^{13}C NMR method revealed only one *trans*-isomer of the zinc(II) complex with cyclam in an aqueous solution of inclusion compound **2**.

Key words: copper, zinc, cyclam, cucurbit[8]uril, inclusion compounds, X-ray diffraction analysis, NMR spectrometry.

Inclusion compounds of metal complexes in the internal cavity of organic cavitand molecules are interesting from the viewpoint of classical coordination chemistry (inclusion results in unusual chemical and physicochemical properties of complexes) and as promising compounds for the synthesis of pharmaceutical preparations of prolong action (the inclusion in the cavitand prevents the biologically active complex from fast decomposition in the organism and decreases its toxicity).[1,2]

Cucurbit[*n*]urils (CB[*n*], $C_{6n}H_{6n}N_{4n}O_{2n}$ ($n = 5—10$))[3—7] represent a relatively new class of organic macrocyclic cavitands compared to such well known receptors in supramolecular chemistry as calixarenes and cyclodextrins. Molecules CB[*n*] possess a rather rigid high-symmetry structure; access to the hydrophobic intramolecular cavity is provided through two portals formed by *n* carbonyl groups. When included in the barrel-like cavity of cucurbit[*n*]uril, the complex can completely be incorporated inside the cavitand, unlike the most part of inclusion compounds of calixarenes and cyclodextrins, which are characterized by only partial immersion of the complex into the cup-shaped cavities.[8] This increases the stability of the adducts with CB[*n*] compared to the indicated cavitands.

Inclusion in CB[8] can affect the geometric parameters of both the guest and host; X-ray diffraction analysis plays an important role in the study of this influence. Inclusion in CB[*n*] almost completely isolates complexes from the environment, changing their chemical and physicochemical properties: the absorption, fluorescence, and NMR spectra of the "guest" change on going from the environment of the solvent (as a rule, these are weakly acidic aqueous solutions) to the nonpolar cavity of the cavitand. NMR spectroscopy is among the most efficient methods for studying inclusion compounds in CB[*n*] in solutions. The good correspondence of the guest size to the host cavity induces an interaction between them and, as a consequence, changes the shielding constants of the contacting atoms of the complex and CB[*n*], which results in a substantial change in the position of resonance of these atoms on going from the initial complex to inclusion compounds.[9—13]

Interest in complexes with cyclam (1,4,8,11-tetraazacyclotetradecane) and its derivatives is caused by their wide use in medicine, for instance, as antiviral drugs.[14—16] To the present time, the inclusion compounds in CB[8] of the nickel(II),[17] iron(II),[18] palladium(II),[19] platinum(II),[20] and copper(II)[21] complexes with cyclam have been synthesized and structurally characterized. In the structures of these compounds, the complex lies in the cavity of the cavitand molecule, while cyclam, except for the copper(II) complex, takes the most stable configuration *trans*-III (of five theoretically possible *trans*-configurations differed in the configuration of the nitrogen atoms (Fig. 1)[22]). Information about the ligand configuration in solutions of the inclusion compounds in CB[8] of complexes with cyclam is lacking. According to the NMR studies, solutions of "free," i.e. not included in the cavitand, complexes with cyclam contain the ligand configuration *trans*-III, which

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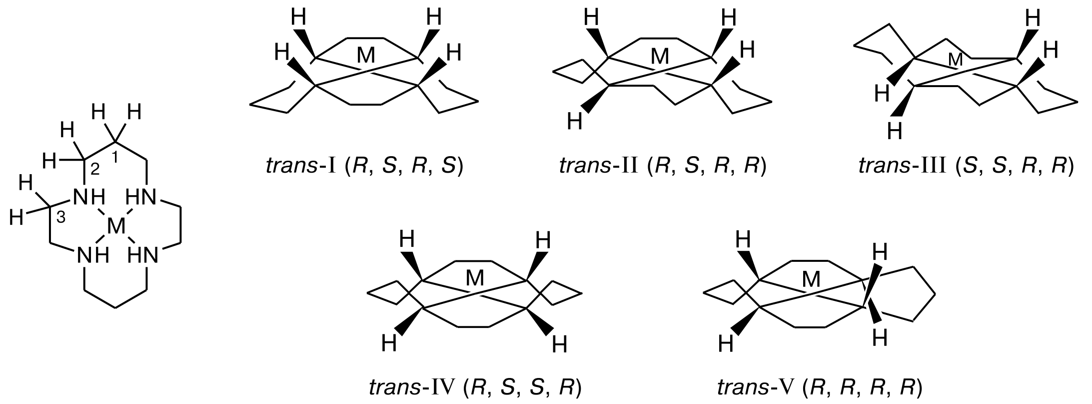

Fig. 1. Structural formula and five theoretically possible *trans*-conformations of the cyclam complexes.

is found in the crystalline state, along with other cyclam isomers of cyclam.[14,23,24]

In the present paper, we report the synthesis of the inclusion compounds in CB[8] of the copper(II) and zinc(II) complexes with the tetraazamacrocyclic ligand cyclam, {[Cu(cyclam)(H_2O)$_2$]@CB[8]}Cl_2 • 18H_2O (**1**) and {[Zn(cyclam)]@CB[8]}Cl_2 • 13H_2O (**2**), and the X-ray diffraction study of inclusion compound **1**. The results of the ^{1}H and ^{13}C NMR study of solutions of these complexes with cyclam and their inclusion compounds are presented.

Results and Discussion

Complex {[Cu(cyclam)(H_2O)$_2$]@CB[8]}Cl_2 • 18H_2O (1). The inclusion complex between cucurbit[8]uril and the copper(II) complex with cyclam {[Cu(cyclam)(H_2O)$_2$]@CB[8]}Cl_2 • 18H_2O was obtained as crystals in 53% yield on reflux of an aqueous solution containing the inclusion adduct of cyclam in cucurbit[8]uril {cyclam@CB[8]} • 4HCl • 18H_2O and copper(II) nitrate taken in a sevenfold excess. Compound **1** is well soluble in water. The IR spectrum of **1** contains the characteristic vibration bands of CB[8] (1800—400 cm^{-1}) and water and also narrow medium-intensity bands at 2926 and 2855 cm^{-1}, which can be attributed to stretching vibrations of the N—H bond in coordinated cyclam.

According to the X-ray diffraction data of single crystals of **1**, the cavity of each CB[8] molecule encapsulates the complex cation of the guest (Fig. 2). In addition to four nitrogen atoms of cyclam forming a planar-square environment of the central atom (Cu—N, 2.000(3) and 2.007(4) Å), the copper atom is additionally weakly coordinated by two water molecules (Cu—O, 2.472(4) Å); thus, the coordination number of the metal is 4 + 2.

Compound **1** was synthesized by the two-step method similar to that proposed earlier[25] from the metal complex with monodentate ligands and the inclusion compound of the polydentate cyclic ligand in the cavitand. Under similar reaction conditions, the inclusion compound {[Cu(cyclam)(H_2O)]@CB[8]}$(NO_3)_2$ • 14H_2O was synthesized from copper(II) nitrate and {cyclam@CB[8]} • • 4HCl • 18H_2O taken in a ratio of 6.3 : 1. The composition of this compound (different from the composition of **1**) was established by mass spectrometry and elemental analysis (no X-ray diffraction data are available). When the reaction is carried out at the same ratio of the reactants but with a lower (compared to the conditions of synthesis of compound **1**) concentration of the

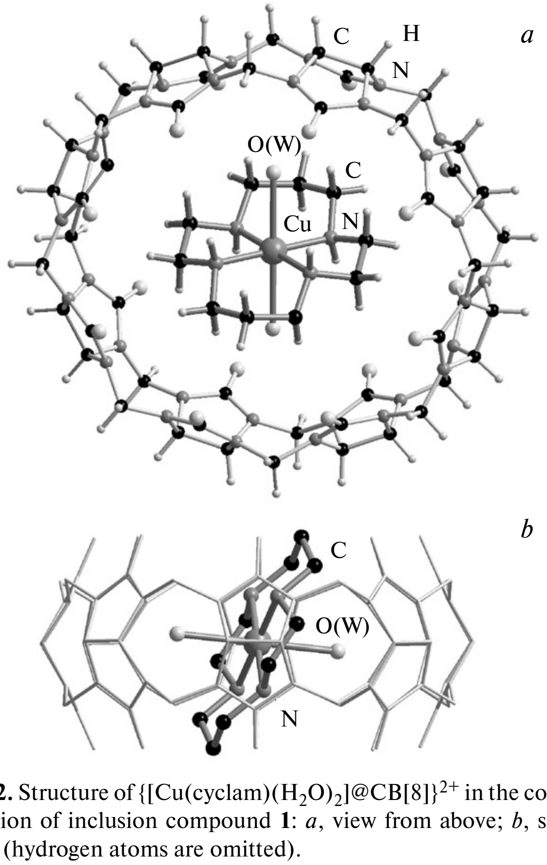

Fig. 2. Structure of {[Cu(cyclam)(H_2O)$_2$]@CB[8]}$^{2+}$ in the composition of inclusion compound **1**: *a*, view from above; *b*, side view (hydrogen atoms are omitted).

initial solution of the copper(II) complex, compound $\{[Cu(cyclam)(H_2O)_{1.3}]@CB[8]\}(CB[8])_{0.5}(NO_3)_2 \cdot 17H_2O$ (**3**) of another composition was obtained in which not all cavitand molecules incoporate the cyclam complex in the cavity.[21] Thus, the composition and structure of the inclusion compounds of the copper(II) complex with cyclam depend substantially on the reaction conditions.

In structure **1**, the plane of the metal complex CuN_4 is substantially inclined relative to the equatorial plane of CB[8] (inclination angle is ~81°; Fig. 2, *b*). Such an inclination of the internal macrocycle plane relative to the external macrocycle is characteristic of both the inclusion compounds between CB[8] and the cyclam complexes (the inclination angle varies from 66 to 77°)[17—21] and the inclusion adduct of noncoordinated cyclam in CB[8] (~59°).[25] Two water molecules occupying the axial positions of the octahedral environment of the copper atom are arranged inside the cavity of CB[8], and structure **1** is analogous to the structure of the encapsulated in CB[8] chloropalladium(IV) complex with cyclam $\{trans\text{-}[Pd(cyclam)Cl_2]@CB[8]\}^{2+}$ in which the axial chloride ligands also lie inside the cavity.[19] The inclusion compounds of the cyclam complexes differ from the ethylenediamine aqua and chloro complexes, $\{trans\text{-}[M(en)_2(H_2O)_2]@CB[8]\}^{n+}$ and $\{trans\text{-}[M(en)_2Cl_2]@CB[8]\}^{n+}$, in which the equatorial positions are occupied by two ethylenediamine ligands smaller in size.[9,17,20,26] The latter are characterized by different orientations of the guest inside the host cavity depending on the axial ligands. In the structures of the inclusion compounds of the chloro complexes, the plane MN_4 is almost perpendicular to the equatorial plane of the cavitand and the axial chloride ligands are arranged inside the cavity of CB[8], whereas in the inclusion compounds of the aqua complexes the plane MN_4 nearly coincides with the equatorial plane of CB[8] and the aqua ligands are arranged in the region of negatively charged portals. The large size of cyclam, which does not allow it to be completely incorporated in the cavity of CB[8], predetermines only one orientation of the complex inside the cavitand in which the axial ligands, including aqua ligands, can be only inside the hydrophobic cavity.

In complex **1** cyclam takes the configuration *trans*-III characteristic of both cyclam itself and its complexes with metals[14]: the six-membered metallocycles exist in the most stable chair conformation, whereas the five-membered metallocycles exist in the most stable skewed conformation (see Fig. 1). Cyclam exists in the same conformation as in the inclusion compounds in CB[8] of other complexes with cyclam.[17—20] The only example[21] of the stabilization in the solid state of unusual cyclam isomers *trans*-I and *trans*-II is the inclusion compound of the copper(II) complex with cyclam **3**. It is assumed that the formation of complexes with these high-energy configurations of the ligand instead of the much more general configuration *trans*-III is due to the formation of hydrogen bonds between the NH groups of incorporated cyclam and the oxygen atoms of one of the portals.

In the crystal structure of **1**, the molecular packing of CB[8] forms one-dimensional channels with the diameter less than 2 Å extending along the axis *c* and filled with water molecules of crystallization and chloride ions. The CB[8] molecule in structure **1** undergoes the ellipsoid distortion typical of the inclusion compounds of this cavitand (Δ_{CH}, the highest difference in the distances between the opposite carbon atoms of the CH groups); the value of distortion of 1.07 Å is comparable with the distortions of CB[8] in other inclusion compounds of the complexes with cyclam (Δ_{CH}, 0.50—1.36 Å).[17—20]

Complex $\{[Zn(cyclam)]@CB[8]\}Cl_2 \cdot 13H_2O$ (2). The inclusion compound of the zinc(II) complex with cyclam of the composition $\{[Zn(cyclam)]@CB[8]\}Cl_2 \cdot 13H_2O$ (**2**) was synthesized in 98% yield as a colorless finely crystalline precipitate from an aqueous solution of the inclusion compound between CB[8] and cyclam $\{cyclam@CB[8]\} \cdot 4HCl \cdot 18H_2O$ and zinc(II) nitrate taken in a 17-fold excess. Compound **2** is highly soluble in water. The IR spectrum of compound **2** contains vibrations bands of CB[8] and water and also medium-intensity bands at 2930 and 2856 cm^{-1}, which can be attributed to stretching vibrations of the N—H bond in cyclam.

The symmetry space group and crystal system of the obtained crystals of **2** (space group R-3, a = 29.1274 Å, c = 26.1643 Å, γ = 120°) coincide with the X-ray diffraction data for compound **1** and their unit cell parameters are close, indicating that inclusion compounds **1** and **2** are of the same type. Attempts to obtain crystals of **2** suitable for full X-ray diffraction analysis with recrystallization from solutions of mineral acids, NaCl, or KCl were unsuccessful.

The composition of compound **2** is given on the basis of the data of elemental analysis and mass spectrometry. The mass spectrum (Fig. 3) contains a set of peaks of different intensities. The peaks assigned to the ions $[CB[8] + Zn(cyclam)]^{2+}$ and $[CB[8] + Zn(cyclam) + H_2O]^{2+}$ are rather intense and their presence indicates the presence of supramolecular adducts "host—guest" in an aqueous solution of **2**.

Studies by NMR spectroscopy. Solutions in D_2O of the copper(II) and zinc(II) complexes with cyclam $[Cu(cyclam)]Cl_2$ и $[Zn(cyclam)]Cl_2$, the inclusion compounds of these complexes in CB[8] (**1** and **2**), CB[8] (DCl/D_2O), cyclam, and its inclusion compound in CB[8] were studied at room temperature by ^1H and ^{13}C NMR and ^1H-^1H COSY spectroscopy. The spectra of CB[8], cyclam, and $\{cyclam@CB[8]\} \cdot 4HCl \cdot 18H_2O$ are similar to those presented in the literature for these compounds.[25,27—29]

In the ^1H NMR spectrum of a solution of the complex $[Cu(cyclam)]Cl_2$, the signals from the protons undergo

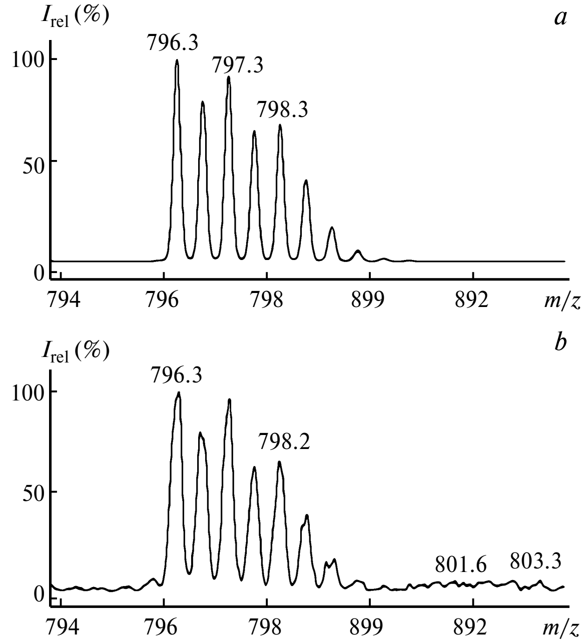

Fig. 3. Fragment of the electrospray mass spectrum of **2**: the calculated (*a*) and experimental (*b*) isotope distributions for $[Zn(cyclam) + CB[8] + H_2O]^{2+}$.

a downfield shift by 0.2—0.4 ppm relative to the spectrum of free cyclam (Fig. 4, spectra *a*, *b*). Complex formation impedes the interconformational (see Fig. 1) transitions of cyclam and changes the shape of some signals in the spectrum. The signal for the protons H(1) at δ 1.8 gains the complicated structure and the signals of the protons H(2) and H(3) are shifted to δ 3.0 and 2.92, respectively, and the earlier broadened signal from the protons of the NH group of cyclam appears (δ 2.15). The shift and broadening of the signals from the cyclam protons were also observed for the complex formation of zinc(II) chloride with the phenylazomethine cyclam derivatives.[30] The number of lines in the ^1H NMR spectrum of the complex $[Cu(cyclam)]Cl_2$ indicates only one isomer of the ligand corresponding in symmetry to the configuration *trans*-III.

The ^{13}C NMR spectrum of the complex $[Cu(cyclam)]Cl_2$ also confirms only one *trans*-III configuration of cyclam (the chemical shifts of the carbon atoms are δ 49.18, 46.17, and 24.68).

In the ^1H and ^{13}C NMR spectra of the inclusion compound of the copper(II) complex with cyclam in CB[8] (**1**), the signals of the carbon nuclei of cyclam are the noise level and the signals of CB[8] are broadened, which does not allow the spectra to be interpreted. This can be due to both paramagnetism of Cu^{II} and the distortion of the symmetry of the "host" upon inclusion (which is also observed in the solid phase).

The ^1H NMR spectrum of the zinc(II) complex with cyclam $[Zn(cyclam)]Cl_2$ indicates in favor of two forms with different cyclam configurations. Heating from room temperature to 320 K insignificantly changes the spectrum, indicating the absence of chemical exchange and kinetic stability of the both complexes in this temperature

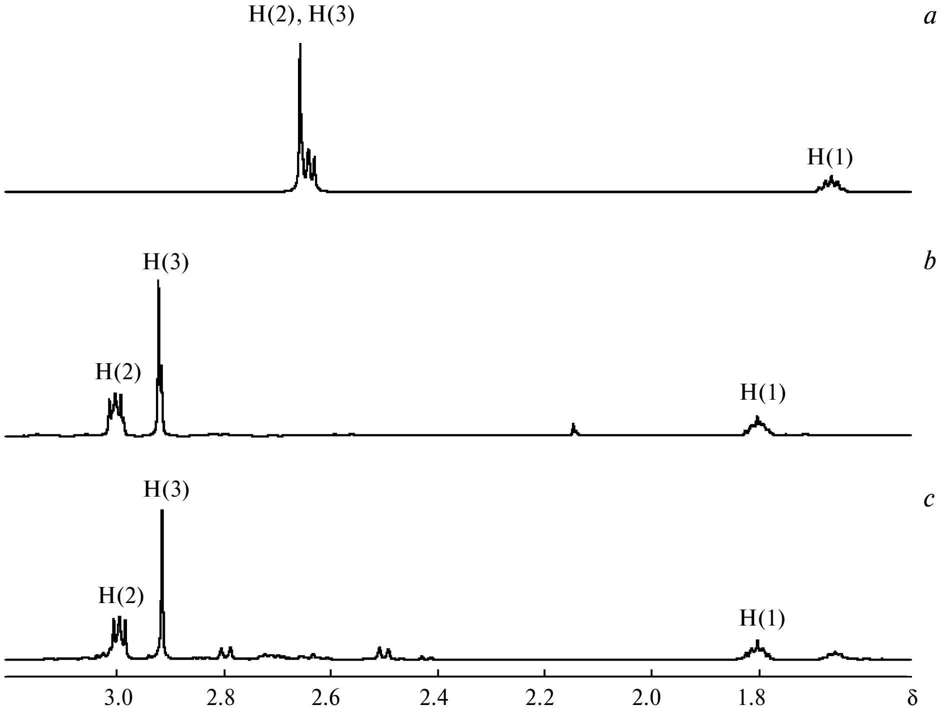

Fig. 4. ^1H NMR spectra of solutions of cyclam (*a*), $[Cu(cyclam)]Cl_2$ (*b*), and $[Zn(cyclam)]Cl_2$ (*c*) in D_2O.

range. The signals of the predominant *trans*-III configuration of the ligand appear at δ 3.0, 2.92, and 1.8 (Fig. 4, spectrum *c*) and almost coincide in position with the signals in the ^{1}H NMR spectrum of the copper(II) complex [Cu(cyclam)]Cl$_2$ (Fig. 4, spectrum *b*). Note the visual effect of the exclusive resemblance of the ^{1}H NMR spectra of the paramagnetic copper(II) complex and diamagnetic zinc(II) complex caused by the arrangement of the spectra in the figure in this scale. More detailed consideration reveals substantial differences in the fine structure of the spectra.

In the spectra of the complex [Zn(cyclam)]Cl$_2$, the signals of the complicated structure in the region from 3.1 to 2.4 ppm and an almost resolved quintet at δ 1.65 are assigned to another configuration of the ligand, which is the configuration *trans*-II according to the symmetry concepts. The ratio of integral intensities of quintets of the protons H(1) (δ 1.8 and 1.65) suggests that the ratio of the forms is approximately 2 : 1.

In the ^{13}C NMR spectrum of a solution of [Zn(cyclam)]Cl$_2$, the signals at δ 49.15, 46.17, and 24.68 are attributed to signals of the complex with the *trans*-III configuration of cyclam; they almost coincide with the corresponding signals of free cyclam and the signals of the complex [Cu(cyclam)]Cl$_2$. The signals of lower intensity at δ 50.50, 50.19, 47.76, 46.37, 27.85, 27.48, and 24.20 are attributed to the *trans*-II configuration of the ligand.

Thus, according to the NMR spectra data, a solution of the zinc(II) complex with cyclam contains two forms of the complex in which the ligand exists in the configurations *trans*-III and *trans*-II. In complexes with various metals cyclam and its derivatives are predominantly met in the configurations *trans*-III and *trans*-I (see Ref. 14). This is, for instance, the zinc(II) complex with the phenylazomethine cyclam derivatives[30] or the nickel(II) complex [Ni(cyclam)](ClO$_4$)$_2$ in which, according to the ^{1}H NMR data at room temperature, the isomer *trans*-I is about 15%.[23,24] The configuration of cyclam *trans*-II is rather rare, it is known for the copper(II) complex with tetramethyl-substituted cyclam,[31] and for unsubstituted cyclam its formation was observed for the first time in inclusion compound **3** (see Ref. 21).

The ^{1}H and ^{13}C NMR spectra of a solution of the inclusion compound of the zinc(II) complex with cyclam in CB[8] (**2**) exhibit the signals corresponding to only one configuration of cyclam, *trans*-III. The signals of protons of the "free" complex [Zn(cyclam)]Cl$_2$ (δ 3.0, 2.92, and 1.80) in the ^{1}H NMR spectrum of inclusion compound **2** undergo a substantial upfield shift (δ 2.56, 2.34, and 1.68) (Fig. 5), which indicates the change in the shielding constants of protons in the cavity of CB[8] and is typical of inclusion compounds in this cavitand.[9—13] The position of signals of the protons is close to that in the inclusion compound in CB[8] of cyclam itself, {cyclam@CB[8]} • 4HCl • 18H$_2$O (δ 2.63, 2.41, and 1.76).[25]

The ^{13}C NMR spectrum of inclusion compound **2** contains the signals at δ 48.88, 45.04, and 24.62 (Fig. 6, spectrum *a*), which undergo a slight upfield shift compared to the signals of the carbon atoms in the spectrum of [Zn(cyclam)]Cl$_2$ (δ 49.15, 46.17, and 24.68) (Fig. 6, spectrum *b*). The signals of inclusion compound **2** coincide completely with those of the carbon atoms of noncoordinated cyclam included in CB[8]. The signals in the ^{1}H and ^{13}C NMR spectra of inclusion compound **2** corresponding to CB[8] are similar to those for this cavitand.[5,25,28]

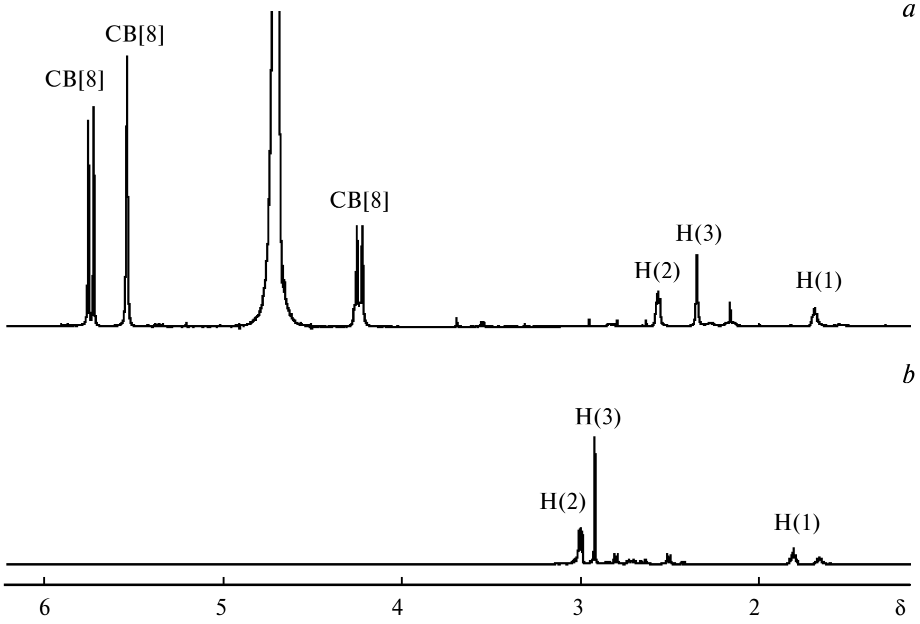

Fig. 5. ^{1}H NMR spectra of solutions of {[Zn(cyclam)]@CB[8]}Cl$_2$ • 13H$_2$O (**2**) (*a*) and [Zn(cyclam)]Cl$_2$ (*b*) in D$_2$O.

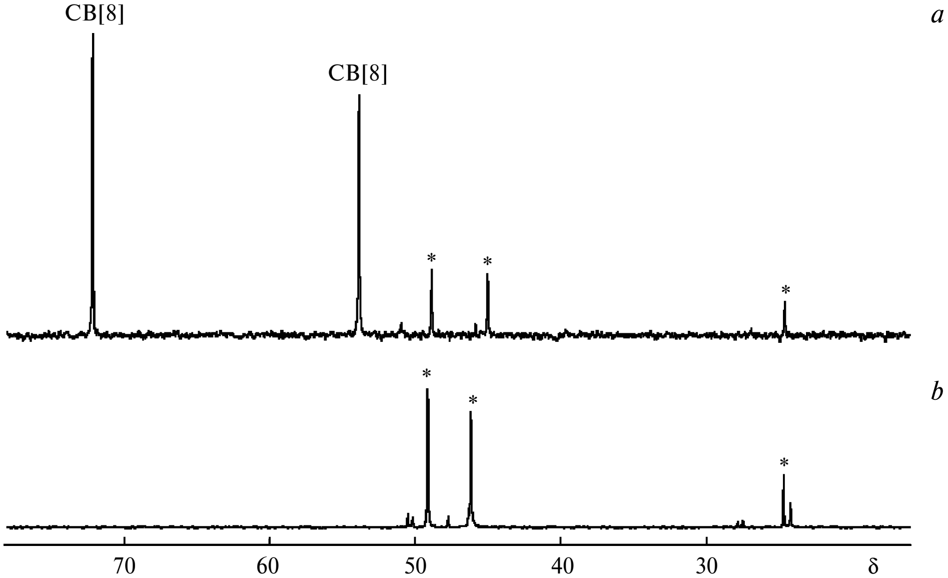

Fig. 6. ^{13}C NMR spectra of solutions of $\{[Zn(cyclam)]@CB[8]\}Cl_2 \cdot 13H_2O$ (**2**) (*a*) and $[Zn(cyclam)]Cl_2$ (*b*) in D_2O (signals of the carbon atoms of cyclam in the configuration *trans*-III are marked with *).

The presence in a solution of inclusion compound **2** of only one cyclam configuration, *trans*-III, and the data of mass spectrometry on the retention of the "host—guest" structure in an aqueous solution of **2** suggest that the same ligand isomer is present in the crystalline phase of $\{[Zn(cyclam)]@CB[8]\}Cl_2 \cdot 13H_2O$.

Thus, acting as a "molecular container," cucurbit[8]uril forms inclusion compounds with the copper(II) and zinc(II) complexes with the cyclic polyamine ligand cyclam. According to the X-ray diffraction data, in the structure of the inclusion compound $\{[Cu(cyclam)(H_2O)_2]@CB[8]\}Cl_2 \cdot 18H_2O$ cyclam takes the most stable configuration *trans*-III, unlike the isomers *trans*-I and *trans*-II of this complex for the inclusion compounds of the different composition known in the literature. The study of the copper(II) and zinc(II) complexes with cyclam, $[Cu(cyclam)]Cl_2$ and $[Zn(cyclam)]Cl_2$, by ^1H and ^{13}C NMR spectroscopy revealed only one configuration of cyclam (*trans*-III) in a solution of the first complex and two configurations (*trans*-III and *trans*-II) in a solution of the second complex. The presence of only one cyclam isomer (*trans*-III) in a solution of the cucurbit[8]uril inclusion compound of the zinc(II) complex with cyclam suggests that the ligand exists in the same configuration in the crystalline phase of the inclusion compound $\{[Zn(cyclam)]@CB[8]\}Cl_2 \cdot 13H_2O$ as well.

Experimental

The initial substances $Cu(NO_3)_2 \cdot 6H_2O$ (analytical purity grade), $Zn(NO_3)_2 \cdot 6H_2O$ (analytical purity grade), cyclam (1,4,8,11-tetraazacyclotetradecane) (reagent grade), and HCl (reagent grade) were used without additional purification. Cucurbit[8]uril,[5] $\{cyclam@CB[8]\} \cdot 4HCl \cdot 18H_2O$,[25] and the copper and zinc complexes $[Cu(cyclam)]Cl_2$ (see Ref. 32) and $[Zn(cyclam)]Cl_2$ (see Ref. 33) were synthesized according to the published procedures.

IR spectra were recorded on a Scimitar FTS 2000 spectrophotometer in KBr pellets. The elemental analyses for C, H, and N were carried out at the Analytical Laboratory of the Institute of Inorganic Chemistry (Siberian Branch of the Russian Academy of Sciences) on a Euro EA 3000 instrument. X-ray diffraction analysis was performed on a Bruker Nonius X8Apex single-crystal diffractometer with a 4K CCD detector.[34] Mass spectra (ESI-MS) were recorded on a Q-TOF I mass spectrometer (Micromass, Manchester, Great Britain). The ^1H and ^{13}C NMR spectra of the compounds in D_2O were obtained on a Bruker Avance 500 spectrometer (chemical shifts are presented in the δ scale and were measured at 500.13 and 125.72 MHz, respectively, relative to the residual signal of the solvent and external standard C_6D_6) at the Laboratory of Physical Chemistry of Condensed Media of the Institute of Inorganic Chemistry (Siberian Branch of the Russian Academy of Sciences).

{Cucurbit[8]uril-1,4,8,11-tetraazacyclotetradecanecopper(II) clathrate dichloride} octadecahydrate, $\{[Cu(cyclam)(H_2O)_2]@CB[8]\}Cl_2 \cdot 18H_2O$ (1). Separately prepared hot solutions of $Cu(NO_3)_2 \cdot 6H_2O$ (0.20 g, 0.678 mmol) in water (5 mL) and $\{cyclam@CB[8]\} \cdot 4HCl \cdot 18H_2O$ (0.20 g, 0.10 mmol) in water (5 mL) were mixed in a round-bottom flask, and the resulting solution was refluxed for 2 h. Needle-like violet crystals were obtained by slow cooling followed by evaporation in air at room temperature. The crystals were filtered off, washed with a small amount of cold water, and dried in air. The yield was 0.107 g (53% based on $\{cyclam@CB[8]\} \cdot 4HCl \cdot 18H_2O$). The product is soluble in hot water, rapidly loses water of crystallization in air, and can be recrystallized from 0.01 *M* solutions of NaCl and KCl to form larger crystals. Found (%): C, 34.6; H, 5.7; N, 24.6. $C_{58}H_{112}Cl_2CuN_{36}O_{36}$. Calculated (%): C, 34.4; H, 5.6; N, 24.9. IR (KBr), ν/cm^{-1}: 3454 s, 3231 sh, 2926 m, 2855 w, 1726 s, 1470 s, 1425 s, 1373 s, 1317 s, 1292 w, 1229 s, 1186 s, 1153 s, 993 w, 968 s, 827 m, 804 s, 758 s, 669 m, 623 w, 442 w.

{Cucurbit[8]uril-1,4,8,11-tetraazacyclotetradecanezinc(II) clathrate dichloride} tridecahydrate, $\{[Zn(cyclam)]@CB[8]\}Cl_2 \cdot 13H_2O$ (2). Separately prepared hot solutions of $Zn(NO_3)_2 \cdot 6H_2O$ (0.20 g, 0.673 mmol) in water (5 mL) and $\{cyclam@CB[8]\} \cdot 4HCl \cdot 18H_2O$ (0.08 g, 0.04 mmol) in water (5 mL) were mixed in a round-bottom flask, and the resulting solution was refluxed for 2 h. Colorless crystals were obtained by slow cooling followed by evaporation in air at room temperature. The crystals were filtered off, washed with a small amount of cold water, and dried in air. The yield was 0.074 g (97% based on $\{cyclam@CB[8]\} \cdot 4HCl \cdot 18H_2O$). The product is soluble in hot water and rapidly loses water of crystallization in air. Found (%): C, 36.8; H, 5.2; N, 26.3. $C_{58}H_{98}Cl_2ZnN_{36}O_{29}$. Calculated (%): C, 36.7; H, 5.2; N, 26.5. IR (KBr), ν/cm^{-1}: 3451 s, 3264 sh, 3005 s, 2930 m, 2856 w, 2363 w, 1724 s, 1640 w, 1470 s, 1425 s, 1373 s, 1317 s, 1290 w, 1227 s, 1188 s, 1152 s, 1026 s, 993 w, 968 s, 831 w, 804 s, 756 s, 671 m, 628 w, 443 w. ESI-MS, m/z (I (%)): 796.3 (15 %) $[CB[8] + Zn(cyclam)]^{2+}$, 805.3 (25%) $[CB[8] + + Zn(cyclam) + H_2O]^{2+}$, 765.2 (100%) $[CB[8] + (cyclam) + 2 H]^{2+}$. ^1H NMR (D_2O), δ: 5.75 (CB[8]), 5.72 (CB[8]), 5.53 (CB[8]), 4.25 (CB[8]), 4.22 (CB[8]), 2.56 (cyclam), 2.34 (cyclam), 1.68 (cyclam). ^{13}C NMR (D_2O), δ: 156.89 (CB[8]), 72.14 (CB[8]), 53.86 (CB[8]), 48.88 (cyclam), 45.04 (cyclam), 24.62 (cyclam).

Table 1. Crystallographic data and diffraction experimental conditions for compound **1**

Parameter	Value
Compound	**1**
Empirical formula	$C_{58}H_{112}Cl_2CuN_{36}O_{36}$
Molecular weight/g mol^{-1}	2024.28
T/K	150(2)
Crystal system	Rhombohedral
Space group	R-3
a/Å	29.0931(4)
b/Å	29.0931(4)
c/Å	26.6721(7)
γ/deg	120
Z	9
V/Å^3	19550.9(6)
d/g cm^{-3}	1.547
μ/mm^{-1}	0.421
$\theta_{min}/\theta_{max}$	2.22/32.57
F(000)	9567
Size/mm	0.45×0.42×0.40
Scan range, θ/deg	1.11—26.37
Range of h, k, l	$-36 \le h \le 36$ $-34 \le k \le 36$ $-24 \le l \le 33$
Number of measured reflections	46812
Number of independent reflections (R_{int})	8895 (0.0873)
Number of reflections with $I > 2\sigma_I$	7747
S Factor on F^2	1.060
R Factor ($I > 2\sigma_I$)	
R_1	0.0784
wR_1	0.2443
R Factor (all data)	
R_2	0.0873
wR_2	0.2544

X-ray diffraction study. The structure of compound **1** was established by X-ray diffraction analysis. Diffraction data were obtained by a standard procedure at 150 K using MoKα radiation (λ = 0.71073 Å) with a graphite monochromator. The crystallographic data and details of diffraction experiments are presented in Table 1. An absorption correction was applied semiempirically by the SADABS program[34] with allowance for intensities of equivalent reflections. Structure **1** was solved by a direct method and refined by full-matrix least squares on F^2 in the anisotopic approximation for non-hydrogen atoms using the SHELX97 program package.[35] Hydrogen atoms of cucurbit[8]uril and organic ligands were localized geometrically and refined in the rigid body approximation. The positions of hydrogen atoms for water molecules of crystallization were not refined. The coordinates of atoms of compound **1** were deposited with the Cambridge Crystallographic Data Centre (CCDC No. 804 338) and are available at the authors.

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References

1. N. J. Wheate, D. P. Buck, A. I. Day, J. G. Collins, *Dalton Trans.*, 2006, 451.
2. T. Utsuki, H. Brem, J. Pitha, T. Loftsson, T. Kristmundsdottir, B. M. Tyler, A. Olivi, *J. Control. Release.*, 1996, **40**, 3, 251.
3. R. Behrend, E. Meyer, F. Rusche, *J. Liebigs Ann. Chem.*, 1905, **339**, 1.
4. W. A. Freeman, W. L. Mock, N. Y. Shih, *J. Am. Chem. Soc.*, 1981, **103**, 7367.
5. A. Day, A. P. Arnold, R. J. Blanch, B. Snushall, *J. Org. Chem.*, 2001, **66**, 8094.
6. J. W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, K. Kim, *Acc. Chem. Res.*, 2003, **36**, 621.
7. L. Isaacs, *Chem. Commun.*, 2009, 619.
8. A. R. Mustafina, V. V. Skripacheva, A. I. Konovalov, *Usp. Khim.*, 2007, **76**, 979 [A. R. Mustafina, V. V. Skripacheva, A. I. Konovalov, *Russ. Chem. Rev.*, 2007, **76**, 917].
9. T. V. Mitkina, M. N. Sokolov, D. Y. Naumov, N. V. Kuratieva, O. A. Gerasko, V. P. Fedin, *Inorg. Chem.*, 2006, **45**, 6950.
10. W. S. Jeon, K. Moon, S. H. Park, H. Chun, Y. H. Ko, J. Y. Lee, E. S. Lee, S. Samal, N. Selvapalam, M. V. Rekharsky,

V. Sindelar, D. Sobransingh, Y. Inoue, A. E. Kaifer, K. Kim, *J. Am. Chem. Soc.*, 2005, **127**, 12984.

11. W. Ong, A. E. Kaifer, *Organometallics*, 2003, **22**, 4181.
12. K. Feng, L.-Z. Wu, L.-P. Zhang, C.-H. Tung, *Dalton Trans.*, 2007, 3991.
13. S. Liu, A. D. Shukla, S. Gadde, B. D. Wagner, A. E. Kaifer, L. Isaacs, *Angew. Chem., Int. Ed.*, 2008, **47**, 2657.
14. X. Liang, P. J. Sadler, *Chem. Soc. Rev.*, 2004, **33**, 246.
15. T. M. Hunter, I. W. McNae, D. P. Simpson, A. M. Smith, S. Moggach, F. White, M. D. Walkinshaw, S. Parsons, P. J. Sadler, *Chem. Eur. J.*, 2007, **13**, 40.
16. T. M. Hunter, S. J. Paisey, H. S. Park, L. Cleghorn, A. Parkin, S. Parsons, P. J. Sadler, *J. Inorg. Biochem.,* 2004, **98**, 713.
17. T. V. Mit´kina, D. Yu. Naumov, O. A. Gerasko, F. M. Dolgushin, X. Visent, R. Yusar, M. N. Sokolov, V. P. Fedin, *Izv. Akad. Nauk*, *Ser. Khim.*, 2004, 2414 [*Russ. Chem. Bull.*, *Int. Ed.*, 2004, **53**, 2519].
18. E. A. Kovalenko, T. V. Mit´kina, O. A. Gerasko, D. G. Samsonenko, D. Yu. Naumov, V. P. Fedin, *Koord. Khim.*, 2011, **37**, 163 [*Russ. J. Coord. Chem.* (*Engl. Transl.*), 2011, **57**].
19. T. V. Mitkina, D. Yu. Naumov, O. A. Gerasko, V. P.Fedin, *Inorg. Chim. Acta.*, 2010, **363**, 4387.
20. E. A. Kovalenko, T. V. Mit´kina, O. A. Gerasko, D. Yu. Naumov, D. G. Samsonenko, V. P. Fedin, *Izv. Akad. Nauk*, *Ser. Khim.*, 2010, 2019 [*Russ. Chem. Bull., Int. Ed.*, 2010, **59**, 2072].
21. S. L. Hart, R. I. Haines, A. Decken, B. D. Wagner, *Inorg. Chim. Acta*, 2009, **362**, 4145.
22. B. Bosnich, C. K. Poon, M. L. Tobe, *Inorg. Chem.*, 1965, **4**, 1102.
23. P. J. Connolly, E. J. Billo, *Inorg. Chem.,* 1987, **26**, 3224.
24. D. T. Pierce, T. L. Hatfield, E. J. Billo, Y. Ping, *Inorg. Chem.*, 1997, **36**, 2950.
25. S.-Y. Kim, I.-S. Jung, E. Lee, J. Kim, S. Sakamoto, K. Yamaguchi, K. Kim, *Angew. Chem., Int. Ed.*, 2001, **40**, 2119.
26. T. V. Mit´kina, D. Yu. Naumov, N. V. Kurat´eva, O. A. Gerasko, V. P. Fedin, *Izv. Akad. Nauk*, *Ser. Khim.,* 2006, 25 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 26].
27. M. E. Haouaj, M. Luhmer, Y. H. Ko, K. Kim, K. Bartik, *J. Chem. Soc.*, *Perkin Trans. 2*, 2001, 804.
28. R. V. Pinjari, S. P. Gejji, *J. Phys. Chem. A*, 2008, **112***,* 12679.
29. SDBSWeb: http://riodb01.ibase.aist.go.jp/sdbs/ (National Institute of Advanced Industrial Science and Technology, 22.10.2010), SDBS No.: 9378.
30. O. Enoki, T. Imaoka, K. Yamamoto, *Org. Lett.*, 2003, **5**, 2547.
31. P. V. Bernhardt, P. C. Sharpe, *Chem. Commun.,* 1996, 1267.
32. A. Urfer, T. A. Kaden, *Helv. Chim. Acta*, 1994, **77**, 23.
33. X. Liang, M. Weishaupl, J. A. Parkinson, S. Parsons, P. A. McGregor, P. J. Sadler, *Chem.-Eur. J.*, 2003, **9**, 4709.
34. APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11). Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
35. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.

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