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Zinc and Cobalt Aqua Complexes with Cucurbit[6]uril: Syntheses and Crystal Structures

I. V. Andrienko[a], **E. A. Kovalenko**[a, *], **I. E. Karmadonova**[a, b], **P. E. Plyusnin**[a, b], **D. G. Samsonenko**[a, b], **and V. P. Fedin**[a, b]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

[b] *Novosibirsk State University, Novosibirsk, 630090 Russia*

**e-mail: e.a.kovalenko@niic.nsc.ru*

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Abstract—Supramolecular complexes $[Zn(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 6.5H_2O$ (**I**), $[Zn(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 7H_2O$ (**II**), and $[Co(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 7H_2O$ (**III**) are synthesized by the slow (for **I** and **III**) and fast (for **II**) cooling (after reflux) of aqueous solutions of a mixture of salts of the corresponding metals and cucurbit[6]uril. According to the X-ray diffraction data (CIF files CCDC nos. 1862494 (**I**), 1862495 (**II**), and 1862496 (**III**)), the supramolecular complexes are the first examples of the direct coordination of the zinc and cobalt atoms to the cucurbit[6]uril molecule. Compounds **I–III** are characterized by X-ray diffraction analysis, thermogravimetry, IR spectroscopy, and elemental analysis.

Keywords: zinc complexes, cobalt complexes, cucurbit[6]uril, X-ray diffraction analysis, supramolecular chemistry, crystal structure

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INTRODUCTION

Interest in metal complexes with macrocyclic cavitands (calixarenes, cyclodextrins, and cucurbit[6]urils) is due to the possibility of preparing from them highly organized supramolecular ensembles combining organic and inorganic building blocks [1, 2].

The ability of cucurbit[6]uril (CB[6]) to bind metal ions in aqueous solutions has been discovered as far as in 1905 [3]. Since CB[6] contains carbonyl groups more polarized than the C–O bonds in crown ethers or cryptands, the interactions between cucurbituril and metal cations are stronger than those with the organic macrocycles [4–11]. A CB[6] molecule is built of six glycoluril moieties linked by methylene bridges and resembles a barrel, whose planes of the bottom and lid contain oxygen atoms of the polarized carbonyl groups (portals) capable of either coordinating the metal ion, or forming hydrogen bonds with metal aqua complexes. The metal complexes are coordinated by the oxygen atoms arranged in the planes of the CB[6] portals and are not included into the cavitand cavity. Thus, the unique structure of CB[6] makes it possible to include organic molecules into the intramolecular cavity and also to form supramolecular adducts or complexes with a wide series of *s*, *p*, *d*, and *f* elements.

In spite of the studies of the reactions of CB[*n*] with transition metal complexes, this field of chemistry still contains many unsolved problems. In particular, this concerns the CB[*n*] compounds with Zn(II). A series of supramolecular architectures are known in which tetrahedra $[ZnCl_4]^{2-}$ occupy nodes when forming the packing of the so-called honeycomb structures [12–23]. No direct interaction of the zinc and oxygen atoms of the cucurbituril portals is observed in these complexes. There are several examples for the direct coordination of the zinc atoms to CB[5] [24, 25] and to substituted CB[6] [26, 27]. No examples are known for unsubstituted CB[6]. The reactions of CB[*n*] with the Co(II) salts are studied even more poorly. Two structures are described where the cobalt complexes occupy cavities formed by various cucurbit[*n*]uril compounds with rare-earth elements [28–30]. In addition, there are examples for the formation of polyrotaxanes based on the cobalt complexes, organic ligands, and CB[*n*] [31, 32] with the chain structure. The inclusion compounds of the Co(II) complexes with the polyamine ligands were synthesized for CB[8] [33–35].

The syntheses, X-ray diffraction data, and physicochemical properties of three new supramolecular cucurbit[6]uril complexes with Zn(II) and Co(II), namely, $[Zn(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 6.5H_2O$ (**I**), $[Zn(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 7H_2O$ (**II**), and $[Co(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 7H_2O$ (**III**), are reported in this work.

EXPERIMENTAL

The reagents $Zn(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ (high-purity grade) were used. Cucurbit[6]uril was synthesized using a described procedure [36]. The syntheses were carried out in glass vials with screw-tops. Analyses to C, H, and N were conducted on a Euro EA 3000 instrument at the Analytical Laboratory of the Nikolaev Institute of Inorganic Chemistry (Siberian Branch, Russian Academy of Sciences). IR spectra were recorded on a Scimitar FTS 2000 spectrophotometer in KBr pellets. Thermogravimetric (TG) studies in a helium atmosphere were carried out using a TG 209 F1 Iris® microbalance (NETZSCH). A sample weight was 10 mg, an Al crucible was used, the gas flow rate was 60 mL/min, and the heating rate was 10 deg/min in the temperature range from 20 to 400°C. The experimental results were processed using the ProteusAnalysis standard software package [37].

Syntheses of complexes I and II. A 1 M aqueous solution (2 mL) of zinc nitrate and cucurbit[6]uril decahydrate ($C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O$, CB[6] $\cdot$ $10H_2O$) (0.020 g, 0.018 mmol) was heated to 100°C and kept at this temperature for 48 h. The bulky colorless crystals of compound **I** as polyhedra were obtained by the slow cooling of the reaction mixture to room temperature for 48 h. The yield was 0.020 g (83% based on CB[6] $\cdot$ $10H_2O$). Colorless stick-shaped crystals of compound **II** were obtained on fast cooling of the reaction mixture to room temperature for 2 h. The yield was 0.010 g (42% based on CB[6] $\cdot$ $10H_2O$). Being taken from the mother liquor, the crystals of compounds **I** and **II** underwent cracking and lost crystallinity. The results of elemental and TG analyses and the IR spectral data for the samples of compounds **I** and **II** dried in air coincide.

For $C_{36}H_{62}N_{26}O_{31}Zn$ (based on $9H_2O_{cryst}$)

Anal. calcd., %	C, 30.4	H, 4.4	N, 25.6
Found, %	C, 30.7	H, 4.2	N, 25.7

IR (ν, cm^{-1}): 3442, 3003, 2955, 2388, 2289, 1740, 1610, 1480, 1416, 1378, 1327, 1299, 1260, 1236, 1191, 1148, 1029, 967, 821, 800, 760, 675, 633, 455.

TG: a mass loss of 8% on heating to 90°C corresponds to the removal of six molecules of water of crystallization, and at the second step the 10% mass loss on heating to 160°C corresponds to the removal of three molecules of water of crystallization and four coordination water molecules.

Synthesis of complex III. A 1 M aqueous solution (2 mL) of cobalt nitrate and CB[6] $\cdot$ $10H_2O$ (0.020 g, 0.018 mmol) was heated to 100°C and kept at this temperature for 48 h. The bulky pink crystals of compound **III** were obtained on cooling the reaction mixture to room temperature for 48 h. Being taken from the mother liquor, the crystals underwent cracking and lost crystallinity. The yield was 0.010 g (42% based on CB[6] $\cdot$ $10H_2O$).

For $C_{36}H_{60}N_{26}O_{30}Co$ (based on $8H_2O_{cryst}$)

Anal.calcd., %	C, 31.0	H, 4.3	N, 26.1
Found, %	C, 31.1	H, 4.1	N, 25.9

IR (ν, cm^{-1}): 3420, 3003, 2956, 2388, 2290, 1740, 1610, 1482, 1417, 1378, 1327, 1300, 1260, 1236, 1191, 1149, 1029, 970, 821, 800, 759, 676, 633, 454.

TG: a mass loss of 5% on heating to 90°C corresponds to the removal of four molecules of water of crystallization, and at the second stage a mass loss of 10% on heating to 160°C corresponds to the removal of four molecules of water of crystallization and four coordination water molecules.

X-ray diffraction analysis. The diffraction data for the single crystals of compounds **I–III** were obtained at 130 K on an Agilent Xcalibur automated diffractometer equipped with an AtlasS2 two-coordinate detector (graphite monochromator, $\lambda(MoK_\alpha) = 0.71073$ Å, ω scan mode). Integration was performed, an absorption correction was applied, and the unit cell parameters were determined using the CrysAlisPro program package [38]. The crystal structures were solved using the SHELXT program [39] and refined by full-matrix least squares in the anisotropic (except for hydrogen atoms) approximation (SHELXL) [40]. The positions of the hydrogen atoms of the organic ligands were calculated geometrically and refined by the riding model. The Zn(II) cations in the structure of compound **I** are disordered over three positions (Zn(1), Zn(2), and Zn(3)) with the relative weights 0.79/0.12/0.09. The coordination environment of the Zn(II) cations arranged in the minor positions (Zn(2) and Zn(3)) were not established because of the low population of these positions. Each Zn^{2+} and Co^{2+} cation in the structures of compounds **II** and **III** is disordered over four equally probable positions. A part of the coordination environment of the Zn^{2+} and Co^{2+} cations is also disordered. The crystallographic data and details of diffraction experiments for compounds **I–III** are presented in Table 1.

The full tables of interatomic distances and bond angles, coordinates of atoms, and parameters of atomic displacements for the complexes were deposited with the Cambridge Crystallographic Data Centre (CIF files CCDC nos. 1862494 (**I**), 1862495 (**II**), and 1862496 (**III**); http://www.ccdc.cam.ac.uk/structures/) and can also be obtained free of charge from the authors.

RESULTS AND DISCUSSION

Compounds **I–III** were obtained by heating a mixture of a 1 M solution of zinc or cobalt nitrate with CB[6] to 100°C for 48 h. Polyhedral single crystals

Table 1. Selected crystallographic data and structure refinement parameters for compounds **I**–**III**

Parameter	Value		
	I	**II**	**III**
Empirical formula	$C_{36}H_{57}N_{26}O_{28.5}Zn$	$C_{36}H_{58}N_{26}O_{29}Zn$	$C_{36}H_{58}N_{26}O_{29}Co$
FW, g/mol	1375.44	1384.45	1378.01
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$Pnnm$	$Pnnm$
a, Å	11.5609(2)	11.5797(3)	11.5454(3)
b, Å	16.1024(3)	16.0615(4)	16.0936(5)
c, Å	29.5339(6)	14.8855(4)	14.7975(4)
V, Å^3	5497.98(18)	2768.51(12)	2749.48(13)
Z	4	2	2
ρ_{calcd}, g/cm^3	1.662	1.661	1.664
μ, mm^{-1}	0.564	0.561	0.430
$F(000)$	2852	1436	1430
Crystal size, mm	0.24 × 0.12 × 0.09	0.32 × 0.26 × 0.19	0.24 × 0.20 × 0.19
Scan range over θ, deg	3.27–25.68	3.38–25.68	3.38–29.06
Range of indices hkl	$-14 \le h \le 15$, $-18 \le k \le 20$, $-37 \le l \le 32$	$-15 \le h \le 14$, $-15 \le k \le 20$, $-13 \le l \le 19$	$-12 \le h \le 15$, $-16 \le k \le 22$, $-19 \le l \le 21$
N_{hkl} measured/independent	22779/10368	7426/2738	11001/3302
R_{int}	0.0246	0.0142	0.0176
N_{hkl} with $I > 2\sigma(I)$	9253	2385	2808
GOOF for F^2	1.046	1.069	1.063
R factors ($I > 2\sigma(I)$)	$R_1 = 0.0587$, $wR_2 = 0.1597$	$R_1 = 0.0820$, $wR_2 = 0.2390$	$R_1 = 0.0742$, $wR_2 = 0.2157$
R factors (for all reflections)	$R_1 = 0.0671$, $wR_2 = 0.1666$	$R_1 = 0.0894$, $wR_2 = 0.2482$	$R_1 = 0.0827$, $wR_2 = 0.2250$
Residual electron density (max/min), e/Å^3	1.339/–0.395	0.702/–0.841	1.469/–0.646

were obtained on slow cooling the reaction mixture for 48 h (syntheses of **I** and **III**). According to the X-ray diffraction data, the single crystals of complexes **I** and **III** have the compositions $[Zn(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 6.5H_2O$ and $[Co(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 7H_2O$, respectively. The fast cooling of the reaction mixture (synthesis of **II**) gives stick-like single crystals that crystallize, according to the X-ray diffraction data, in the space group $Pnnm$ (unlike $P2_12_12_1$ for **I**) and have the composition $[Zn(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 7H_2O$. Different conditions of cooling the reaction mixture in the case of compounds **I** and **II** result in the formation of crystals of different shapes. A more ordered phase with a lower symmetry crystallizes on slow cooling, whereas the fast cooling results in the crystallization of a more disordered phase with a higher symmetry.

Being taken from the mother liquor, the crystals of compounds **I**–**III** undergo cracking and lose crystallinity. The crystals of compounds **I**–**III** are insoluble in water, methanol, and ethanol. According to the TG analyses performed for the freshly prepared samples, the content of water in them is higher than that in the samples selected for X-ray diffraction analysis.

In the structure of complex **I**, the Zn(II) atom exists in the octahedral environment consisting of two oxygen atoms of the carbonyl groups of the CB[6] molecule (Zn–O 2.124(5) and 2.200(4) Å) and four oxygen atoms of the aqua ligands (Zn–O 2.026(5)–2.092(5) Å). Thus, the complex cation $[Zn(H_2O)_4(CB[6])]^{2+}$ is formed (Fig. 1a).

The crystals of compounds **II** and **III** are isostructural. The Zn(II) atoms in the structure of compound **II** and Co(II) in compound **III** are also in the distorted octahedral environment consisting of two oxygen

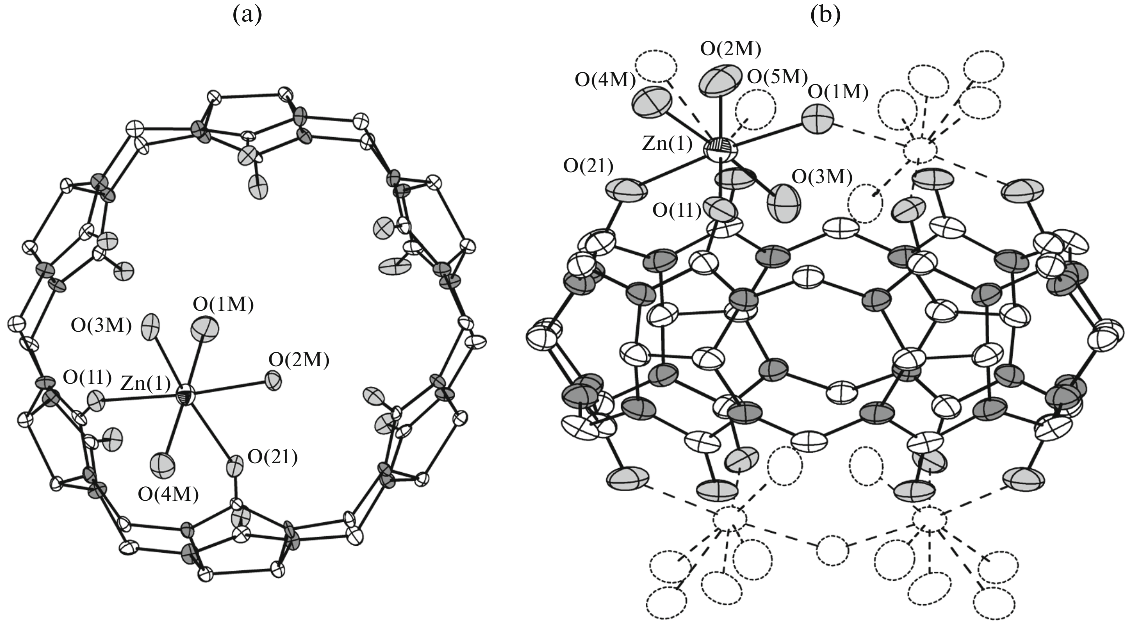

Fig. 1. Coordination environment of the Zn(II) cation in the structures of compounds (a) **I** and (b) **II**. Ellipsoids of 50% probability. Hydrogen atoms are omitted. For compound **II**, alternative positions of the Zn(II) cations and aqua ligands are shown by dashed lines.

atoms of the carbonyl groups of the CB[6] molecule (Zn–O 2.103(3) and 2.315(3) Å for **II**; Co–O 2.075(3) and 2.308(3) Å for **III**) and four aqua ligands (Zn–O 1.864(8)–2.113(4) Å; Co–O 1.934(5)–2.097(3) Å). The center of the CB[6] molecule lies in the partial position with the symmetry $2/m$, resulting in the disordering of the Zn^{2+} cation with its coordination environment over four equally populated positions (Fig. 1b).

The Zn^{2+} cations in the structure of compound **I** are disordered over three positions (Zn(1), Zn(2), and Zn(3)), whereas each Zn^{2+} and Co^{2+} cation in compounds **II** and **III**, respectively, is disordered over four equally probable positions. The above described complex cations $[M(H_2O)_4(CB[6])]^{2+}$ (M = Zn, Co) in the structures of compounds **I**–**III** are linked by hydrogen bonds between the aqua ligands, carbonyl groups of the CB[6] molecules, and molecules of water of crystallization to form chains parallel to the crystallographic axis *a*. The chains of the adjacent layers are shifted relative to each other by half a translation along the *a* axis (Fig. 2). Channels directed along the *a* axis are formed in the space between the chains, and nitrate anions are located in the channels. The nitrate anions, aqua ligands, and molecules of water of crystallization form a single branched network of hydrogen bonds: $O\cdots O$ 2.67–2.98 Å for **I**, 2.63–3.01 Å for **II**, and 2.54–3.00 Å for **III**.

The IR spectra of complexes **I**–**III** exhibit stretching vibration bands of the O–H molecules of water of crystallization in a range of 3700–3100 cm^{-1}, N–H vibration bands are observed at 3100–2980 cm^{-1}, those of the C–H groups are observed at 2980–2890 cm^{-1}, and the vibrations of the C=O groups of CB[6] are observed in a range of 1743–1740 cm^{-1}. The absorption bands of nitrate anions in the spectra of the complexes appear at 1378 cm^{-1}.

The TG results for compounds **I**–**III** show that at a heating rate of 10°C/min the water molecules are removed in a range of 20–160°C in two stages, and the process is accompanied by endothermic effects. The mass loss at the first stage at 90°C is 8% for compounds **I** and **II** and 5% for compound **III** corresponding to the removal of six and four molecules of water of crystallization, respectively. The overall loss of the crystallization and coordination water at two stages is 18 and 15%, respectively. Heating above 250°C leads to the complete thermal destruction (Fig. 3).

Based on the data of elemental and TG analyses, we can present the compositions of the polycrystalline samples as follows: $[Zn(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 9H_2O$ for the compounds obtained by the syntheses of **I** and **II** and $[Co(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 8H_2O$ for the compound obtained by the synthesis of **III**.

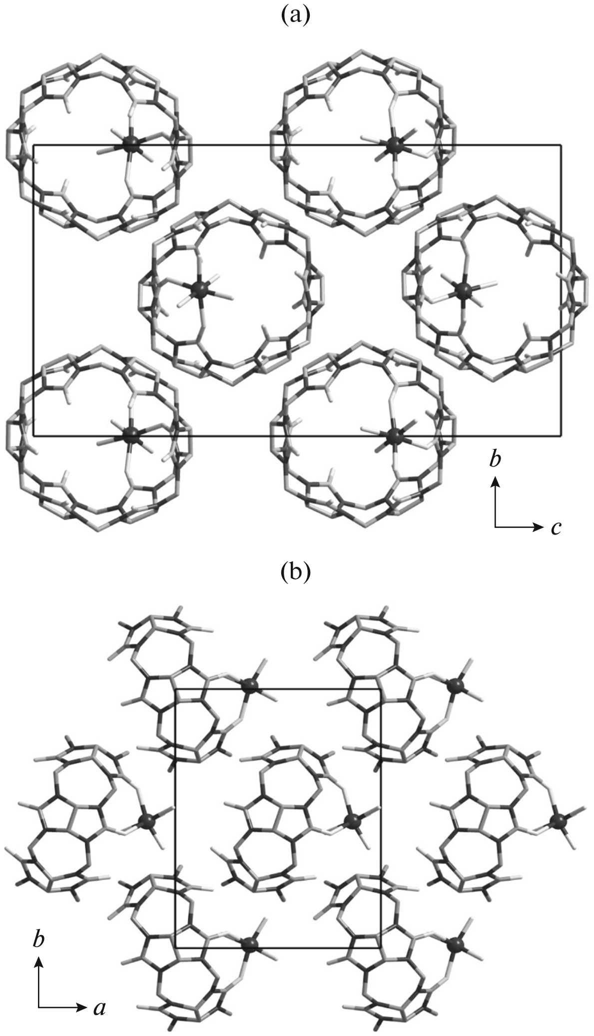

Fig. 2. Crystal packing in the structures of compounds (a) **I** and (b) **II**. Hydrogen atoms are omitted. The positions of the Zn(II) cations are shown by dark balls. Only one of the alternative positions of the Zn(II) cations of the aqua ligands is shown.

The single zinc complex with the CB[6] derivative in which the direct coordination of the carbonyl groups of the macrocycle to the Zn^{2+} cation is observed [26] has been synthesized and structurally characterized before the present work. Several Zn(II) compounds with cucurbit[5]uril were described [24, 25]. Published examples of the complexes with the direct coordination of the carbonyl groups of cucurbiturils to the Co^{2+} cations are lacking. Thus, the compounds obtained in this work are the first zinc(II) and cobalt(II) complexes with nonfunctionalized cucurbit[6]uril.

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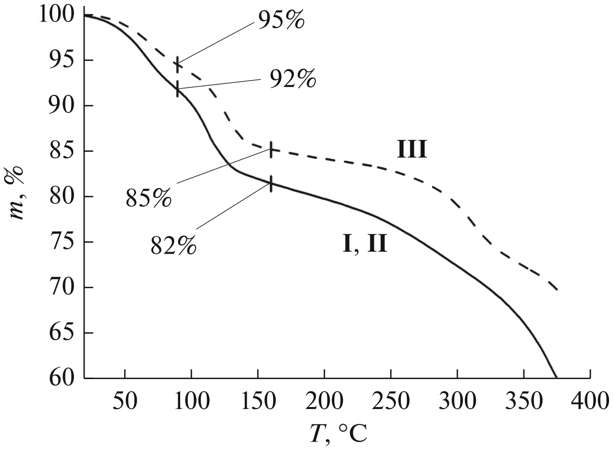

Fig. 3. TG curves for compounds (solid line) Zn$(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 9H_2O$ and (dashed line) $[Co(H_2O)_4(C_{36}H_{36}N_{24}O_{12})](NO_3)_2 \cdot 8H_2O$.

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