

Supramolecular approach to crystallization of polynuclear chromium(III) aqua hydroxo complexes: synthesis and crystal structures of complexes $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$ and $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$ with cucurbit[*n*]uril (*n* = 7, 8)

O. A. Gerasko, E. A. Mainicheva, D. Yu. Naumov, and V. P. Fedin*

A. V. Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
3 prosp. Akad. Lavrentieva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383) 330 9489. E-mail: cluster@che.nsk.su

Supramolecular compounds of the compositions $\{[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8](\text{C}_{42}\text{H}_{42}\text{N}_{28}\text{O}_{14})_2\}(\text{NO}_3)_4 \cdot 18.75\text{H}_2\text{O}$ (**1**) and $\{[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}](\text{C}_{48}\text{H}_{48}\text{N}_{32}\text{O}_{16})_3\}(\text{NO}_3)_6 \cdot 55\text{H}_2\text{O}$ (**2**) were synthesized from aqueous solutions of chromium(III) nitrate and the macrocyclic cavitand cucurbit[*n*]uril ($\text{C}_{6n}\text{H}_{6n}\text{N}_{4n}\text{O}_{2n}$, where *n* = 7 or 8, respectively). According to the X-ray diffraction study, the polynuclear chromium aqua complexes are disposed in cavities formed by the cucurbit[*n*]uril molecules and are linked to these molecules through hydrogen bonds between the hydroxo and aqua ligands of the polycations and the portal oxygen atoms of the macrocycles. Compound **1** is the first example of supramolecular compounds of cucurbit[7]uril with metal aqua complexes. The isolation of the supramolecular adduct with cucurbit[8]uril **2** in the single-crystalline state allows the determination of the structure of the tetranuclear chromium aqua complex having an adamantane-like structure, $[\text{Cr}_4(\mu_2\text{-OH})_6(\text{H}_2\text{O})_{12}]^{6+}$, which has been previously unknown in the solid state.

Key words: chromium, aqua complexes, cucurbituril, supramolecular compound, crystal structure.

The hydrolysis of Cr^{III} compounds is better studied than the corresponding processes of other transition metal compounds due to high kinetic stability of chromium(III) aqua complexes.^{1,2} The formation of hydroxo- and oxo-bridged chromium compounds as a result of hydrolysis is an important step in the leather-making process.³ It was hypothesized⁴ that Cr_4 fragments bound to small atoms or groups, for example, to O, OH, Cl, or S, are present in a low-molecular-weight chromium-containing compound isolated from biological sources. It is the opinion⁵ that the dinuclear hydroxo-bridged chromium(III) complex serves as an active site of the metalloenzyme responsible for glucose degradation in living organisms.

Polynuclear chromium(III) hydroxo complexes (di-, tri-, tetra-, penta-, and hexanuclear), which are formed upon the addition of sodium hydroxide to an aqueous solution of Cr^{III} perchlorate, can be separated by ion exchange chromatography.⁶ Studies of these oligomers in solution by different physicochemical methods^{6–11} suggested a number of possible structures of polynuclear aqua complexes.^{6,12} However, the problems of isolating oligomers in the solid phase and obtaining direct structural information are still with us today.

The supramolecular approach based on the use of noncoordinating ligands, whose donor atoms can form hydrogen bonds with aqua ligands of the complexes, is one of the most useful methods for crystallization of polynuclear aqua complexes. Macroanions (anionic capsules), such as the inclusion compound of the macrocyclic cavitand calix[4]arene with the sodium 18-crown-6 complex $[\{\text{Na}@(18\text{-crown-6})(\text{OH}_2)_2\}@\{(p\text{-sulfonatocalix[4]arene})_2\}]^{7-}$ and the inclusion compound of calix[4]arene with the tetraprotonated form of cyclam $[\{\text{H}_4\text{cyclam}\}@\{(p\text{-sulfonatocalix[4]arene})_2\}]^{4-}$,^{13,14} were used as outer-sphere ligands for crystallization of polynuclear chromium aqua complexes. The di-,^{13,14} tri-,¹³ and tetranuclear¹³ chromium aqua complexes $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$, $[\text{Cr}_3(\text{OH})_4(\text{H}_2\text{O})_{10}]^{5+}$, and $[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}]^{6+}$, respectively, were isolated from an aqueous solution as supramolecular compounds with the above-mentioned macroanions, and these compounds were structurally characterized. It should be noted that the latter complex can be selectively isolated from a solution containing a mixture of all oligomers. In the structures of the resulting compounds, the polynuclear chromium aqua complexes are located in the

cavities formed by the macroanions and are linked to the latter by both hydrogen bonds of the aqua ligands of the complex with the oxygen atoms of the SO_3^- groups of calixarene and cation-anion interactions. The dinuclear chromium complex was isolated as the supramolecular compound with mesitylene-2-sulfonate $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8][(\text{H}_3\text{C})_3\text{C}_6\text{H}_2\text{SO}_3]_4 \cdot 4\text{H}_2\text{O}$ (see Ref. 15) and the complex of this salt with 18-crown-6 $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8][(\text{H}_3\text{C})_3\text{C}_6\text{H}_2\text{SO}_3]_4 \cdot \text{C}_{12}\text{H}_{24}\text{O}_6 \cdot 3\text{H}_2\text{O}$.¹⁶

In the present study, we applied the supramolecular approach to the isolation of polynuclear chromium(III) aqua complexes with the use of the organic macrocyclic cavitand cucurbit[*n*]uril. The cucurbit[*n*]uril molecule ($\text{CB}[n]$, $\text{C}_{6n}\text{H}_{6n}\text{N}_{4n}\text{O}_{2n}$ ($n = 5-8$)) consists of *n* methylene-bridged glycoluril fragments and has a barrel-like shape containing polarized carbonyl groups (portals) in the planes of the lid and the bottom.¹⁷⁻¹⁹

Earlier,²⁰⁻²³ we have successfully used cucurbit[6]uril for crystallization of polynuclear Zr, Hf, Sr, U, Mo, Al, Ga, and In aqua complexes. In the supramolecular products, the aqua hydroxo complexes are linked to the macrocycle by hydrogen bonding between the hydroxo and aqua ligands of the complexes and the portal oxygen atoms of cucurbit[6]uril. In the present study, we synthesized the dinuclear and tetranuclear chromium aqua complexes from aqueous solutions of chromium(III) nitrate as supramolecular compounds with cucurbit[7]uril and cucurbit[8]uril with the compositions $\{[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8](\text{CB}[7])_2\}(\text{NO}_3)_4 \cdot 18.75\text{H}_2\text{O}$ (**1**) and $\{[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}](\text{CB}[8])_3\}(\text{NO}_3)_6 \cdot 55\text{H}_2\text{O}$ (**2**), respectively.

Results and Discussion

Earlier, we have demonstrated²⁴ that the addition of cucurbit[6]uril to an aqueous solution of chromium(III) nitrate gave rise to the supramolecular compound $\{[\text{Cr}(\text{H}_2\text{O})_6](\text{CB}[6])\}(\text{NO}_3)_3 \cdot 13\text{H}_2\text{O}$, in which the mononuclear octahedral aqua complex is linked to CB[6] by hydrogen bonding between the coordinated water molecules and the carbonyl groups of the macrocycle. This compound has a chain structure, in which the molecules of the aqua complex and cucurbit[6]uril are arranged one above another and are linked by hydrogen bonding. To synthesize polynuclear chromium aqua complexes and isolate them as supramolecular compounds, we carried out the reactions of cucurbit[6]uril with aqueous solu-

tions of chromium(III) nitrate or sulfate with varying the reaction conditions, such as the total concentration of the metal, pH (by adding NaOH, KOH, or ammonia), and the temperature. However, all experiments afforded the compounds of CB[6] with mononuclear complexes only. For the reactions with cucurbit[*n*]urils of larger size, we found the conditions, which provided the isolation of polynuclear chromium aqua complexes in the solid phase.

Violet-green crystals with the composition $\{[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8](\text{CB}[7])_2\}(\text{NO}_3)_4 \cdot 18.75\text{H}_2\text{O}$ (**1**) were grown by slow diffusion of ethanol vapor into a saturated aqueous solution of chromium(III) nitrate and cucurbit[7]uril (pH = 2.3). Crystals of **1** are soluble in water at high temperature. According to the X-ray diffraction study (Table 1), complex **1** is a supramolecular compound of the dinuclear chromium aqua complex with cucurbit[7]uril in which the aqua complex : CB[7] ratio is 1 : 2. The structure of $[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$ in **1** (Fig. 1) is analogous to that of the cation in the dinuclear chromium aqua complexes synthesized earlier.¹³⁻¹⁶ The metal atoms are in a distorted octahedral environment and are linked to each other by two bridging hydroxo groups ($\text{Cr}(1)-\text{O}(5)$, 1.948(3) Å; $\text{Cr}(2)-\text{O}(5)$ 1.950(3) Å). Each chromium atom is additionally coordinated by four water molecules ($\text{Cr}(1)-\text{O}(1)$, 1.990(3) Å; $\text{Cr}(1)-\text{O}(2)$, 2.000(3) Å; $\text{Cr}(2)-\text{O}(3)$, 1.982(3) Å; $\text{Cr}(2)-\text{O}(4)$, 2.006(3) Å). The Cr...Cr nonbonded distance is 3.0235(1) Å. On the whole, the bond lengths and bond angles in the dinuclear fragment differ only slightly from the corresponding parameters for the known dinuclear chromium aqua complexes.

In the structure of **1**, the dinuclear aqua complexes are located in the cavities formed by four cucurbit[7]uril molecules (Fig. 2) and are linked to the latter by numerous hydrogen bonds between the hydroxo and aqua ligands of the complex and the oxygen atoms of the carbonyl groups at each CB[7] portal ($\text{O} \cdots \text{O}$, 2.53–2.96 Å). The cucurbit[7]uril molecules are arranged at nearly a right angle to each other; the angle between the planes formed by the portal oxygen atoms of the adjacent molecules is 84°. The adjacent CB[7] molecules are in rather close proximity and are linked to each other by hydrogen bonds between the carbonyl groups of one molecule

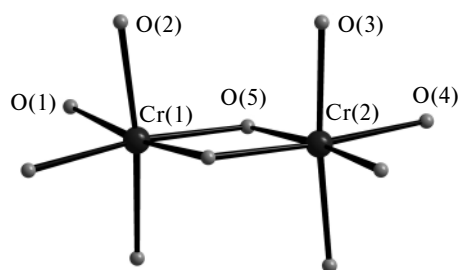


Fig. 1. Structure of the dinuclear chromium aqua complex $[\text{Cr}_2(\mu_2\text{-OH})_2(\text{H}_2\text{O})_8]^{4+}$ in compound **1**.

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

Parameter	1	2
Empirical formula	C ₈₄ H _{139.50} Cr ₂ N ₆₀ O _{68.75}	C ₁₄₄ H ₂₈₄ Cr ₄ N ₁₀₂ O ₁₃₉
Molecular weight/g mol ⁻¹	3194.06	5876.42
<i>T</i> /K	150(2)	150(2)
Crystal system	Cubic	Hexagonal
Space group	<i>Ia</i> 3	<i>R</i> -3
Unit cell parameters		
<i>a</i> /Å	45.9434(11)	30.0467(6)
<i>c</i> /Å		24.3737(8)
<i>V</i> /Å ³	96977(4)	19056.6(8)
<i>Z</i>	24	3
<i>d</i> /g cm ⁻³	1.313	1.536
μ/mm ⁻¹	0.238	0.294
Transmission, max/min	0.9255/0.9066	0.9600/0.9545
<i>F</i> (000)	39876	9120
Crystal dimensions/mm	0.42×0.35×0.33	0.16×0.15×0.14
θ-Scan range, deg	1.09–25.35	2.23–25.35
Ranges of <i>h</i> , <i>k</i> , <i>l</i> indices	–55 ≤ <i>h</i> ≤ 38 –29 ≤ <i>k</i> ≤ 55 –55 ≤ <i>l</i> ≤ 55	–36 ≤ <i>h</i> ≤ 36 –35 ≤ <i>k</i> ≤ 36 –17 ≤ <i>l</i> ≤ 29
Number of measured reflections	221112	37828
Number of independent reflections (<i>R</i> _{int})	14817 (0.0456)	7652 (0.0430)
Number of reflections with <i>I</i> > 2σ(<i>I</i>)	14817	7652
Number of parameters	1085	1031
<i>S</i> factor based on <i>F</i> ²	1.050	1.086
<i>R</i> factors based on reflections with <i>I</i> > 2σ(<i>I</i>)		
<i>R</i> ₁	0.0708	0.0900
<i>wR</i> ₂	0.1934	0.2523
<i>R</i> factors (based on all reflections)		
<i>R</i> ₁	0.1556	0.1254
<i>wR</i> ₂	0.2309	0.2801
Residual electron density (max/min)/e Å ⁻³	0.542/–0.376	1.550/–0.992

and the CH and CH₂ groups of another molecule (*d*_{Cp}(O...H–C) = 2.48 Å). The formation of a system of O...H–C hydrogen bonds between the adjacent CB[*n*] molecules was documented for the (H₃O)₅{(CH₃)₂CO@CB[7]}(SO₄)_{2.5}·15H₂O compound, in the crystal structure of which the CB[7] molecules are packed in a herringbone fashion,²⁵ and for the {[La(H₂O)₆(SO₄)](CB[6])}(NO₃)·12H₂O complex having a chain structure.²⁶

Green crystals of compound **2** were grown by keeping an aqueous solution of chromium nitrate, cucurbit[8]uril, and sodium hydroxide in a sealed tube at pH 4.4 for three days at 95 °C. Crystals of **2** are insoluble in water at high temperature. The X-ray diffraction study showed that complex **2** is a supramolecular compound of the tetranuclear chromium aqua complex [Cr₄(OH)₆(H₂O)₁₂]⁶⁺ with cucurbit[8]uril. The chromium and oxygen atoms in the aqua complex are disordered over two positions, one of which is shown in Fig. 3. The chromium atoms in [Cr₄(OH)₆(H₂O)₁₂]⁶⁺ are in a slightly distorted octahedral environment formed by three oxygen atoms of the termi-

nal water molecules and three oxygen atoms of the μ₂-bridging hydroxo groups that link the metal atoms in pairs. The {Cr₄(μ₂-OH)₆} fragment of the complex has an adamantane-like structure (in Fig. 3, this fragment is indicated by thicker lines), in which four chromium atoms occupy the vertices of a slightly distorted tetrahedron, and six oxygen atoms of the hydroxo groups are located above the edges of this tetrahedron. This structural type has been previously unknown for tetranuclear chromium aqua complexes. Earlier,⁶ only cyclic structures have been proposed for tetranuclear aqua complexes based on the study of aqueous solutions of Cr^{III}. The structure of one of these compounds with the composition [Cr₄(OH)₆(H₂O)₁₂]⁶⁺ (involved in the supramolecular compound with the macroanion [{Na@{(18-crown-6)(OH)₂}}@{(*p*-sulfonatocalix[4]arene)₂}}]^{7–}) was established by X-ray diffraction.¹³ The cation in this compound exists as an eight-membered ring consisting of alternating four chromium atoms (located in the vertices of the rhombus) and four oxygen atoms of the μ₂-bridging hydroxo groups. Two opposite chromium atoms in the

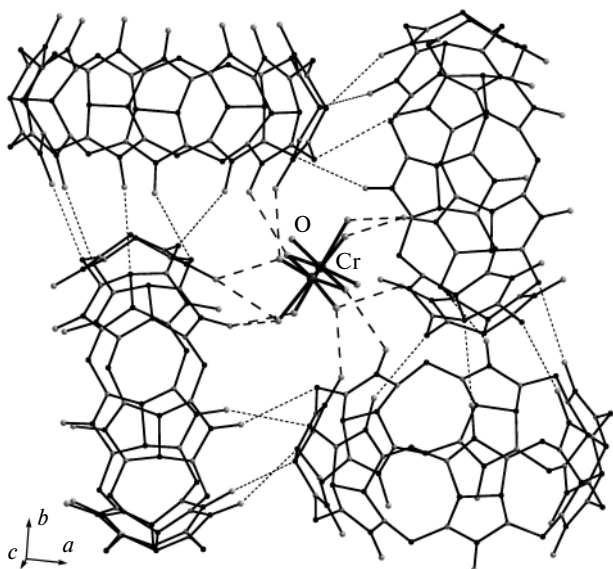


Fig. 2. Packing of the CB[7] molecules and the dinuclear Cr^{III} aqua complexes in the structure of **1**. The hydrogen bonds between the hydroxo and aqua ligands of the complex and CB[7] are indicated by dashed lines; the hydrogen bonds between the CB[7] molecules, by dotted lines.

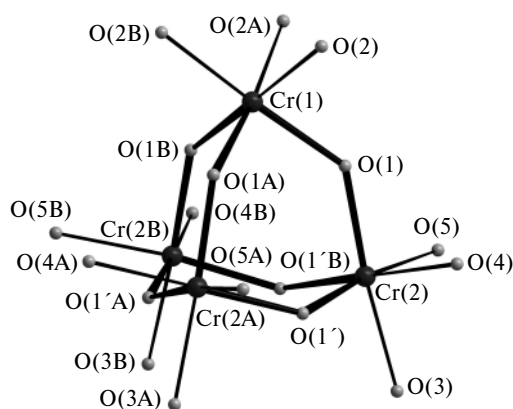


Fig. 3. Structure of the tetranuclear chromium aqua complex $[\text{Cr}_4(\mu_2\text{-OH})_6(\text{H}_2\text{O})_{12}]^{6+}$ in compound **2**. The adamantane-like fragment of the complex is shown by thicker lines.

ring are additionally linked to each other by two μ_2 -bridging hydroxo groups. The adamantane-like structure was described only for chromium complexes with organic ligands, such as $[\text{Cr}_4(\text{OH})_6(\text{C}_5\text{Me}_5)_4](\text{BF}_4)_2$ (**3**)²⁷ and $[\text{Cr}_4(\text{OH})_6(\text{tach})_4](\text{ClO}_4)_n(\text{CF}_3\text{SO}_3)_{6-n}$ (**4**) (tach is 1,3,5-triaminocyclohexane).²⁸ The bond lengths and bond angles in the tetranuclear aqua complex of compound **2** are given in Table 2. The average Cr—O bond length in the bridging hydroxo groups of the adamantane fragment is 1.931(3) Å, which is slightly shorter than the analogous distances in chromium complexes with organic ligands ($d_{\text{aver}} = 1.952(8)$ and 1.973(6) Å in **3** and **4**, respectively). The Cr...Cr nonbonded distances ($d_{\text{aver}} = 3.566(2)$ Å) are

Table 2. Selected geometric parameters for the tetranuclear chromium aqua complex in compound **2**

Bond	<i>d</i> /Å	Angle	ω /deg
Cr(1)—O(2)	2.005(6)	O(1)—Cr(1)—O(1A)	93.12(13)
Cr(1)—O(1)	1.940(3)	O(1)—Cr(1)—O(2)	85.43(19)
Cr(2)—O(1)	1.921(3)	O(1)—Cr(1)—O(2A)	91.89(19)
Cr(2)—O(1')	1.903(3)	O(1)—Cr(1)—O(2B)	174.9(2)
Cr(2)—O(1'B)	1.958(3)	O(1)—Cr(2)—O(1'B)	94.17(15)
Cr(2)—O(3)	2.032(6)	O(1)—Cr(2)—O(1')	95.95(15)
Cr(2)—O(4)	2.025(6)	O(1)—Cr(2)—O(3)	174.9(2)
Cr(2)—O(5)	2.019(6)	O(1)—Cr(2)—O(4)	86.5(2)
Cr(1)...Cr(2)	3.577(2)	O(1)—Cr(2)—O(5)	90.6(2)
Cr(2)...Cr(2A)	3.5540(17)	Cr(1)—O(1)—Cr(2)	135.80(17)
		Cr(2)—O(1')—Cr(2A)	134.02(17)

also somewhat shorter than those in complexes **3** and **4** ($d_{\text{aver}} = 3.669(2)$ and 3.668(9) Å, respectively).

In the crystal structure of **2**, the tetranuclear chromium aqua complexes are located in the cavities formed by six cucurbit[8]uril molecules (Figure 4 shows only four molecules; two other molecules are located above and below the plane of the figure) and are linked to the cucurbit[8]uril molecules by numerous hydrogen bonds between the hydroxo and aqua ligands of the polycation and the oxygen atoms of the carbonyl groups at each cucurbit[8]uril portal (O...O, 2.49–2.98 Å). Six cucurbit[8]uril molecules that form the cavity are arranged at

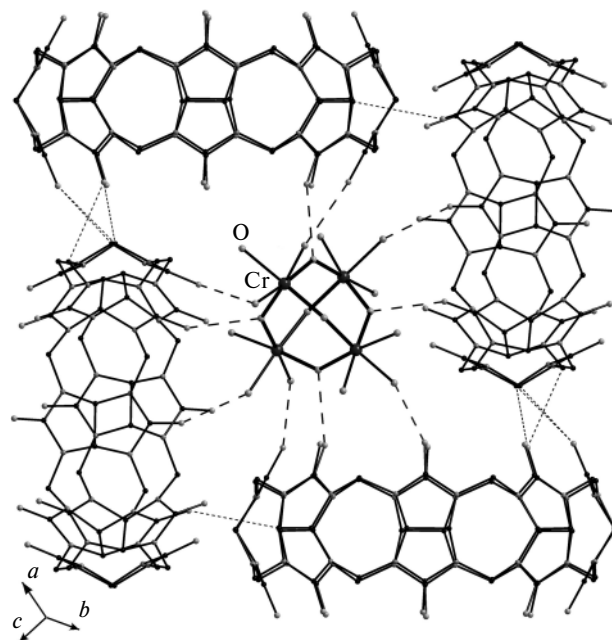


Fig. 4. Packing of the CB[8] molecules and the tetranuclear Cr^{III} aqua complexes in the structure of **2**. The hydrogen bonds between the hydroxo and aqua ligands of the complex and CB[8] are indicated by dashed lines; the hydrogen bonds between the CB[8] molecules, by dotted lines.

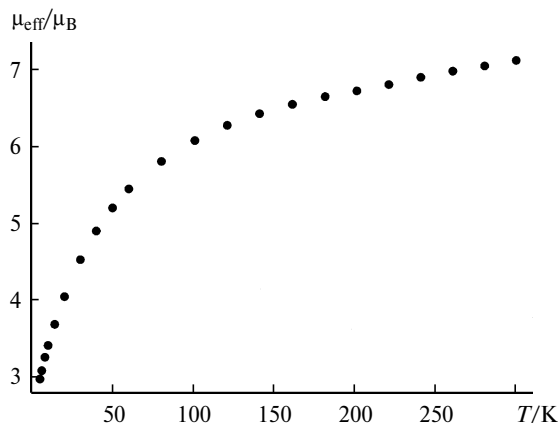


Fig. 5. Temperature dependence of the effective magnetic moment for compound **2**.

nearly a right angle to each other; the angle between the planes formed by the portal oxygen atoms of the adjacent molecules is 89° . The average length of the hydrogen bonds $d_{\text{aver}}(\text{O}\cdots\text{H}-\text{C})$ between the adjacent CB[8] molecules is 2.44 \AA . In the structure of **2**, the water solvent molecules and the nitrate anions are located between the polycations and the CB[8] molecules.

The magnetic properties of complex **2** were studied in the temperature range of 2–300 K in magnetic field of 5 kOe (Fig. 5). The effective magnetic moment at 300 K is 7.1β . For four independent noninteracting Cr^{III} ions ($S = 3/2$), the calculated effective magnetic moment is 7.75β . The lower magnetic moment of complex **2** indicates that weak antiferromagnetic interactions between the paramagnetic Cr^{III} ions occur even at room temperature. Antiferromagnetic interactions were found²⁸ also in the tetranuclear chromium complex with triaminocyclohexane **4**, in which μ_{eff} is 6.9β at 296 K.

The IR spectra of complexes **1** and **2** show a broad stretching band in the $3700\text{--}2800 \text{ cm}^{-1}$ region belonging to different types of H_2O molecules and hydroxy groups involved in hydrogen bonding. In the $1800\text{--}400 \text{ cm}^{-1}$ region, the bands associated with vibrations of cucurbit[7]uril and cucurbit[8]uril were distinguished. The absorption band of nitrate anions is observed at 1384 cm^{-1} .

To conclude, we demonstrated that the macrocyclic cavitands cucurbit[*n*]urils of larger size ($n = 7$ or 8) can be used for the isolation of polynuclear chromium aqua complexes in the solid phase from aqueous solutions. Supramolecular compounds are formed by numerous hydrogen bonds between the hydroxo and aqua ligands of the complex and the oxygen atoms of cucurbit[*n*]urils. Apparently, the packing of large cucurbit[*n*]uril molecules plays the structuring role in compounds **1** and **2**. The size of the cavities between these cucurbit[*n*]uril molecules allows the encapsulation of polycations. Cucurbit[*n*]urils of larger size form, correspondingly, larger cavities, which can encapsulate higher-nuclearity polycations. Com-

pound **1** is the first example of supramolecular compounds of cucurbit[7]uril with metal aqua complexes. The preparation of the supramolecular compound with cucurbit[8]uril **2** in the single-crystalline state allowed us to establish the structure of the tetranuclear adamantane-like chromium aqua complex $[\text{Cr}_4(\mu_2\text{-OH})_6(\text{H}_2\text{O})_{12}]^{6+}$, which has been previously unknown in the solid state.

Experimental

The starting chromium nitrate of high purity grade was used without additional purification. Cucurbit[*n*]urils ($n = 7$ and 8) were synthesized according to a known procedure.¹⁸ The IR spectra were recorded on a SCIMITAR FTS 2000 Fourier-transform spectrometer in the $4000\text{--}400 \text{ cm}^{-1}$ region. The elemental analysis for C, H, N was carried out in the Laboratory of Microanalysis of the Novosibirsk Institute of Organic Chemistry, 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.²⁹ The magnetic properties were measured on a SQUID Quantum Design magnetometer.

Octaaquadi(μ_2 -hydroxo)dichromium(III)-bis{cucurbit[7]uril} tetranitrate crystal hydrate, $\{[\text{Cr}_2(\text{OH})_2(\text{H}_2\text{O})_8]-(\text{C}_{42}\text{H}_{42}\text{N}_{28}\text{O}_{14})_2\}(\text{NO}_3)_4 \cdot 18.75\text{H}_2\text{O}$ (1**).** Cucurbit[7]uril $\text{C}_{42}\text{H}_{42}\text{N}_{28}\text{O}_{14} \cdot 17\text{H}_2\text{O}$ (0.015 g, 0.011 mmol) was added to an aqueous solution (3 mL) of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.60 g, 1.5 mmol). The reaction mixture was heated until cucurbit[7]uril was completely dissolved. The solution (pH 2.3) was cooled to room temperature and kept in ethanol vapor for 7 days until violet-green polyhedral crystals were obtained. The crystals were filtered off, washed with ethanol and diethyl ether, and dried in air for 1 day. The yield was 0.015 g (92 % based on consumed cucurbit[7]uril). Found (%): C, 31.38; H, 4.08; N, 26.15. $\text{C}_{84}\text{H}_{139.50}\text{Cr}_2\text{N}_{60}\text{O}_{68.75}$. Calculated (%): C, 31.55; H, 4.41; N, 26.28. IR (v/cm^{-1}): 3420 (s), 2924 (m), 1769 (w), 1734 (s), 1702 (w), 1655 (w), 1558 (w), 1539 (w), 1506 (w), 1472 (s), 1420 (s), 1384 (s), 1375 (s), 1322 (s), 1227 (s), 1185 (s), 1152 (w), 1029 (m), 965 (s), 826 (m), 802 (s), 756 (m), 669 (s), 624 (m), 550 (m), 444 (m).

Dodecaquaahexa(μ_2 -hydroxo)tetrachromium(III)-tris{cucurbit[8]uril} hexanitrate crystal hydrate, $\{[\text{Cr}_4(\text{OH})_6(\text{H}_2\text{O})_{12}]-(\text{C}_{48}\text{H}_{48}\text{N}_{32}\text{O}_{16})_3\}(\text{NO}_3)_6 \cdot 55\text{H}_2\text{O}$ (2**).** A solution (1 mL) of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.20 g, 0.5 mmol) and cucurbit[8]uril $\text{C}_{48}\text{H}_{48}\text{N}_{32}\text{O}_{16} \cdot 20\text{H}_2\text{O}$ (0.020 g, 0.013 mmol) and a 1 M NaOH aqueous solution (1 mL, 0.189 mmol) were placed in a tube. The tube was sealed and kept at 95°C for 3 days. The green polyhedral crystals that formed were filtered off (pH 4.4), washed with ethanol and diethyl ether, and dried in air for 1 day. The yield was 0.017 g (73% based on consumed cucurbit[8]uril). Found (%): C, 29.23; H, 4.81; N, 24.82. $\text{C}_{144}\text{H}_{284}\text{Cr}_4\text{N}_{102}\text{O}_{139}$. Calculated (%): C, 29.43; H, 4.87; N, 24.31. IR (v/cm^{-1}): 3429 (s), 3007 (w), 2930 (w), 1726 (s), 1641 (w), 1475 (s), 1426 (s), 1384 (s), 1318 (s), 1295 (w), 1231 (s), 1191 (s), 1156 (m), 1028 (m), 994 (m), 970 (s), 912 (w), 831 (m), 808 (s), 759 (s), 674 (s), 633 (m), 544 (w), 448 (m).

X-ray diffraction study. The crystallographic characteristics and the X-ray data collection and refinement statistics for compounds **1** and **2** are given in Table 1. The X-ray diffraction data

sets were collected according to a standard procedure at 150 K using graphite-monochromated MoK α radiation ($\lambda = 0.71073$). Semiempirical absorption corrections were applied based on the intensities of equivalent reflections. The structures were solved by direct methods and refined by the full-matrix least-squares method based on F^2 with anisotropic displacement parameters for nonhydrogen atoms using the SHELXTL program package.²⁹ The hydrogen atoms of cucurbit[n]urils were positioned geometrically and refined using a riding model. The hydrogen atoms of the water molecules were not located. The atomic coordinates of compounds **1** and **2** were deposited with the Cambridge Structural Database (CCDC 638252 and CCDC 638253, respectively) and can be obtained from the authors.

This study was financially supported by the Russian Foundation for Basic Research and the Russian Academy of Sciences (Program of Basic Research No. 7 of the Division of Chemistry and Materials Science of the Russian Academy of Sciences and the Integration Interdisciplinary Project of the Siberian Branch of the Russian Academy of Sciences No. 41).

References

1. D. T. Richens, *The Chemistry of Aqua Ions*, John Wiley and Sons, Oxford, 1997, 261.
2. J. Springborg, *Adv. Inorg. Chem.*, 1988, **32**, 55.
3. K. H. Gustavson, *The Chemistry of the Tanning Process*, Academic, New York, 1956.
4. A. Yamamoto, O. Wada, and H. Suzuki, *Eur. J. Biochem.*, 1987, **165**, 627.
5. E. Gonzalez-Vergara, J. Hegenauer, P. Saltmann, M. Sabat, and J. A. Ibers, *Inorg. Chim. Acta*, 1982, **66**, 115.
6. H. Stunzi and W. Marty, *Inorg. Chem.*, 1983, **22**, 2145.
7. M. Ardon and R. A. Plane, *J. Am. Chem. Soc.*, 1959, **81**, 3197.
8. R. W. Kolaczowski and R. A. Plane, *Inorg. Chem.*, 1964, **3**, 322.
9. M. E. Thompson and R. E. Connick, *Inorg. Chem.*, 1981, **20**, 2279.
10. J. E. Finholt, M. E. Thompson, and R. E. Connick, *Inorg. Chem.*, 1981, **20**, 4151.
11. H. Stunzi, F. P. Rotzinger, and W. Marty, *Inorg. Chem.*, 1984, **23**, 2160.
12. P. Andersen, *Coord. Chem. Rev.*, 1989, **94**, 47.
13. A. Drljaca, M. J. Hardie, C. L. Raston, and L. Spiccia, *Chem. Eur. J.*, 1999, **5**, N8, 2295.
14. S. Airey, A. Drljaca, M. J. Hardie, and C. L. Raston, *Chem. Commun.*, 1999, 1137.
15. L. Spiccia, H. Stoeckli-Evans, W. Marty, and R. Giovanoli, *Inorg. Chem.*, 1987, **26**, 474.
16. A. Drljaca, D. C. R. Hockless, B. Moubaraki, K. S. Murray, and L. Spiccia, *Inorg. Chem.*, 1997, **36**, 1988.
17. W. A. Freeman, *Acta Crystallogr.*, 1984, **40B**, 382.
18. A. Day, A. P. Arnold, R. J. Blanch, and B. Snushall, *J. Org. Chem.*, 2001, **66**, 8094.
19. J. W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, and K. Kim, *Acc. Chem. Res.*, 2003, **36**, 621.
20. O. A. Gerasko, M. N. Sokolov, and V. P. Fedin, *Pure Appl. Chem.*, 2004, **76**, N9, 1633.
21. O. A. Gerasko, E. A. Mainicheva, D. Yu. Naumov, N. V. Kuratieva, M. N. Sokolov, and V. P. Fedin, *Inorg. Chem.*, 2005, **44**, 4133.
22. E. A. Mainicheva, O. A. Gerasko, L. A. Sheludyakova, D. Yu. Naumov, M. I. Naumova, and V. P. Fedin, *Izv. Akad. Nauk, Ser. Khim.*, 2006, **55**, 261 [*Russ. Chem. Bull., Int. Ed.*, 2006, **55**, 267].
23. E. A. Mainicheva, O. A. Gerasko, and V. P. Fedin, *Vestn. MITKhT [Bull. Lomonosov Moscow State Academy of Fine Chemical Technology]*, 2006, **6**, 53 (in Russian).
24. D. G. Samsonenko, O. A. Gerasko, T. V. Mit'kina, J. Lipkowski, A. V. Virovets, D. Fenske, and V. P. Fedin, *Koord. Khim.*, 2003, **29**, 178 [*Russ. J. Coord. Chem.*, 2003, **29**, 178 (Engl. Transl.)].
25. I. Hwang, W. S. Jeon, H.-J. Kim, D. Kim, H. Kim, N. Selvapalam, N. Fujita, S. Shinkai, and K. Kim, *Angew. Chem. Int. Ed.*, 2007, **46**, 210.
26. D. G. Samsonenko, J. Lipkowski, O. A. Gerasko, A. V. Virovets, M. N. Sokolov, V. P. Fedin, J. G. Platas, R. Hernandez-Molina, and A. Mederos, *Eur. J. Inorg. Chem.*, 2002, 2380.
27. D. Wormsbacher, K. M. Nicholas, and A. L. Rheingold, *J. Chem. Soc., Chem. Commun.*, 1985, 721.
28. J. Glerup, H. Weihe, P. A. Goodson, and D. J. Hodgson, *Inorg. Chim. Acta*, 1993, **212**, 281.
29. APEX2 (Version 1.08), SAINT (Version 7.03), SADABS (Version 2.11), and SHELXTL (Version 6.12). Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.

Received March 14, 2007