Synthesis and crystal structures of supramolecular compounds of polynuclear aluminum(III) aqua hydroxo complexes with cucurbit[6]uril

E. A. Mainicheva, O. A. Gerasko, L. A. Sheludyakova, D. Yu. Naumov, M. I. Naumova, 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 di-, trideca-, and triacontanuclear aluminum aqua hydroxo complexes, *viz.*, $[Al_2(OH)_2(H_2O)_8]^{4+}$, $[Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]^{7+}$, and $[Al_{30}O_8(OH)_{56}(H_2O)_{26}]^{18+}$, respectively, with the organic macrocyclic cavitand cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12}$) were prepared by evaporation of aqueous solutions of aluminum nitrate and cucurbit[6]uril after the addition of pyridine, ammonia, KOH, or NaOH at pH 3.1—3.8. X-ray diffraction study demonstrated that the aqua hydroxo complexes are linked to the macrocycle through hydrogen bonds between the hydroxo and aqua ligands of the polycations and the portal oxygen atoms of cucurbit[6]uril.

Key words: aqua complexes, aluminum, cucurbit[6]uril, supramolecular compound, crystal structure.

Polynuclear hydrolysis products prevail in chemistry of aqueous solutions of aluminum(III) compounds in wide pH and concentration ranges.[1,2] The control over the degree of hydrolysis and, consequently, the degree of polymerization of aluminum aqua ions plays an important role in geochemistry, biology, edaphology, and catalyst production.[3—6] Polynuclear aluminum hydroxo complexes are involved as the major components in aluminum sols, which are used as precursors of various ceramic materials.[7,8] Numerous potentiometric, kinetic, and spectroscopic studies of the formation of aluminum aqua hydroxo complexes revealed a large series of compounds $Al_p(OH)_q^{(3p-q)+}$ with different degrees of polymerization and a variable OH/Al ratio. However, solid-state isolation of these complexes from aqueous solutions presents difficulties because of their kinetic lability and high rates of ligand exchange. The polynuclear aqua complex containing 13 Al atoms, which is the most abundant aluminum form in organic acidic soils, has been studied in most detail.[9] The aqua hydroxo complex of composition $[\varepsilon\text{-}Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]^{7+}$ is the ε isomer of the Keggin structure (ε-Al_{13}),[10] in which the central AlO_4 tetrahedron shares vertices with 12 edge-sharing AlO_6 octahedra.[11,12] Recently, transformation products of the ε-Al_{13} aqua complex, *viz.*, the aqua complexes $[\delta\text{-}Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]^{7+}$ and $[Al_{30}O_8(OH)_{56}(H_2O)_{26}]^{18+}$, have been isolated from an aqueous solution of the former complex subjected to thermal treatment, and the resulting complexes have been structurally characterized.[13—15] The dinuclear $[Al_2(OH)_2(H_2O)_8]^{4+}$, octanuclear $[Al_8(OH)_{14}(H_2O)_{18}]^{10+}$, and tridecanuclear $[Al_{13}(OH)_{24}(H_2O)_{26}]^{15+}$ (Anderson structure[10]) cations belong to another type of polynuclear aluminum aqua complexes, in which all metal atoms are in an octahedral coordination (AlO_6).[16—18] The aluminum aqua hydroxo complexes were isolated from aqueous solutions and structurally characterized as salts with SO_4^{2-}, SeO_4^{2-}, or Cl^- anions. The use of large anions, such as polyoxometallates, enabled the ε-Al_{13} and δ-Al_{13} forms and the $[W_2Al_{28}O_{18}(OH)_{48}(H_2O)_{24}]^{12+}$ heteropolycation to be synthesized and structurally characterized.[19,20] An ε-Al_{13} compound with a complex polyanion, which consists of two sulfonatocalix[4]arene molecules and an encapsulated sodium complex with 18-crown-6, was documented.[21]

In the present study, we report a new supramolecular approach to the solid-state isolation of polynuclear aluminum aqua complexes from aqueous solutions. The di-, trideca-, and triacontanuclear aqua complexes were obtained as supramolecular compounds **1**—**4** with the organic macrocyclic cavitand cucurbit[6]uril. X-ray diffraction study demonstrated that these compounds have the following compositions: $\{[Al_2(OH)_2(H_2O)_8](Py@@C_{36}H_{36}N_{24}O_{12})_2\}(NO_3)_4\cdot16H_2O$ (**1**), $\{[Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]_2(C_{36}H_{36}N_{24}O_{12})_3\}(NO_3)_{14}\cdot6H_2O$ (**2**), $K_2\{[Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]_2(C_{36}H_{36}N_{24}O_{12})_3\}(NO_3)_{16}\cdot36H_2O$ (**3**), and $\{[Na_2(OH)_2(H_2O)(C_{36}H_{36}N_{24}O_{12})]_2[Al_{30}O_8(OH)_{56}(H_2O)_{26}]\}(NO_3)_{18}\cdot56H_2O$ (**4**).

Results and Discussion

Earlier,[22—27] we have demonstrated that organic macrocyclic cavitands cucurbit[n]urils ($C_{6n}H_{6n}N_{4n}O_{2n}$,

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 261—268, February, 2006.

n = 5—8 (CB[n])) can be used for solid-state isolation of polynuclear aqua complexes of different metals (Zr, Hf, Sr, U, Mo, and Ga) from aqueous solutions.

The cucurbit[n]uril molecule has a barrel-like shape and can form hydrogen bonds with aqua ligands due to the presence of polarized carbonyl groups at the ends (portals).[28—30] As a rule, polynuclear cationic metal aqua complexes have a high charge, and coordinated water molecules in these complexes possess rather strong acidic properties, which is favorable for the formation of hydrogen bonds with the carbonyl oxygen atoms of cucurbit[n]urils. Large sizes of polynuclear aqua complexes promotes the formation of an extensive hydrogen bond network due to a large contact surface area.

In aqueous solutions of aluminum salts at low pH (<3), aluminum is present as the hydrated $[Al(H_2O)_6]^{3+}$ cation. A crystallographic analysis of alums and other hydrates showed that aluminum has an octahedral coordination with six water molecules. Earlier,[31] we have demonstrated that the addition of cucurbit[6]uril to an aqueous solution of aluminum chloride (pH 2.5) led to the formation of the supramolecular compound $[Al(H_2O)_6](C_{36}H_{36}N_{24}O_{12})Cl_3 \cdot 18H_2O$, in which the octahedral aqua complex is linked to CB[6] through hydrogen bonds between the carbonyl groups of the macrocycle and the water molecules. An increase in pH leads to H^+ abstraction from the coordinated water molecules and polymerization of the aqua ions through the bridging hydroxo ligands. In the present study, we added pyridine, ammonia, potassium hydroxide, or sodium hydroxide to a solution of aluminum(III) nitrate and cucurbit[6]uril to increase the basicity of the solution, pH of the resulting solutions being varied from 2.7 to 4.0. At pH > 4, an amorphous precipitate of aluminum hydroxide was obtained in all cases. At certain pH and reagent ratios, we succeeded in isolating supramolecular adducts of polynuclear aluminum aqua complexes with cucurbit[6]uril from solution.

Colorless air-stable crystals of compound **1** were grown by slow evaporation of an aqueous solution of aluminum nitrate and cucurbit[6]uril after the addition of pyridine to pH 3.1 in air.

X-ray diffraction study showed that complex **1** is a supramolecular compound of the dinuclear aluminum aqua complex with cucurbit[6]uril, in which the aqua complex/CB[6] ratio is 1 : 2 (Fig. 1). The $[Al_2(OH)_2(H_2O)_8]^{4+}$ cation in compound **1** is structurally similar to the dinuclear cation in the $[Al_2(OH)_2(H_2O)_8](YO_4)_2 \cdot 2H_2O$ complexes (Y = S or Se).[15] The metal atoms are in an octahedral coordination and are linked to each other by two bridging hydroxo groups (Al—O, 1.891(4), 2.161(5), 1.868(4), and 1.873(5) Å). Each aluminum atom is additionally coordinated by four water molecules (Al—O, 1.803(4)—2.084(4) Å). The dinuclear aqua complex in compound **1** is linked to two cucurbit[6]uril molecules through hydrogen bonds between three aqua ligands and two carbonyl oxygen atoms at each portal of CB[6] (O...O, 2.53—2.96 Å). In complex **1**, the octahedral coordination environment of the metal atoms is somewhat more distorted than that in the $[Al_2(OH)_2(H_2O)_8](YO_4)_2 \cdot 2H_2O$ complex. The Al—O distances in molecule **1** are in the range of 1.803(4)—2.161(5) Å, whereas these distances in $[Al_2(OH)_2(H_2O)_8](YO_4)_2 \cdot 2H_2O$ are in the range of 1.87—1.95 Å. The average metal—oxygen distance in the dinuclear cation of **1** (1.94 Å) is longer than the Al—O distances in the above-mentioned complexes (1.89 Å). In the crystal of **1**, the aqua complexes and cucurbit[6]uril molecules are linked to each other through hydrogen bonds to form chains along the a axis (see Fig. 1). The

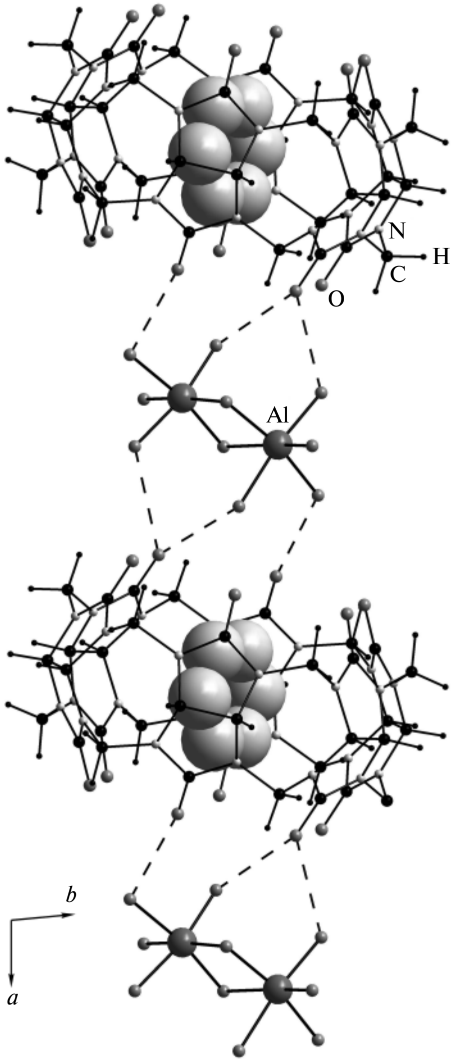

Fig. 1. Fragment of the $[\{[Al_2(OH)_2(H_2O)_8](Py@@C_{36}H_{36}N_{24}O_{12})\}^{4+}]_\infty$ chain in the structure of **1**. Hydrogen bonds are indicated by dashed lines. The pyridine molecules included in cucurbit[6]uril are represented by large-diameter balls.

water molecules of crystallization, the nitrate anions, and the cucurbit[6]uril molecules, which are not linked to the aqua complexes, are located between the chains. The cavity of each CB[6] molecule encapsulates one pyridine molecule, resulting in a distortion of the cavitand. The difference between the largest and smallest diameters of CB[6] (distances between the opposite carbon atoms of CH groups) is 1.29 Å.

The tridecanuclear aluminum aqua complex was isolated as supramolecular compounds **2** and **3** from a solution of aluminum nitrate and cucurbit[6]uril after the addition of ammonia and a KOH solution, respectively (pH 3.8). The compounds were obtained as air-stable colorless crystals. The Al_{13} polyoxo cations in complexes **2** and **3** are structurally similar to the tridecanuclear aluminum aqua complex prepared earlier[11,12] as the sulfate and selenate salts. This is the ε isomer of the Keggin structure, in which the central AlO_4 tetrahedron shares vertices with four Al_3O_{13} groups consisting of three edge-sharing AlO_6 octahedra (Fig. 2). In compounds **2** and **3**, the coordination environment of the central aluminum atom is more distorted compared to other known structures. The Al—O distances in the aqua complex are 1.802(3), 1.802(3), 1.826(4), and 1.853(4) Å (aver., 1.820 Å) in compound **2** and 1.818(3), 1.820(2), 1.820(2), and 1.842(3) Å (aver., 1.825 Å) in compound **3**, whereas these distances in the selenate salt are equal to each other (1.831 Å) and the Al—O distances in the sulfate salt are 1.833 and 1.843 Å. The average metal—oxygen distances in the octahedral coordination environment of aluminum are 2.01 (Al—O), 1.87 (Al—OH), and 1.94 Å (Al—OH_2) in compound **2** and 2.01, 1.86, and 1.94 Å, respectively, in compound **3**, which agree well with the average bond lengths in the structure of the above-described ε-Al_{13} aqua complex (2.03, 1.85, and 1.95 Å, respectively).

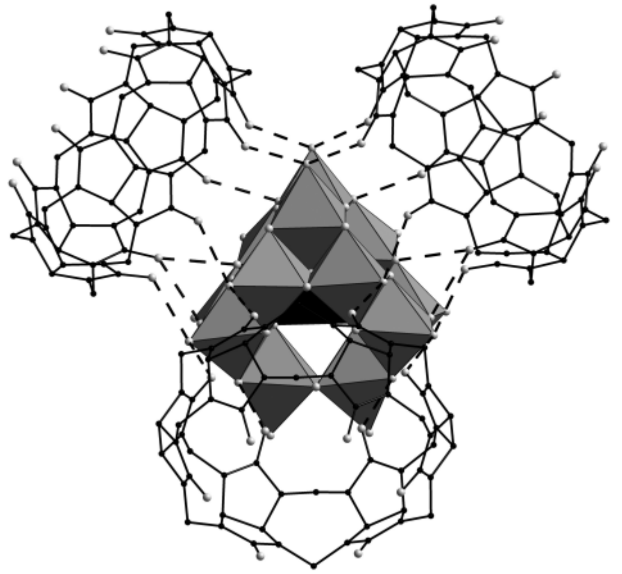

Fig. 2. Structure of the supramolecular adduct of ε-Al_{13} with cucurbit[6]uril molecules in compounds **2** and **3**. Hydrogen bonds are indicated by dashed lines. The hydrogen atoms are omitted. The coordination environment of the aluminum atoms is represented by polyhedra: the AlO_4 tetrahedron is shown in black and the AlO_6 octahedra are shown in gray.

The ε-Al_{13} polyoxo cation can be described as a truncated tetrahedron. Each hexagonal plane of this polyhedron is formed by six bridging oxygen atoms of the OH ligands and six terminal oxygen atoms of the H_2O ligands. The arrangement of these ligands match very well with the shape and sizes of the portals of cucurbit[6]uril. In supramolecular compounds **2** and **3**, three of four hexagonal planes of each ε-Al_{13} polyoxo cation are linked to three CB[6] molecules through hydrogen bonds between six hydroxo and aqua ligands of the polycation and six portal oxygen atoms of cucurbit[6]uril. The planes of the portals are virtually parallel to the faces of the tetrahedral ε-Al_{13} polyoxo cation (angles are 0.01—1.93°). The O...O distances are in the range of 2.63—2.77 Å.

The 12-membered hexagonal ring consisting of six ε-Al_{13} aqua complexes and six cucurbit[6]uril molecules is the main structural unit in the crystal lattices of compounds **2** and **3** (Fig. 3). The polycations are located at the vetices of the hexagons so that three adjacent rings are linked to each other by these polycations, and the hexagonal rings are distorted analogously to cyclohexane in a chair conformation due to the tetrahedral shape of ε-Al_{13}. In the crystal structure, these layers consisting of hexagons are packed in stacks along the *a* axis in such a way that the ε-Al_{13} polycation of one layer lies virtually above the center of the hexagonal ring of another layer. The distance between the aluminum aqua complexes of the adjacent layers is ~7 Å. The solvate water molecules and the nitrate anions are located between the supramolecular layers. In the structure of **3** (Fig. 4), one of four Al_3O_{13} fragments in all Al_{13} polycations of the adjacent layers is coordinated to the potassium atom by two hydroxo groups (K—O, 2.826(4) and 2.710(3) Å). The potassium atom is disordered over two positions and is additionally coordinated by two oxygen atoms of two NO_3^- anions and one water molecule. The coordination of an alkali metal by the hydroxo groups of Al_{13} was found in the Na-δ-$[Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}][SO_4]_4 \cdot 19H_2O$ complex,[14] which is supposedly responsible for the transformation of the ε-Al_{13} form of the polycation into the isomeric δ-Al_{13} form. In the latter, the Al_3O_{13} fragment coordinated by the sodium atom is rotated about the C_3 axis of the central AlO_4 tetrahedron by 60°. In compound **3**, coordination to the potassium atom does not cause such a rotation.

Under analogous conditions (pH 3.5), the addition of a NaOH solution to a solution of aluminum nitrate and cucurbit[6]uril, unlike the above-described experiments with an ammonia solution (synthesis of compound **2**) or a KOH solution (synthesis of compound **3**), did not lead to

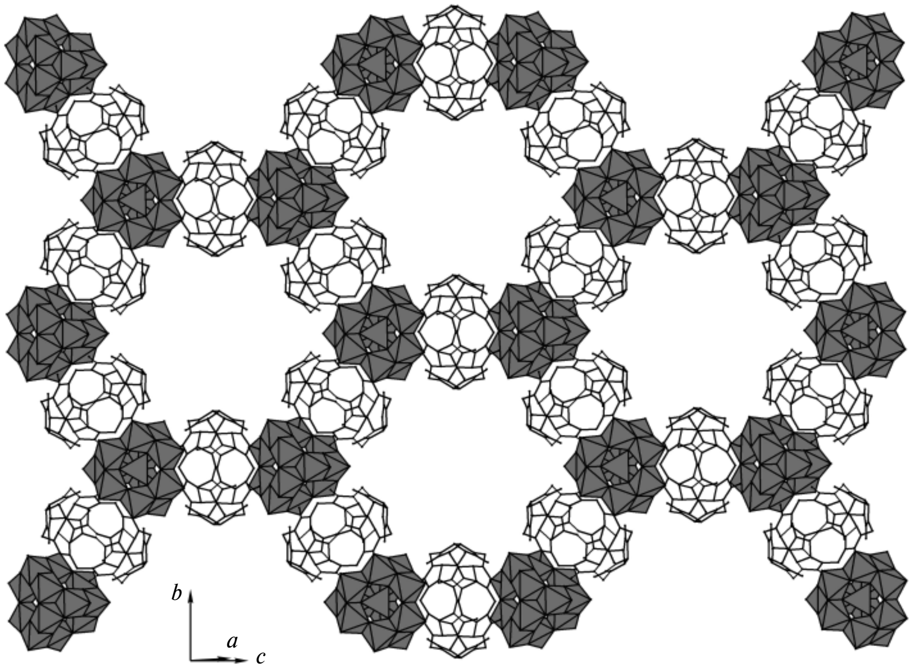

Fig. 3. Structure of the layer consisting of the hexagonal rings formed by the ε-Al_{13} aqua complexes and cucurbit[6]uril molecules in the structures of **2** and **3**. The coordination environment of the aluminum atoms is represented by polyhedra.

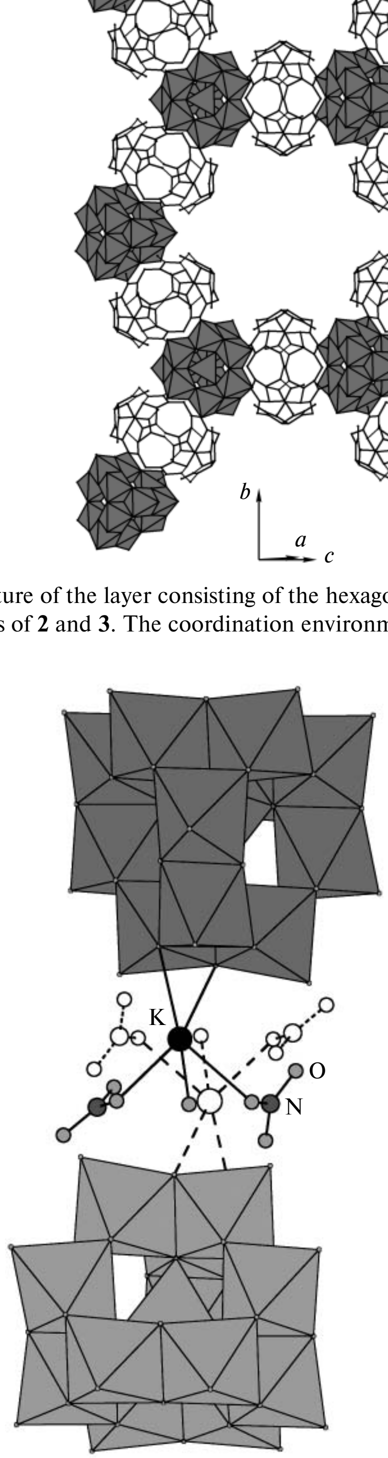

Fig. 4. Coordination environment of the potassium atom in compound **3**. One of the disordered positions is indicated by dashed lines. The coordination environment of the aluminum atoms is represented by polyhedra. The ε-Al_{13} aqua complexes of the adjacent layers are differently colored.

the formation of the tridecanuclear aqua complex. The precipitate containing no aluminum (based on incomplete X-ray diffraction data and the IR spectrum, where Al—O stretching bands are absent), which was obtained upon storage for 1 day, was filtered off. After 1 month, air-stable colorless crystals of **4** were isolated from the mother liquor.

X-ray diffraction data showed that compound **4** is a supramolecular adduct of the triacontanuclear aqua complex $[Al_{30}O_8(OH)_{56}(H_2O)_{26}]^{18+}$ with cucurbit[6]uril (Fig. 5). In the Al_{30} polycation, two tridecanuclear δ-Al_{13} fragments are linked to each other by a bridge consisting of four vertex-sharing AlO_6 octahedra (in Fig. 5, these octahedra are shown in dark-gray). The Al_3O_{13} fragment (in Fig. 5, it is dashed) coordinated by these bridging octahedra is rotated relative to the central tetrahedron in δ-Al_{13} by 60°. In AlO_4, the Al—O bond with the oxygen atom bound to this fragment is the longest one in the distorted tetrahedral environment of the central aluminum atom (1.841(3), 1.786(3), 1.791(3), and 1.791(3) Å). As a whole, the structure of Al_{30} in compound **4** is analogous to that of the triacontanuclear polyoxo cation in the $[Al_{30}O_8(OH)_{56}(H_2O)_{26}][SO_4]_9 \cdot xH_2O$ complex.**[14,15]**

In supramolecular compound **4**, the Al_{30} aqua complex is linked to four cucurbit[6]uril molecules through hydrogen bonds between the hydroxo and aqua ligands of the polycation, on the one hand, and the portal oxygen atoms of CB[6], on the other hand (O...O, 2.73—2.88 Å). The rotation of the Al_3O_{13} fragment in the δ form of the polycation leads to distortion of the hexagonal planes

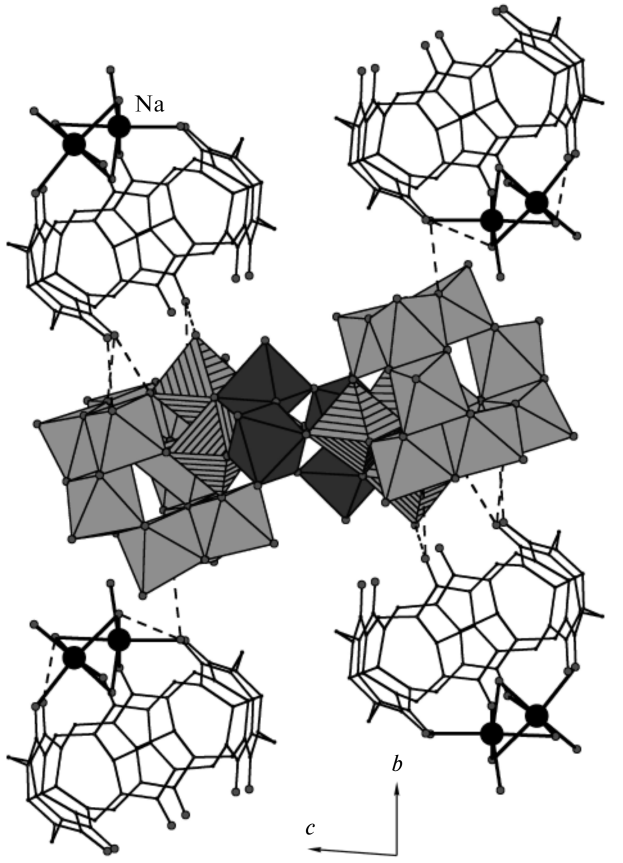

Fig. 5. Fragment of the $[\{[Al_{30}O_8(OH)_{56}(H_2O)_{26}](C_{36}H_{36}N_{24}O_{12})_2\}^{18+}]_\infty$ chain in the structure of **4**. Hydrogen bonds are indicated by dashed lines. The coordination environment of the aluminum atoms is represented by polyhedra: the AlO_6 octahedra, through which two δ-Al_{13} fragments are linked to each other, are shown in dark-gray, and the Al_3O_{13} fragments rotated with respect to the central tetrahedron in δ-Al_{13} are dashed.

characteristic of the ε-Al_{13} form, due to which the geometric correspondence between Al_{30} and the portals of cucurbit[6]uril is worse. Compound **4** differs from compounds **2** and **3** in that only three portal oxygen atoms of two CB[6] molecules and one oxygen atom of two other CB[6] molecules are involved in hydrogen bonding. The supramolecular adducts of Al_{30} with four cucurbit[6]uril molecules form chains, between which the solvate water molecules and the nitrate anions are located. In the crystal, these chains are parallel to each other and are extended along the *a* axis to form alternating organic and inorganic layers along the *b* axis (Fig. 6). The distance between the adjacent polycations is rather short (shortest distance between the oxygen atoms of the adjacent Al_{30} fragments is 3.80 Å).

The portal of each CB[6] molecule is bound to the $\{Na_2(OH)_2(H_2O)\}$ dimer, in which the sodium atoms are linked to each other by two hydroxo bridges and one water molecule (Na—O, 2.333(5)—2.483(5) Å). Each Na atom (coordination number is 6) is coordinated by the portal oxygen atoms of two carbonyl groups of CB[6] and the water molecule. The other two carbonyl groups at the portal are involved in hydrogen bonds with two hydroxo bridges, through which the sodium atoms are linked to each other, and with the hydroxo group of the Al_{30} aqua complex. Coordination by alkali and alkaline-earth metals is characteristic of the chemistry of cucurbit[6]uril, each portal of the macrocycle being coordinated to two small cations, such as K^+, Na^+, or Rb^+.[32—35]

The IR spectra of compounds **1**—**4** show a broad stretching band in the 3700—2800 cm^{-1} region corresponding to different types of water and hydroxy groups involved in hydrogen bonding (Fig. 7). In addition to the characteristic stretching bands of cucurbit[6]uril, the spectra show absorption bands of the nitrate anions (1384 cm^{-1}), Al—O stretching bands at 800—400 cm^{-1} characteristic of the AlO_4 and AlO_6 coordination polyhedra,[36] and absorption bands of pyridine (1612 and 1543 cm^{-1}) for compound **1**. The Al_{13} polycation is characterized by stretching bands of the Al—O bonds involved in the tetrahedral environment of the metal atom at 729 cm^{-1} and bands of the Al—O bonds involved in the octahedral environment at 627 (Al—OH), 546 (Al—O), and 492 cm^{-1} (Al—OH_2).[37] In the spectra of compounds **2** and **3**, the bands at 739 and 730 cm^{-1} can be assigned to Al—O stretching vibrations of the AlO_4 tetrahedron. The Al—O stretching bands of the octahedral environment of aluminum (Al—OH, Al—O, and Al—OH_2) in the spectra of these compounds are observed at 634, 549, and 496 cm^{-1}, respectively, for compound **2** and at 634, 548, and 492 cm^{-1} for compound **3**. It is difficult to distinguish the Al—O stretching band of the tetrahedral environment of aluminum in the spectrum of **4**. Apparently, this is associated with the fact that it appears at higher frequencies compared to compounds **2** and **3** due to the shorter Al—O distances in the tetrahedra and overlap of this band with the absorption band of cucurbit[6]uril (760 cm^{-1}). The absorption bands at 634, 608, 566, 536, and 491 cm^{-1} can be assigned to Al—O vibrations of the octahedral environment of aluminum. In the spectrum of compound **1**, Al—O vibrations are observed at 630 cm^{-1} and as a broad band in the 610—470 cm^{-1} region.

To summarize, we demonstrated that the macrocyclic cavitand cucurbit[6]uril can be used for solid-state isolation of polynuclear aluminum aqua complexes from aqueous solutions. High charges and large sizes of the aqua complexes favor the formation of stable supramolecular compounds with cucurbit[6]uril due to hydrogen bonding between the hydroxo and aqua ligands of the polycations and the portal oxygen atoms of CB[6]. Conceivably, the use of larger cucurbit[*n*]urils (*n* = 7 or 8) will make it possible to perform solid-state isolation of higher-nuclearity aluminum polyoxy cations, whose existence in

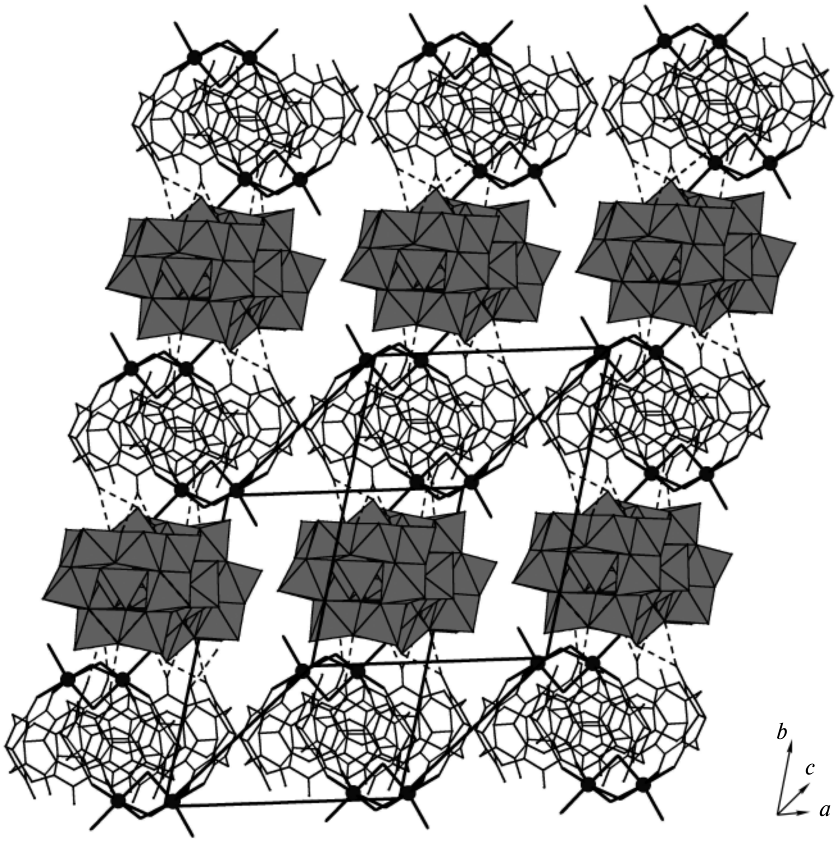

Fig. 6. Fragment of the crystal structure of **4**. Hydrogen bonds are indicated by dashed lines. The coordination environment of the aluminum atoms is represented by polyhedra. The solvate water molecules and the nitrate anions are omitted.

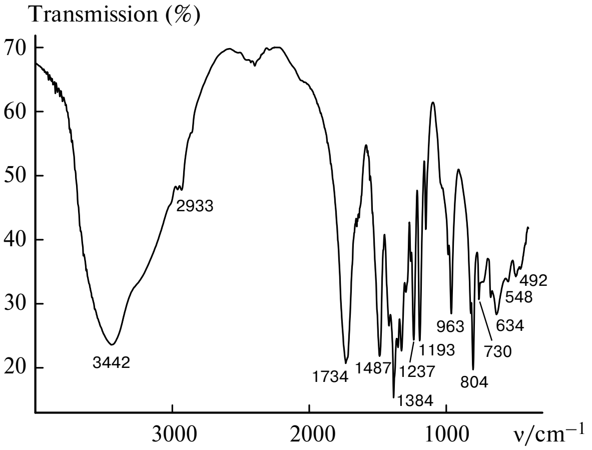

Fig. 7. IR spectrum of compound **3**.

aqueous solutions has been postulated based on analysis of ^{27}Al NMR spectra.[15]

Experimental

The starting aluminum nirate $Al(NO_3)_3 \cdot 9H_2O$ (high-purity grade) was used without additional purification. Cucurbit[6]uril ($C_{36}H_{36}N_{24}O_{12} \cdot 10H_2O$) was synthesized from glyoxal, carbamide, and paraformaldehyde in an acidic medium followed by recrystallization from HCl.[38] Elemental analyses were carried out at the N. N. Vorozhtsov Novosibirsk Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences. X-ray diffraction studies were performed on Bruker SMART CCD and Bruker Nonius X8Apex single-crystal diffractometers equipped with a 4K CCD detector.[39] The IR spectra were recorded on a SCIMITAR FTS 2000 Fourier-transform spectrometer in KBr pellets in the 400—4000 cm^{-1} region.

Octaaquadi(μ_2-hydroxo)dialuminum(III)-bis{cucurbit[6]uril(pyridine) clathrate} tetranitrate hexadecahydrate, {[$Al_2(OH)_2(H_2O)_8$](Py@$C_{36}H_{36}N_{24}O_{12}$)$_2$}(NO_3)$_4 \cdot 16H_2O$ (1). Pyridine (0.095 g, 1.2 mmol) was added to a solution (6 mL) of $Al(NO_3)_3 \cdot 9H_2O$ (1.125 g, 3.0 mmol) to pH 3.1 and then cucurbit[6]uril (0.050 g, $4.3 \cdot 10^{-2}$ mmol) was added. The reaction mixture was heated on a water bath until cucurbit[6]uril was completely dissolved. The resulting solution was slowly concentrated in air at room temperature. After 7 day, colorless crystals of **1** that formed were filtered off and dried in air for 1 day. The yield was 0.032 g (52% based on consumed cucurbit[6]uril). Found (%): C, 32.31; H, 4.48; N, 25.70. $C_{82}H_{132}Al_2N_{54}O_{62}$. Calculated (%): C, 33.73; H, 4.56; N, 25.90. IR (ν/cm^{-1}): 3429 (s), 3114 (w), 3000 (w), 2933 (w), 1733 (s), 1650 (w), 1612 (w), 1543 (m), 1475 (s), 1417 (m), 1384 (s), 1324 (s), 1281 (s), 1235 (s), 1188 (s), 1144 (s), 1029 (m), 983 (m), 962 (s), 818 (m), 799 (s), 759 (s), 675 (s), 630 (m), 610—470 (m).

Bis{dodecaaquatetraeicosa(μ_2-hydroxo)tetra(μ_4-oxo)tridecaaluminum(III)}tris{cucurbit[6]uril} tetradecanitrate hexahydrate, $\{[Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]_2(C_{36}H_{36}N_{24}O_{12})_3\}(NO_3)_{14}\cdot 6H_2O$ (2). A 1 *M* aqueous NH_3 solution (6 mL) was added to a solution (6 mL) of $Al(NO_3)_3\cdot 9H_2O$ (1.125 g, 3.0 mmol). Then the reaction mixture was heated on a water bath until the precipitate was completely dissolved and then cooled to room temperature. Cucurbit[6]uril (0.010 g, $8.9\cdot 10^{-3}$ mmol) was added, and the mixture was heated until the latter compound was completely dissolved. The resulting solution was concentrated in air at room temperature, pH 3.8. After 1 day, colorless crystals of **2** that formed were filtered off and dried in air for 1 day. The yield was 0.016 g (93% based on consumed cucurbit[6]uril). Found (%): C, 20.72; H, 4.65; N, 20.02. $C_{108}H_{298}Al_{26}N_{86}O_{162}$. Calculated (%): C, 21.28; H, 4.93; N, 19.76. IR (ν/cm^{-1}): 3441 (s), 3240 (w), 1734 (s), 1643 (w), 1484 (s), 1412 (w), 1384 (s), 1327(s), 1296 (m), 1259 (m), 1238 (s), 1194 (s), 1150 (s), 1076 (w), 1047 (m), 988 (m), 964 (s), 821 (m), 804 (s), 761 (s), 739 (m), 676 (s), 634 (s), 549 (w), 496 (w), 461 (w).

Dipotassium bis{dodecaaquatetraeicosa(μ_2-hydroxo)tetra-μ_4-oxotridecaaluminum(III)}tris{cucurbit[6]uril} hexadecanitrate hexaeicosahydrate, $K_2\{[Al_{12}(AlO_4)(OH)_{24}(H_2O)_{12}]_2(C_{36}H_{36}N_{24}O_{12})_3\}(NO_3)_{16}\cdot 36H_2O$ (3). Cucurbit[6]uril (0.010 g, $8.9\cdot 10^{-3}$ mmol) was added to a solution (5 mL) of $Al(NO_3)_3\cdot 9H_2O$ (0.938 g, 2.5 mmol). The reaction mixture was heated until cucurbit[6]uril was completely dissolved and then cooled

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

Parameter	1	2	3	4
Molecular formula	$C_{82}H_{132}Al_2N_{54}O_{62}$	$C_{108}H_{298}Al_{26}N_{86}O_{162}$	$C_{108}H_{276}Al_{26}K_2N_{88}O_{200}$	$C_{72}H_{300}Al_{30}N_{66}Na_4O_{230}$
Molecular weight/ g mol^{-1}	2920.38	6095.80	6787.85	6673.14
T/K	150(2)	150(2)	150(2) K	150(2)
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$C2/c$	$C2/m$	$P\bar{1}$
Unit cell parameters:				
a/Å	15.0326(8)	30.3575(16)	30.5446(15)	14.9028(7)
b/Å	19.6101(9)	24.5062(10)	24.7906(11)	20.3749(7)
c/Å	23.2186(12)	18.9267(10)	18.9289(9)	21.8147(11)
α/deg	65.2810(10)	90	90	83.8200(10)
β/deg	74.3620(10)	100.7990(10)	100.7090(10)	84.2990(10)
γ/deg	88.2770(10)	90	90	70.4690(10)
V/Å^3	5960.5(5)	13831.1(12)	14083.7(11)	6192.3(5)
Z	2	2	2	1
ρ_{calc}/g cm^{-3}	1.627	1.464	1.601	1.789
μ/mm^{-1}	0.153	0.207	0.251	0.276
Transmission, max/min	0.9344/0.9247	0.9442/0.9217	0.9284/0.9018	0.9167/0.8857
F(000)	3048	6364	7032	3468
Crystal dimensions/mm	0.52×0.48×0.45	0.40×0.32×0.28	0.42×0.34×0.30	0.45×0.35×0.32
Scan range, θ/deg	1.01—25.35	1.08—25.35	1.07—25.35	1.36—25.35
Ranges of				
h	$-17 \le h \le 18$	$-36 \le h \le 35$	$-36 \le h \le 36$	$-17 \le h \le 17$
k	$-21 \le k \le 23$	$-14 \le k \le 28$	$-19 \le k \le 29$	$-23 \le k \le 23$
l	$-27 \le l \le 27$	$-22 \le l \le 22$	$-18 \le l \le 22$	$-12 \le l \le 26$
Number of measured reflections	35319	40980	37147	36822
Number of independent reflections (R_{int})	21278 (0.0212)	12773 (0.0433)	13222 (0.0271)	22166 (0.0497)
Number of reflections with $I > 2\sigma(I)$	10706	6775	8831	11574
Число рефлексов	21278	12773	13222	22166
Number of parameters in refinement	1810	1058	1082	1981
S factor based on F^2	1.345	1.122	1.080	1.052
R factor based on reflections with $[I > 2\sigma(I)]$:				
R_1	0.0692	0.0665	0.0522	0.0560
wR_2	0.1487	0.1484	0.1090	0.1473
R factor (for all reflections):				
R_1	0.1113	0.1369	0.0827	0.1159
wR_2	0.1604	0.1692	0.1216	0.1616
Residual electron density (max/min)/e Å^{-3}	0.267/–0.297	0.455/–0.410	0.356/–0.314	1.059/–0.412

to room temperature. An aqueous KOH solution (5 mL, 0.28 g, 5.0 mmol) was added with stirring at high temperature until the precipitate was completely dissolved. The resulting solution was concentrated in air at room temperature, pH 3.8. After 1 day, colorless crystals of **3** that precipitated were filtered off and dried in air for 1 day. The yield was 0.013 g (70% based on consumed cucurbit[6]uril). Found (%): C, 18.57; H, 3.80; N, 18.08. $C_{108}H_{276}Al_{26}K_2N_{88}O_{200}$. Calculated (%): C, 19.11; H, 4.10; N, 18.16. IR (ν/cm^{-1}): 3442 (s), 2933 (w), 1734 (s), 1653 (w), 1636 (w), 1558 (w), 1487 (s), 1418 (m), 1384 (s), 1352 (m), 1326 (s), 1295 (m), 1259 (m), 1237 (s), 1193 (s), 1149 (s), 1024 (w), 986 (m), 963 (s), 821 (m), 804 (s), 761 (m), 730 (m), 675 (m), 634 (s), 548 (m), 492 (m), 458 (m).

Bis{cucurbit[6]uril-aquadi(μ_2-hydroxo)disodium}hexaeicosaaqua-hexapentacosa(μ_2-hydroxo)octa(μ_4-oxo)-eicosaluminum(III) octadecanitrate hexapentacosahydrate, $\{[Na_2(OH)_2(H_2O)(C_{36}H_{36}N_{24}O_{12})]_2[Al_{30}O_8(OH)_{56}(H_2O)_{26}]\}(NO_3)_{18} \cdot 56H_2O$ (4). Cucurbit[6]uril (0.020 g, $1.7 \cdot 10^{-2}$ mmol) was added to a solution (10 mL) of $Al(NO_3)_3 \cdot 9H_2O$ (2 g, 5.3 mmol). Then the reaction mixture was heated until the former compound was completely dissolved and then cooled to room temperature. An aqueous NaOH solution (10 mL, 0.4 g, 10.0 mmol) was added with stirring at high temperature until the precipitate was completely dissolved. The resulting solution was concentrated in air at room temperature, pH 3.5. After 1 day, the precipitate that formed (16 mg) was filtered off. The mother liquor was concentrated for 30 days, after which colorless crystals of **4** were obtained. The yield was 0.004 g (7% based on consumed cucurbit[6]uril). Found (%): C, 13.10; H, 3.84; N, 14.05. $C_{72}H_{300}Al_{30}N_{66}Na_4O_{230}$. Calculated (%): C, 12.96; H, 4.53; N, 13.85. IR (ν/cm^{-1}): 3441 (s), 2976 (w), 1729 (s), 1636 (s), 1485 (s), 1417 (w), 1385 (s), 1354 (w), 1328 (m), 1294 (m), 1260 (m), 1238 (s), 1194 (s), 1150 (s), 1072 (m), 1051 (w), 966 (s), 820 (m), 803 (s), 760 (m), 691 (w), 676 (m), 634 (m), 608 (sh), 566 (w), 536 (m), 491 (sh), 459 (w), 445 (w).

X-ray diffraction study. The crystallographic characteristics and details of X-ray diffraction study for crystals of compounds **1—4** are given in Table 1. X-ray data sets were collected according to a standard procedure at 150 K. In all experiments, Mo-Kα radiation (λ = 0.71073 Å) and a graphite monochromator were used. 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 against F^2 with anisotropic displacement parameters for all nonhydrogen atoms using the SHELX97 program package.[40] The hydrogen atoms of cucurbit[6]uril and pyridine were calculated geometrically and refined using a riding model. The hydrogen atoms of the water molecules were not revealed.

The crystallographic data were deposited with the Cambridge Structural Database and can also be obtained from the authors.

This study was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32304) and the Russian Academy of Sciences (Program of the Division of Chemistry and Materials Science of the Russian Academy of Sciences "Chemistry and Physical Chemistry of Supramolecular Systems and Atomic Clusters").

References

1. M. J. Taylor and P. J. Brothers, in *Chemistry of Aluminium, Gallium, Indium and Thallium*, Ed. A. J. Downs, Blackie Academic and Professional, Glasgow, 1993, 111.
2. D. T. Richens, *The Chemistry of Aqua Ions*, John Wiley and Sons, Oxford, 1997, 143.
3. R. J. P. Williams, *Coord. Chem. Rev.*, 1996, **141**, 1.
4. D. R. Parker and P. M. Bertsch, *Environ. Sci. Technol.*, 1992, **26**, 914.
5. R. Burch, *Pillared Clays. Catalysis Today*, *V. 2*, *3*. Elsevier, New York, 1988.
6. V. V. Molchanov and R. A. Buyanov, *Usp. Khim.*, 2000, **65**, 476 [*Russ. Chem. Rev.*, 2000, **65** (Engl. Transl.)].
7. L. F. Nazar, G. Fu, and A. D. Bain, *J. Chem. Soc.*, *Chem. Commun.*, 1992, 251.
8. J. J. Brinker, in *Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing*, Eds J. J. Brinker and G. W. Scherer, Academic Press, New York, 1990.
9. D. Hunter and D. S. Ross, *Science*, 1991, **251**, 1056.
10. M. T. Pope, *Heteropoly and Isopoly Oxometalates*, Springer Verlag, Berlin, 1983.
11. G. Johansson, *Arkiv Kemi*, 1963, **20**, 305.
12. G. Johansson, *Arkiv Kemi*, 1963, **20**, 321.
13. G. Fu and L. F. Nazar, *Chem. Mater.*, 1991, **3**, 602.
14. J. Rowsell and L. F. Nazar, *J. Am. Chem. Soc.*, 2000, **122**, 3777.
15. L. Allouche, C. Gerardin, T. Loiseau, G. Ferey, and F. Taulelle, *Angew. Chem.*, *Int. Ed.*, 2000, **39**, 511.
16. G. Johansson, *Acta Chem. Scand.*, 1962, **16**, 403.
17. W. H. Casey, M. M. Olmstead, and B. L. Phillips, *Inorg. Chem.*, 2005, **44**, 4888.
18. W. Seichter, H.-J. Mogel, P. Brand, and D. Salah, *Eur. J. Inorg. Chem.*, 1998, 795.
19. J. H. Son, Y.-U. Kwon, and O. H. Han, *Inorg. Chem.*, 2003, **42**, 4153.
20. J. H. Son, Y.-U. Kwon, and O. H. Han, *Inorg. Chem.*, 2004, **43**, 1929.
21. A. Drljaca, M. J. Hardie, and C. L. Raston, *J. Chem. Soc.*, *Dalton Trans.*, 1999, 3639.
22. O. A. Gerasko, A. V. Virovets, D. G. Samsonenko, A. A. Tripol´skaya, V. P. Fedin, and D. Fenske, *Izv. Akad. Nauk, Ser. Khim.*, 2003, 562 [*Russ. Chem. Bull.*, *Int. Ed.*, 2003, **52**, 585].
23. T. V. Mitkina, O. A. Gerasko, M. N. Sokolov, D. Yu. Naumov, and V. P. Fedin, *Izv. Akad. Nauk, Ser. Khim.*, 2004, 80 [*Russ. Chem. Bull.*, *Int. Ed.* 2004, **53**, 80].
24. O. A. Gerasko, M. N. Sokolov, and V. P. Fedin, *Pure Appl. Chem.*, 2004, **76**, 1633.
25. O. A. Gerasko, D. G. Samsonenko, A. A. Sharonova, A. V. Virovets, Ya. Lipkovski, and V. P. Fedin, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 325 [*Russ. Chem. Bull.*, *Int. Ed.*, 2002, **51**, 346].
26. D. G. Samsonenko, O. A. Gerasko, A. V. Virovets, and V. P. Fedin, *Izv. Akad. Nauk, Ser. Khim.*, 2005, 1513 [*Russ. Chem. Bull.*, *Int. Ed.*, 2005, **54**, 1557].
27. O. A. Gerasko, E. A. Mainicheva, D. Yu. Naumov, N. V. Kuratieva, M. N. Sokolov, and V. P. Fedin, *Inorg. Chem.*, 2005, **44**, 4133.
28. W. A. Freeman, *Acta Cryst.*, 1984, **B40**, 382.

29. J. W. Lee, S. Samal, N. Selvapalam, H.-J. Kim, and K. Kim, *Acc. Chem. Res.*, 2003, **36**, 621.
30. J. Lagona, P. Mukhopadhyay, S. Chakrabarti, and L. Isaacs, *Angew. Chem.*, *Int. Ed.*, 2005, **44**, 4844.
31. D. G. Samsonenko, M. N. Sokolov, A. V. Virovets, N. V. Pervukhina, and V. P. Fedin, *Eur. J. Inorg. Chem.*, 2001, 167.
32. Y. M. Jeon, J. Kim, D. Whang, and K. Kim, *J. Am. Chem. Soc.*, 1996, **118**, 9790.
33. J. Heo, J. Kim, D. Whang, and K. Kim, *Inorg. Chim. Acta*, 2000, **297**, 307.
34. J. Heo, S.-Y. Kim, D. Whang, and K. Kim, *Angew. Chem. Int. Ed.*, 1999, **38**, 641.
35. F. Zhang, T. Yajima, Y.-Z. Li, G.-Z. Xu, H.-L. Chen, Q.-T. Liu, and O. Yamauchi, *Angew. Chem.*, *Int. Ed.*, 2005, **44**, 3402.
36. A. N. Lazarev, *Kolebatel´nye spektry i stroenie silikatov* [*Vibrational Spectra and Structures of Silicates*], Nauka, Leningrad, 1968, 347 pp. (in Russian).
37. S. M. Bradley, R. A. Kydd, and C. A. Fyfe, *Inorg. Chem.*, 1992, **31**, 1181.
38. W. A. Freeman, W. L. Mock, and N.-Y. Shih, *J. Am. Chem. Soc.*, 1981, **103**, 7367.
39. *APEX2 (Version 1. 08)*, *SAINT (Version 7. 03)*, *and SADABS (Version 2. 11). Bruker Advanced X-ray Solutions*, Bruker AXS Inc., Madison, Wisconsin, USA, 2004.
40. G. M. Sheldrick. *SHELXS97 and SHELXL97. Programs for the Refinement of Crystal Structures*, Göttingen University, Göttingen, Germany, 1997.

Received October 28, 2005