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Reviews

Supramolecular compounds of cucurbituril with molybdenum and tungsten chalcogenide cluster aqua complexes

M. N. Sokolov, D. N. Dybtsev, and V. P. Fedin★

Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences,
3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation.
Fax: +7 (383 2) 34 4489. E-mail: cluster@che.nsk.su

The review surveys the synthesis and structures of a new class of supramolecular compounds composed of the macrocyclic cavitand cucurbituril and molybdenum or tungsten chalcogenide clusters. The structural motifs of supramolecular compounds and factors influencing their formation are considered.

Key words: molybdenum, tungsten, cluster compounds, cucurbituril, supramolecular compounds, crystal structure.

Introduction

The chemical design of nanosized molecular complexes and supramolecular compounds from low-molecular-weight building blocks in solutions at room temperature is a challenge of modern chemistry.[1—12] Highly ordered supramolecular compounds with desired structures and properties can be constructed from molecular building blocks capable of being involved in highly specific controlled molecular interactions, for example, through hydrogen bonding. To increase the strength, directionality, and specificity of weak hydrogen bonds for the construction of solid-state compounds, it is necessary to use rather large building blocks capable of generating extensive hydrogen bond networks.

The present review surveys the synthesis and structures of organic-inorganic supramolecular compounds formed from triangular thio- and seleno-bridged molybdenum and tungsten aqua complexes or their heterometallic mono- and bis-cuboidal derivatives (Fig. 1)[13—15] and organic macrocyclic cavitand cucurbituril. Crystallization of aqua complexes with the use of cucurbituril ($C_{36}H_{36}N_{24}O_{12}$) not only made it possible for the first time to isolate a series of new cluster aqua complexes from solutions and structurally characterize these complexes but also led to the discovery of a new type of supramolecular compounds.

Cucurbituril is an organic macrocyclic cavitand with the symmetry D_{6h} possessing an inner cavity (Fig. 2). Cucurbituril was first synthesized by condensation of glyoxal, urea, and formaldehyde by Behrend in 1905[16] and was structurally characterized by Freeman as late as 1981.[17—21] The cucurbituril molecule contains two symmetrical portals consisting of six O atoms of carbonyl

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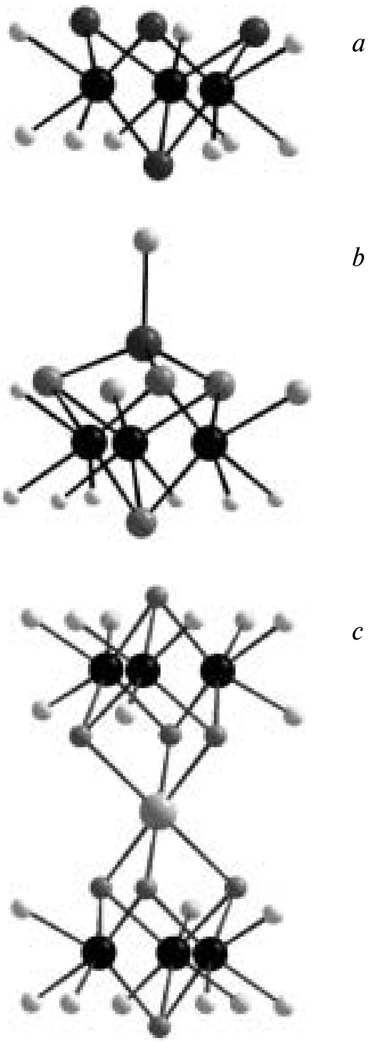

Fig. 1. Cluster aqua complexes $[M_3Q_4(H_2O)_9]^{4+}$ (*a*), $[M_3M'Q_4(H_2O)_9]^{n+}$ (*b*), and $[M_6M'Q_8(H_2O)_{18}]^{8+}$ (*c*).

groups. It is convenient to represent the molecule as an empty barrel without a bottom and lid whose inner cavity is sufficiently large to include small guest molecules, for example, pyridine or tetrahydrofuran. Cucurbituril is virtually insoluble in water and other organic solvents but is readily soluble in some mineral acids (HCl, H_2SO_4), formic acid, and aqueous solutions of alkali metal salts.[22—25]

Analysis of the structural data demonstrated that six carbonyl groups of each portal of cucurbituril fit well in size and symmetry to six aqua ligands located in *cis* positions with respect to the μ_3-bridging chalcogen atom in the triangular cluster aqua complexes $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo or W; Q = S or Se) or with respect to the μ_3-chalcogen atom, which links only the Mo/W atoms in cuboidal heterometallic complexes. Triangular and cuboidal aqua complexes have rather high positive charges, exhibit pronounced acidic properties, and can serve as good hydrogen bond donors. In contrast, the O atoms of the polarized carbonyl groups of cucurbituril are potential hydrogen bond acceptors.

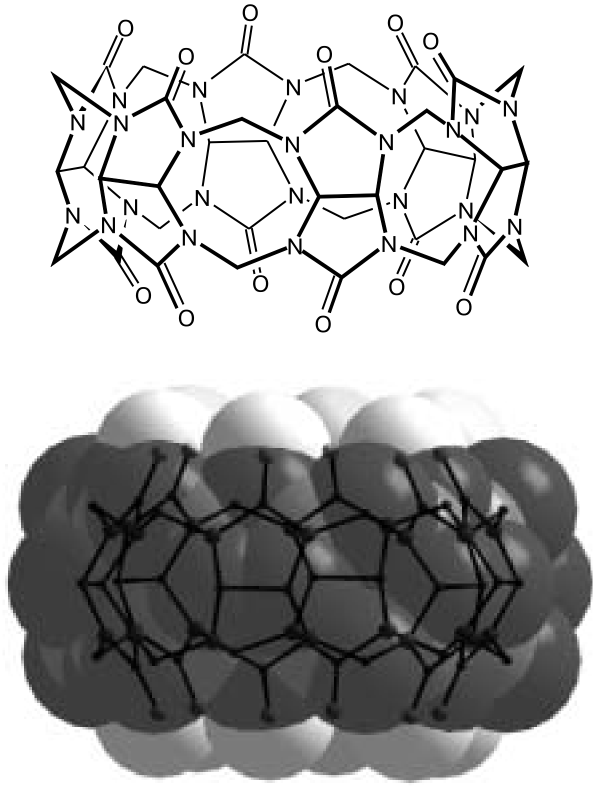

Fig. 2. Cucurbituril molecule ($C_{36}H_{36}N_{24}O_{12}$) (H atoms are omitted).

The geometric and functional complementarity gives rise to extensive hydrogen bond networks involving cucurbituril molecules and triangular/cuboidal aqua complexes resulting in the formation of very stable hybrid organic-inorganic supramolecular compounds. The cluster : cucurbituril ratio in supramolecules can be either 1 : 1 (only one portal is closed by the cluster complex, "barrel with one lid") or 2 : 1 (both portals of cucurbituril are closed, "barrel with two lids") (Fig. 3). The latter type of supramolecules is of interest because the cavity inside the cucurbituril molecule is isolated to form a supramolecular container in which small molecules can be enclosed.

In spite of the fact that the energy of each individual hydrogen bond is low, extensive complementary hydrogen bond networks (in the examples under consideration, up to 12 hydrogen bonds can be formed between the cucurbituril molecule and aqua complexes) provide the formation of very stable supramolecular compounds. All crystalline compounds described below are insoluble or weakly soluble in aqueous solutions of hydrochloric acid in which the starting reagents are readily soluble.

As can be seen from Fig. 3, *a*, *b*, which shows the structures of supramolecular adducts belonging to struc-

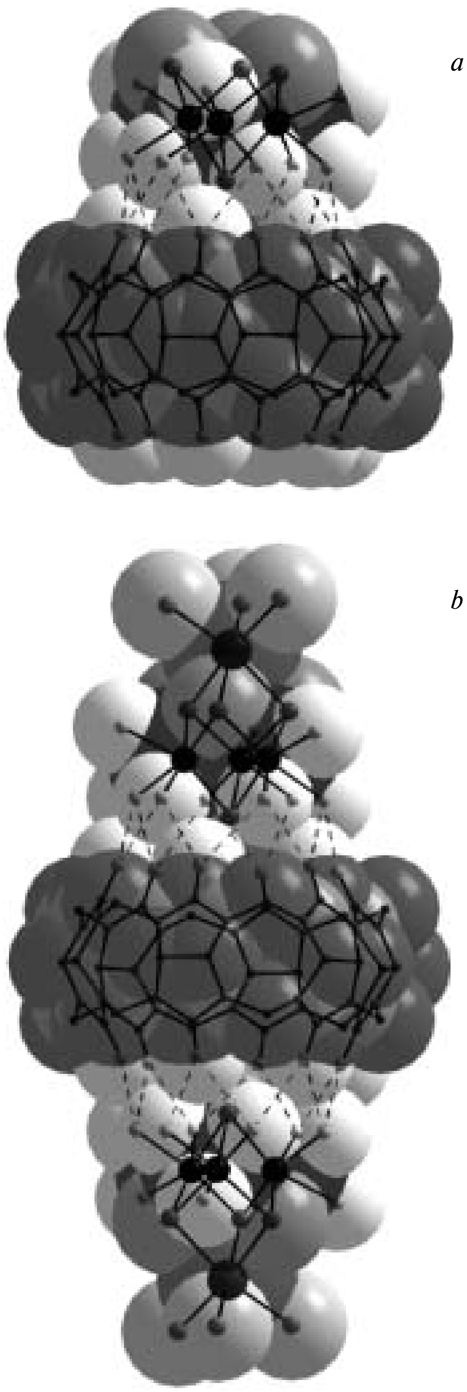

Fig. 3. Structures of supramolecular adducts with a cluster : cucurbituril ratio of 1 : 1 ("barrel with one lid") (*a*) and 2 : 1 ("barrel with two lids") (*b*).

tural types described as a "barrel with one lid" and a "barrel with two lids," there is a good compatibility between the size and symmetry of large building blocks used for the construction of supramolecular compounds. The length of the hydrogen bond between cucurbituril and cluster complexes varies over a wide range (2.6—3.1 Å). The remaining geometric parameters (distances and bond angles) in cluster aqua complexes and cucurbituril remain virtually unchanged upon the formation of supramolecular adducts. In a supramolecule, the cluster complex is oriented in such a way that the μ_3-bridging chalcogen atom is always directed inside the portal of cucurbituril, whereas the coordinatively unsaturated μ_2-chalcogen atoms (in triangular clusters) or heterometal atoms (in cuboidal clusters) are directed outward. Such an arrangement of triangular clusters in supramolecules makes possible the formation of additional chalcogen—chalcogen contacts between the clusters (see below).

The structures of supramolecular compounds formed in chalcogenide cluster—cucurbituril systems depend on the nature of the cluster, the presence of guest molecules in the cavity of cucurbituril, the reagent ratio (cluster : cucurbituril), and the concentration of hydrochloric acid. In solutions of hydrochloric acid, cluster aqua complexes produce different mixed chloro aqua complexes whose compositions depend on the nature of the metal and chalcogen atoms. The substitution of water molecules in aqua complexes by halide ligands decreases the positive charge of the complex and this factor should also influence the composition and structure of the resulting supramolecular compound.

Synthesis and structures of supramolecular compounds of cucurbituril with triangular chalcogenide clusters

The $\{[W_3S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}Cl_2 \cdot 10H_2O$ complex (1) (see Ref. 26). The complex was synthesized from a mixture of dilute solutions of $[W_3S_4(H_2O)_9]^{4+}$ and cucurbituril in HCl (2—2.5 mol L^{-1}). As can be seen from the formula, the cluster : cucurbituril ratio in complex **1** is 1 : 1. Single-crystal X-ray diffraction study of **1** showed that the triangular W_3S_4 fragment is coordinated by two Cl^- ligands in *trans* positions with respect to the μ_3-S atom to form the $[W_3S_4(H_2O)_7Cl_2]^{2+}$ cations. The latter are bound to one portal of cucurbituril by hydrogen bonds involving six H_2O molecules in *cis* positions with respect to the μ_3-S atom (Fig. 4, *a*). The O...O distances between the portal of cucurbituril and the cluster complex are in the range of 2.638—2.826 Å. The crystal packing of the resulting cationic $\{[W_3S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}^{2+}$ supramolecules can be described as consisting of herringbone-like layers parallel to the *bc* plane. These layers are composed of zigzag chains extended along the *c* axis, which are built from the supramolecular adducts linked by additional hydrogen bonds (d(O...O) = 2.65 Å) (see Fig. 4, *b*). The layers alternate with each other along the *a* axis to give a two-layer packing of the *AB AB AB* type (see Fig. 4, *c*).

It should be emphasized that supramolecular adducts in which both portals of cucurbituril are closed by cluster

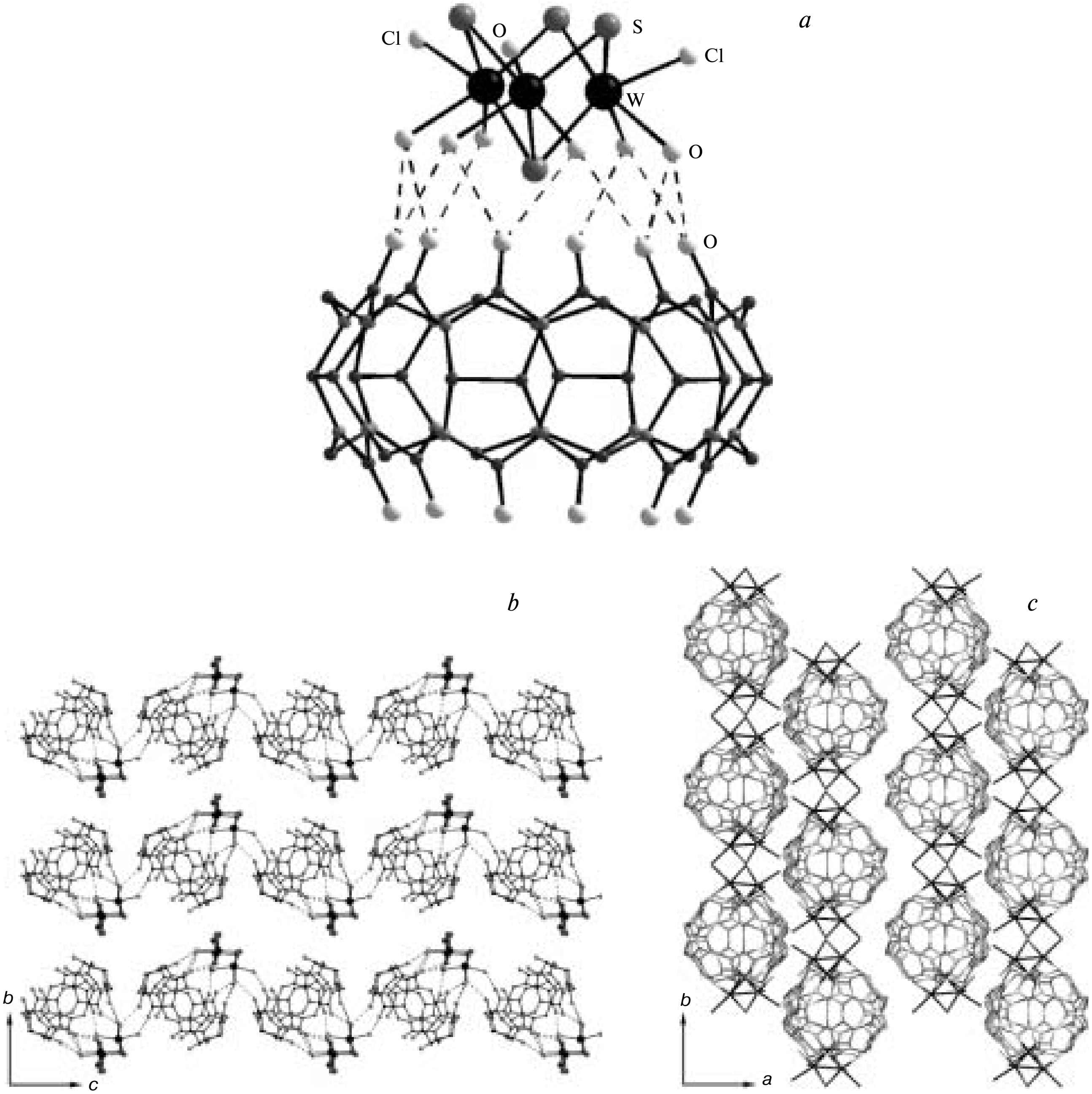

Fig. 4. Structure of the supramolecular adduct $\{[W_3S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}Cl_2 \cdot 10H_2O$ (**1**): the $\{[W_3S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}^{2+}$ supramolecule (*a*), the packing of the supramolecules (one layer) (*b*), and the packing of the layers (*c*).

lids were not obtained in 2—2.5 *M* HCl solutions regardless of the reagent ratio used. Compound **1** was generated even in the presence of a very large (100-fold!) excess of the tungsten sulfide cluster.

The $\{[W_3S_4(H_2O)_8Cl](PyH{\subset}C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 15.5H_2O$ complex (2) (see Ref. 27). As the above-described compound, complex **2** was prepared by crystallization from a 2 *M* HCl solution containing the cluster complex $[W_3S_4(H_2O)_9]^{4+}$ and cucurbituril with the only difference that pyridine was added to the mixture. X-ray diffraction study demonstrated that the inclusion of the guest molecule (pyridinium cation) leads to formation of two types of supramolecules in the case of compound **2**. In one type of supramolecules, the cavity of the cucurbituril molecule contains the pyridinium cation and both portals are closed by the cluster complexes $[W_3S_4(H_2O)_8Cl]^{3+}$ as lids through a network of complementary hydrogen bonds involving six carbonyl groups of the portal and six aqua ligands (two ligands at each W atom) located in *cis* positions with respect to the μ_3-S ligand of the cluster. The O...O distances are in the range of 2.627—3.081 Å. Another type of supramolecules is formed by cucurbituril molecules, which contain pyridinium cations in their cavities and whose portals are not closed by cluster lids. The ratio between both types of supramolecules in the structure is 1 : 1. Hence, the total cluster : cucurbituril ratio in compound **2** remains equal to 1 : 1, *i.e.*, is identical with that found in compound **1**, which was prepared in the absence of pyridine. The van der Waals radius of the pyridine molecule (5.9 Å) is larger than the inner diameter of the portal of cucurbituril (4.2 Å) and the formation of the inclusion compound is, apparently, accompanied by deviations of the O atoms forming the portals from their positions.

Two types of the supramolecules ($\{[W_3S_4(H_2O)_8Cl]_2(PyH{\subset}C_{36}H_{36}N_{24}O_{12})\}^{7+}$ and $\{PyH{\subset}C_{36}H_{36}N_{24}O_{12}\}^{+}$ cations) are linked in slightly distorted hexagonal layers parallel to the *bc* plane (Fig. 5, *a*, *b*). In the crystal packing, both types of layers alternate in such a way that the cucurbituril molecules

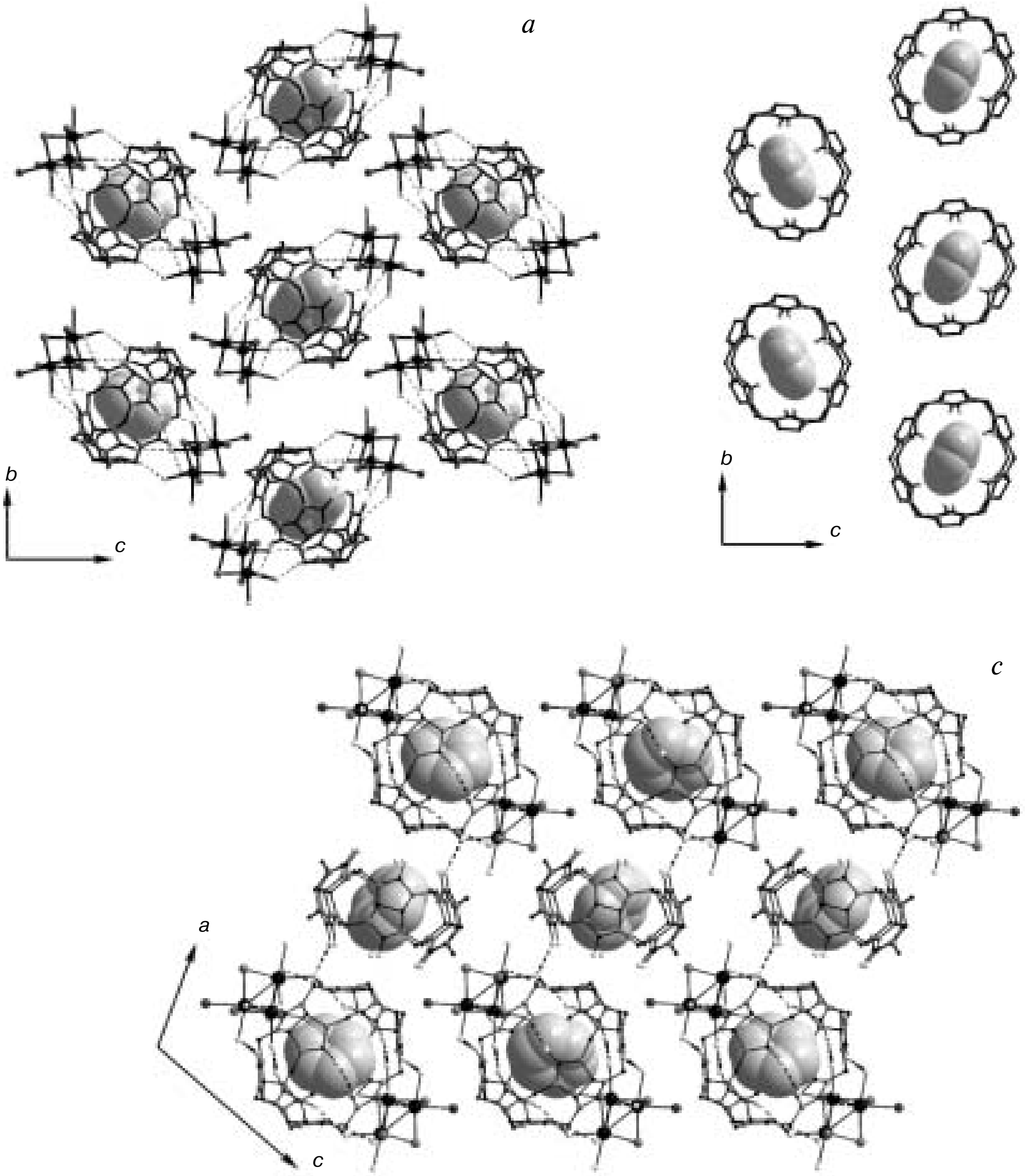

Fig. 5. Structure of the supramolecular adduct $\{[W_3S_4(H_2O)_8Cl](PyH{\subset}C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 15.5H_2O$ (**2**): a layer of the $\{[W_3S_4(H_2O)_8Cl]_2(PyH{\subset}C_{36}H_{36}N_{24}O_{12})\}^{7+}$ supramolecules (*a*); a layer of the $[PyH{\subset}C_{36}H_{36}N_{24}O_{12}]^{+}$ supramolecules (*b*), and the packing of the layers (*c*).

with the "noncoordinated" portals are sandwiched between the adjacent supramolecules and the pyridinium cation is fixed in the cavity of the cucurbituril molecule (see Fig. 5, *c*). The layers are linked by short (2.66 Å) O...O hydrogen bonds (see Fig. 5, *c*).

The inclusion of the pyridinium cation (guest) in the cavity of cucurbituril (host) leads to the mutual distortion of both molecules. The cross-section of the cucurbituril molecule with the symmetry D_{6h} perpendicular to the sixfold axis can be represented as a circle. The formation of a guest—host compound leads to a slight elongation of the cucurbituril molecule so that the circle is transformed into an ellipsoid. These distortions can be seen in Fig. 5, *b*. The guest molecule (pyridinium cation) contracts upon incorporation into the cavity of cucurbituril. Hence, upon the formation of an inclusion compound, the sizes of both the guest and host molecules adapt to each other, with consequent distortions of their structures.

The $(H_9O_4)\{[W_3S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_3 \cdot 16.15H_2O$ complex (3) (see Ref. 28). The third compound in the $[W_3S_4(H_2O)_9]^{4+}$—cucurbituril system was prepared in a 6—8 *M* hydrochloric acid solution. Platelet-like red-lilac hexagonal crystals were isolated from the reaction mixture. X-ray diffraction study demonstrated that the cucurbituril molecules are linked to the triangular sulfide-bridged cluster complexes $[(W_3S_4(H_2O)_6Cl_3)]^+$ through a system of hydrogen bonds ("barrel with two lids"). These bond lengths are in the range of 2.78—2.94 Å. The molecular container is occupied by a water molecule disordered over six positions (Fig. 6, *a*). These supramolecular adducts are linked in chains through hydrogen bonds between the $[H_9O_4]^+$ cations and the chloride ligands coordinated to the W atoms in *trans* positions with respect to μ_3-S. The O—H...Cl hydrogen bond length is 3.11 Å. The interaction of two cluster complexes through the $[H_9O_4]^+$ cation is shown in Fig. 6, *b*.

The supramolecular chains (see Fig. 6, *c*) form a honeycomb-like structure containing channels with the van der Waals diameter of ~5 Å. Each channel includes six supramolecular chains and is occupied by water molecules of solvation and chloride anions.

Therefore, crystallization of the triangular tungsten sulfide cluster with cucurbituril at a higher concentration of hydrochloric acid leads to coordination of three negatively charged chloride ligands to the sulfide cluster complex. Apparently, this coordination hinders the formation of short contacts between the μ_2-S ligands of the adjacent triangular clusters (see below). However, an increase in acidity leads to the incorporation of hydroxonium ions into the crystal structure, and the latter ions are involved in O—H...Cl hydrogen bonds, which link the clusters of the adjacent supramolecules of the "barrel-with-two-lids" type giving rise to the supramolecular chains in the structure of **3**.

The structures of **1—3** exemplify that the formation of supramolecular compounds based on cucurbituril is very sensitive to changes in the reaction conditions (the presence of guest molecules in the cavity of cucurbituril or the concentration of hydrochloric acid).

The $\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](PyH\subset C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 17H_2O$ complex (4) (see Ref. 26). Compound **4** was prepared in a 2.5 *M* hydrochloric acid solution containing the triangular molybdenum cluster $[Mo_3S_4(H_2O)_9]^{4+}$ and cucurbituril in a ratio of 2 : 1 in the presence of pyridine. X-ray diffraction study demonstrated that compound **4** consists of cucurbituril molecules whose portals are closed by the $[Mo_3S_4(H_2O)_6Cl_3]^+$ and $[Mo_3S_4(H_2O)_7Cl_2]^{2+}$ cluster cations through hydrogen bonds (d(O...O) = 2.61—2.73 Å) (Fig. 7, *a*). The molecular container includes the pyridinium cation (in the IR spectrum of **4**, ν(N—H) = 3320 and 3171 cm^{-1}).

The $\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](PyH\subset C_{36}H_{36}N_{24}O_{12})\}^{4+}$ supramolecules are linked in infinite chains along the $\{\bar{1}, 2, 3\}$ direction (see Fig. 7, *b*) by short nonbonded S...S interactions (d(S—S) = 2.984—3.330 Å). These distances are noticeably shorter than twice the van der Waals radius of the S atom (~3.6 Å).[29]

The supramolecular chains are arranged in a hexagonal packing (see Fig. 7, *c*). The space between these chains is occupied by Cl$^-$ anions and water molecules. Free pyridinium cations were not detected.

The $\{[W_3Se_4(H_2O)_8Cl]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_6 \cdot 12H_2O$ complex (5) (see Ref. 30). Supramolecular compound **5** was prepared from a 2.5 *M* HCl solution containing the triangular tungsten selenide complex $[W_3Se_4(H_2O)_9]^{4+}$ and cucurbituril. X-ray diffraction study demonstrated that the structure consists of the supramolecules of the "barrel-with-two-lids" type (Fig. 8, *a*). The O...O distances between the O atoms of the portals of cucurbituril and the O atoms of the water molecules coordinated to the selenide clusters are in the range of 2.75—3.00 Å. The cavity of the molecular container is empty.

Like in the structure of **4**, the $\{[W_3Se_4(H_2O)_8Cl]_2(C_{36}H_{36}N_{24}O_{12})\}^{6+}$ cationic supramolecules are linked in one-dimensional chains along the {1, 0, 1} direction by nonbonded Se...Se interactions (see Fig. 8, *b*). The Se...Se distance is 3.73 Å (van der Waals radius of the Se atom is 1.95 Å).[29] Therefore, the molecules are linked in the supramolecular chains through both the hydrogen bonds between the clusters and cucurbituril molecules and nonbonded Se...Se interactions between the triangular clusters. In the crystal, the chains are packed in a hexagonal fashion (see Fig. 8, *c*). The deviations from the ideal hexagonal packing are insignificant. The space between the chains is occupied by chloride anions and water molecules of solvation.

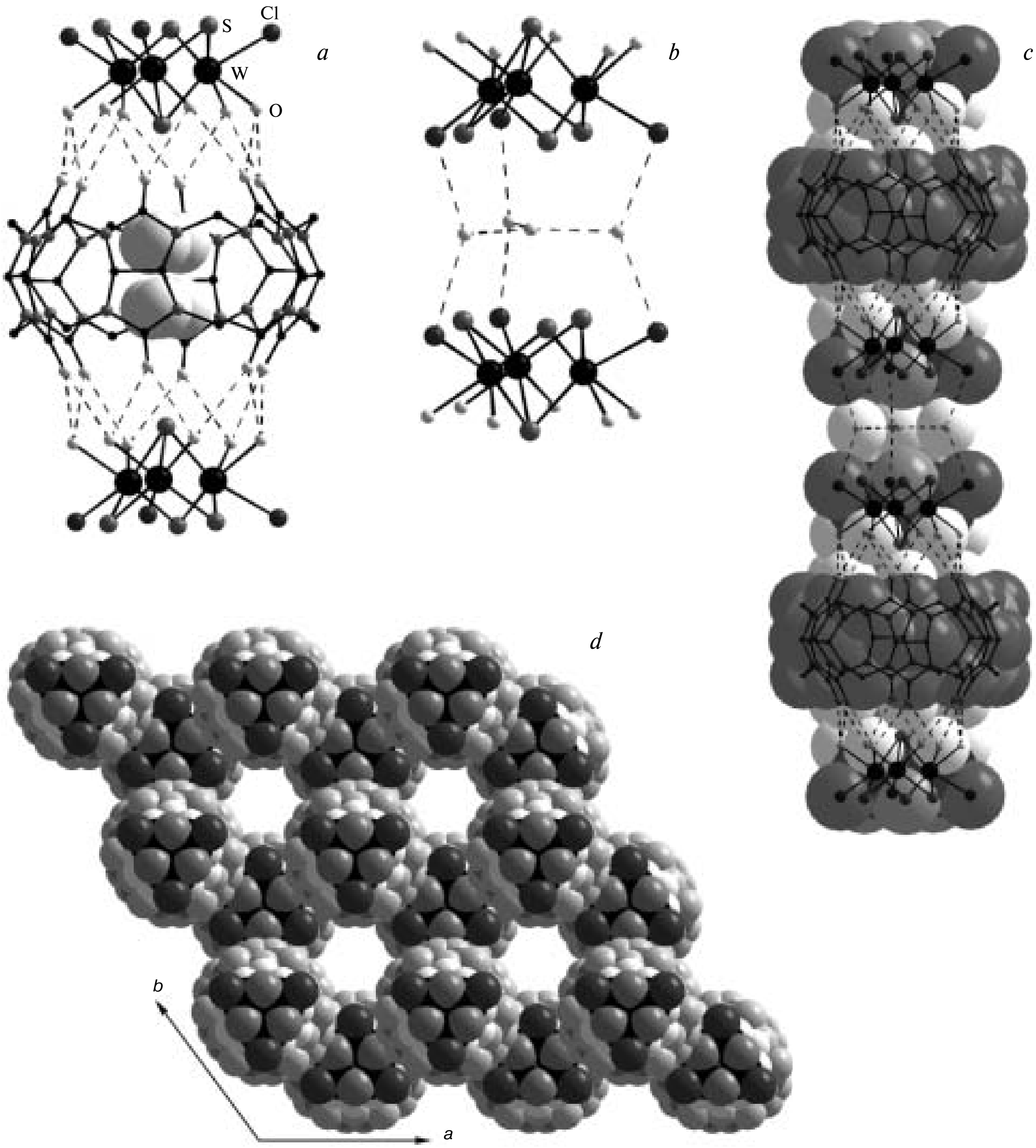

Fig. 6. Structure of the supramolecular adduct $(H_9O_4)\}[W_3S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_3 \cdot 16.15H_2O$ (**3**): the $\{[W_3S_4(H_2O)_6Cl_3]_2(H_2O{\subset}C_{36}H_{36}N_{24}O_{12})\}^{2+}$ supramolecule (*a*); bonding of the supramolecules through the $[H_3O \cdot 3H_2O]^+$ cation (*b*); the structure of the supramolecular chain (view perpendicular to the *c* axis) (*c*); the honeycomb-like packing of the chains (view along the *c* axis) (*d*).

The $\{[W_3Se_4(H_2O)_6Cl_3]_2(PyH{\subset}C_{36}H_{36}N_{24}O_{12})\}Cl_3 \cdot 18H_2O$ complex (6) (see Ref. 31). Green crystals of compound **6** were prepared in 60% yield by adding pyridine to the reaction mixture containing cucurbituril and $[W_3Se_4(H_2O)_9]^{4+}$ in a 3 *M* HCl solution. The crystals consist of the cationic supramolecular adducts of the "barrel-with-two-lids" type. The structure of $\{[W_3Se_4Cl_3(H_2O)_6]_2[PyH{\subset}C_{36}H_{36}N_{24}O_{12}]\}^{3+}$ is shown

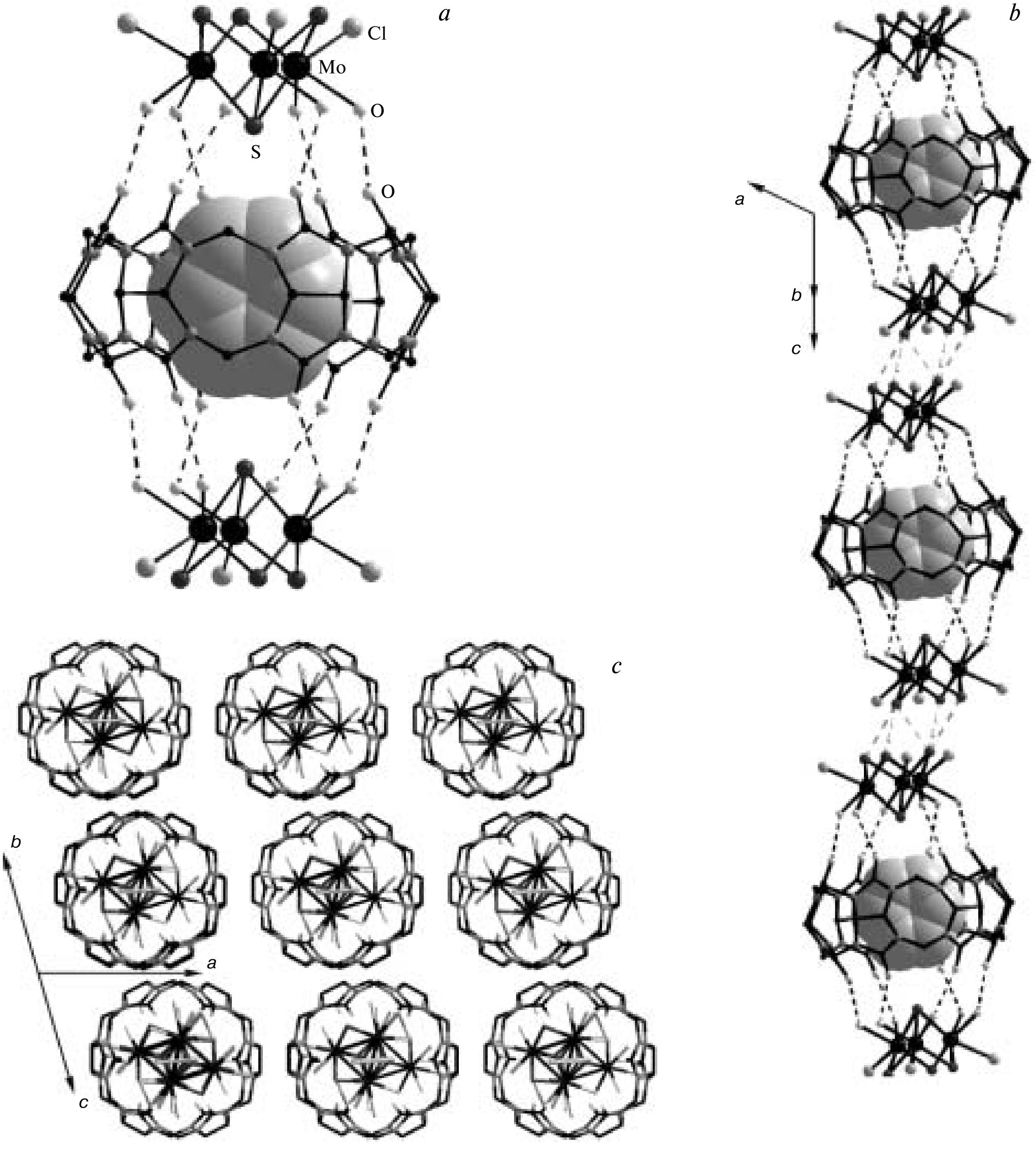

Fig. 7. Structure of the supramolecular adduct $\{[Mo_3S_4(H_2O)_6Cl_3][Mo_3S_4(H_2O)_7Cl_2](PyH{\subset}C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 17H_2O$ (**4**): the $\{[Mo_3S_4(H_2O)_6Cl_2X]_2(PyH{\subset}C_{36}H_{36}N_{24}O_{12})\}^{4+}$ supramolecule ($X = 0.5\ Cl^- + 0.5\ H_2O$) (*a*); bonding of the supramolecules into chains (*b*); the packing of the supramolecular chains (*c*).

in Fig. 9, *a*. Each W atom of the trinuclear $[W_3Se_4(H_2O)_6Cl_3]^+$ cluster is coordinated by the Cl atom located in the *trans* position with respect to the μ_3-Se ligand and by two water molecules in *cis* positions. These six water molecules are involved in hydrogen bonds with six O atoms of the cucurbituril molecule (d(O...O) = 2.68—3.01 Å) thus forming lids, which efficiently close both portals of the cucurbituril molecule containing the protonated pyridine molecule in the cavity. By analogy with compounds **2** and **4**, the incorporation of PyH^+ into the cavity leads to distortions of both the cucurbituril and guest molecules. The N atoms of the pyridinium cation

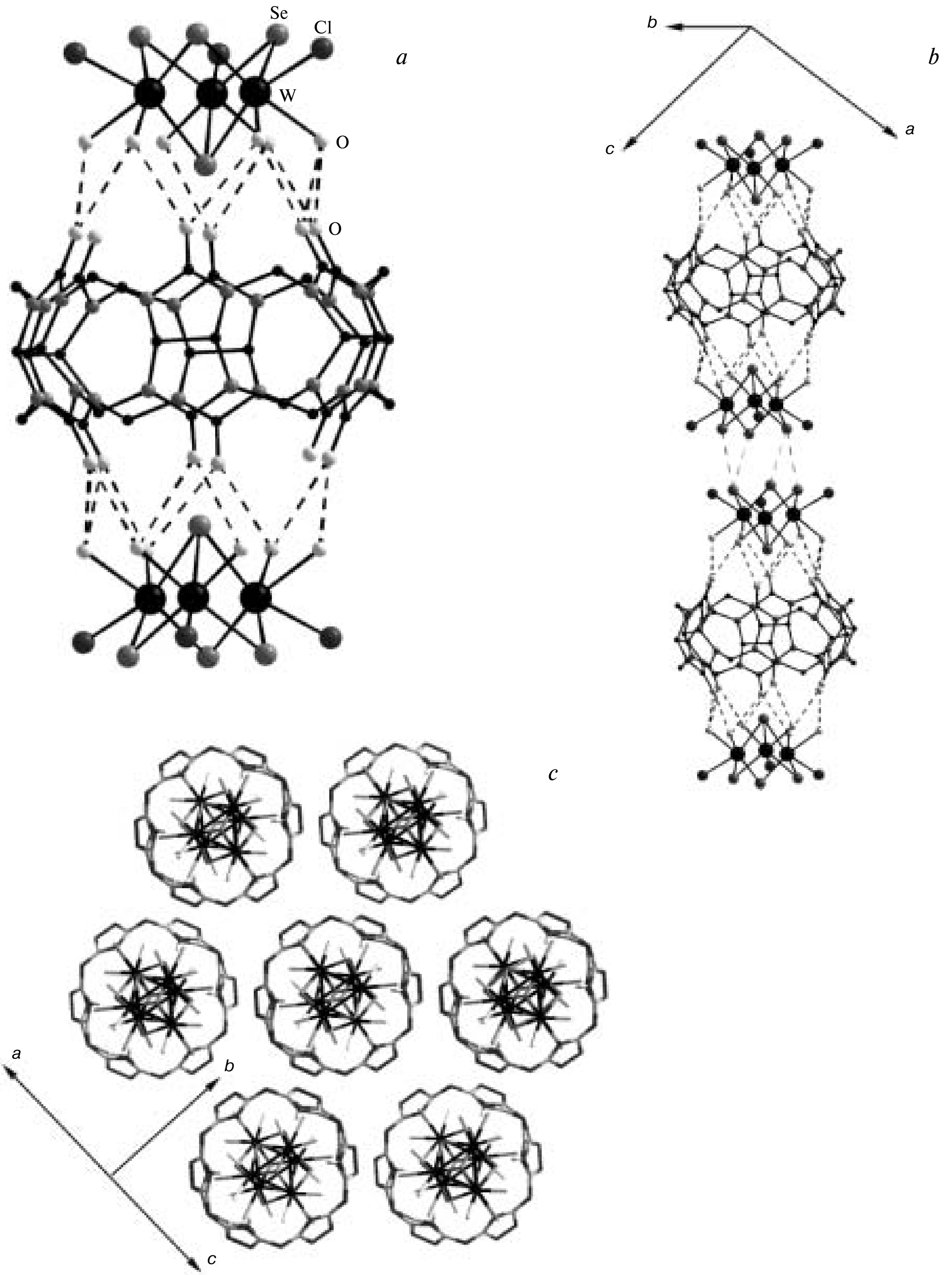

Fig. 8. Structure of the supramolecular adduct $\{[W_3Se_4(H_2O)_8Cl]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_6 \cdot 12H_2O$ (**5**): the $\{[W_3Se_4(H_2O)_8Cl]_2(C_{36}H_{36}N_{24}O_{12})\}^{6+}$ supramolecule (*a*); bonding of the supramolecules in chains (*b*); the packing of the supramolecular chains (*c*).

and the C atoms are disordered over six positions. The bridging μ_2-Se atoms of the adjacent clusters are linked in the $\{W_3Se_4\}_2$ dimers by short (compared to the sum of the van der Waals radii of 3.9 Å) nonbonded Se...Se interactions (3.59—3.72 Å). The cucurbituril molecules linked by these dimers are located one above the other to form

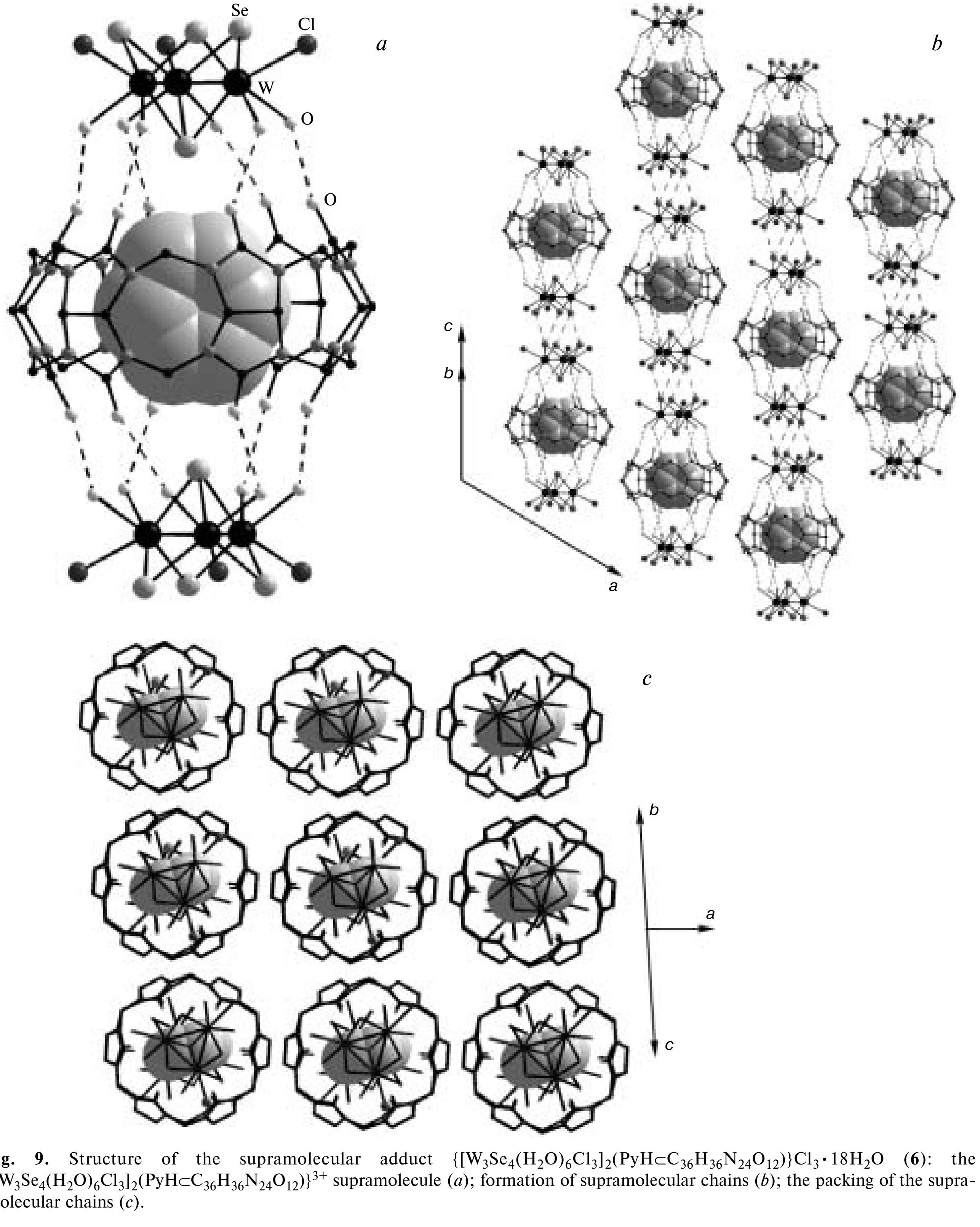

Fig. 9. Structure of the supramolecular adduct $\{[W_3Se_4(H_2O)_6Cl_3]_2(PyH{\subset}C_{36}H_{36}N_{24}O_{12})\}Cl_3\cdot18H_2O$ (**6**): the $\{[W_3Se_4(H_2O)_6Cl_3]_2(PyH{\subset}C_{36}H_{36}N_{24}O_{12})\}^{3+}$ supramolecule (*a*); formation of supramolecular chains (*b*); the packing of the supramolecular chains (*c*).

infinite linear chains (see Fig. 9, *b*). If the chains are represented as cylinders, these cylinders form a square packing (see Fig. 9, *c*). The hexagonal packing of the linear chains in the crystals of compound **5** is denser than the square packing in the crystals of **6**. The looser packing of the latter compound is consistent with an increase in the hydration number (18 H_2O molecules in **6** instead of 12 H_2O molecules in **5**).

Therefore, a comparison of the structures of compounds **5** and **6** shows that in the $[W_3Se_4(H_2O)_9]^{4+}$—cucurbituril system (unlike the analogous structures with tungsten sulfide clusters **1** and **2**), the incorporation of the pyridinium cation as the guest into the cavity of the cucurbituril molecule does not influence the main parameters of the supramolecular adducts, their tendency to form chains through short chalcogen—chalcogen contacts is retained, but the mode of packing of the supramolecular chains in the crystal changes.

The $\{[Mo_3Se_4(H_2O)_8Cl]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_6 \cdot 16H_2O$ complex (7) (see Ref. 32). Complex **7** was prepared as needle-like brown crystals by mixing equimolar amounts of the triangular cluster $[Mo_3Se_4(H_2O)_9]^{4+}$ and cucurbituril in a 2 *M* hydrochloric acid solution. According to the results of X-ray diffraction study, compound **7** is isostructural with tungsten complex **5** described above. The molecules are linked in chains by hydrogen bonds between the selenide clusters and cucurbituril molecules and by nonbonded Se...Se interactions between the triangular clusters (Se...Se distance is 3.70 Å).

The $(H_3O)_2\{[Mo_3Se_4Cl_5(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})\} \cdot 15H_2O$ complex (8) (see Ref. 32). Complex **8** was prepared by the reaction of $[Mo_3Se_4(H_2O)_9]^{4+}$ with cucurbituril in a 6 *M* HCl solution. An increase in the concentration of HCl leads to an increase in the number of chloride ligands coordinated to the cluster. According to the results of X-ray diffraction analysis, the triangular clusters occur in the anionic $[Mo_3Se_4Cl_5(H_2O)_4]^-$ form. The Mo atoms are coordinated by four Cl^- ligands in *cis* positions with respect to the μ_3-Se atom. As a result, the cucurbituril molecules and the chloro aqua complexes in **8** are not involved in complementary hydrogen bonding. The structure of compound **8** contains the dimeric cluster aggregates $[Mo_3Se_4Cl_5(H_2O)_4]_2{}^{2-}$ linked to each other by short Se...Se contacts (*d*(Se...Se) = 2.96—3.43 Å). The cluster : cucurbituril ratio (2 : 1) is equal to that found in compound **7**, which was prepared in the same system but with the use of a 2 *M* HCl solution. However, the crystal structures of compounds **7** and **8** are radically different. The structure of compound **7** consists of polymeric chains formed through hydrogen bonds between the cucurbituril molecules and the cationic $[Mo_3Se_4(H_2O)_8Cl]^{3+}$ complexes as well as through nonbonded Se...Se interactions between the triangular clusters. An increase in the concentration of hydrochloric acid to 6 mol L^{-1} hinders the formation of supramolecular adducts with cucurbituril and leads to substantial structural changes. The chain structure (**7**) is transformed into the island structure (**8**), which consists of alternating pseudohexagonal layers of two types. One layer is composed of the cucurbituril molecules (Fig. 10, *a*), whereas another layer is built from dimeric cluster aggregates held by short nonbonded Se...Se interactions (see Fig. 10, *b*). The layers are located one above the other with a shift of 1/2 of the transverse translation (see Fig. 10, *c*).

The formation of short Q...Q contacts between the adjacent triangular clusters is typical of the M_3Q_4 and M_3Q_7 clusters (M = Mo or W; Q = S or Se).[33] In some cases, the Q...Q distances are noticeably shorter than the corresponding sums of the van der Waals radii (van der Walls radii of the S and Se atoms are 1.85 and 1.95 Å, respectively).[29] The Cambridge Structural Database (CSDB)[34] contains 23 compounds in which such interactions occur. In all structures, the nonbonded Q...Q interactions give rise to the centrosymmetrical $\{M_3Q_4...Q_4M_3\}$ dimers. Based solely on the structural data, it can be stated that Se...Se contacts are, on the whole, stronger than S...S contacts. In some compounds, the Se...Se distances are shorter than 3 Å and, hence, can be considered as weak covalent bonds.

We believe that Q...Q interactions play an important structure-forming role in supramolecular ensembles of cucurbituril with triangular Mo and W chalcogenide aqua complexes and that these interactions are, presumably, equally important to hydrogen bonds.

The $(H_3O)_4\{[M_3S_7Cl_6]_2(C_{36}H_{36}N_{24}O_{12})\} \cdot 8H_2O$ complexes (M = W (**9**), M = Mo (**10**)) (see Ref. 35). Compounds **9** and **10** are isostructural. The $[M_3S_7Cl_6]^{2-}$ cluster anion has a structure typical of such clusters. The metal atoms are coordinated by the μ_3-S ligand and μ_2-S_2 disulfide ligands (IR spectra of **9** and **10** have stretching vibrations of the S—S bond at 554 and 542 cm^{-1}, respectively). In addition, each metal atom is coordinated by two Cl^- ligands, which indicates that the $M_3S_7{}^{4+}$ clusters have a higher affinity for halide ions than $M_3S_4{}^{4+}$. Specific nonbonded interactions in complexes **9** and **10**, like those in compounds **4—7**, are responsible for dimerization of the $[M_3S_7Cl_6]^{2-}$ anions. These anions are linked by six S...Cl contacts (3.16—3.42 Å) and two S...S contacts (3.16—3.32 Å) (Fig. 11, *a*). The crystal packing consists of four alternating layers of the dimeric cluster anions and cucurbituril molecules parallel to the *ab* plane (see Fig. 11, *b*). The space between the layers is occupied by hydroxonium cations and water molecules of solvation.

Supramolecular compounds of heterometallic cuboidal aqua complexes with cucurbituril

Coordination of the heterometal atom by three coordinatively unsaturated μ_2-bridging chalcogen atoms of the triangular $[M_3(\mu_3\text{-}Q)(\mu_2\text{-}Q)_3(H_2O)_9]^{4+}$ complexes gives

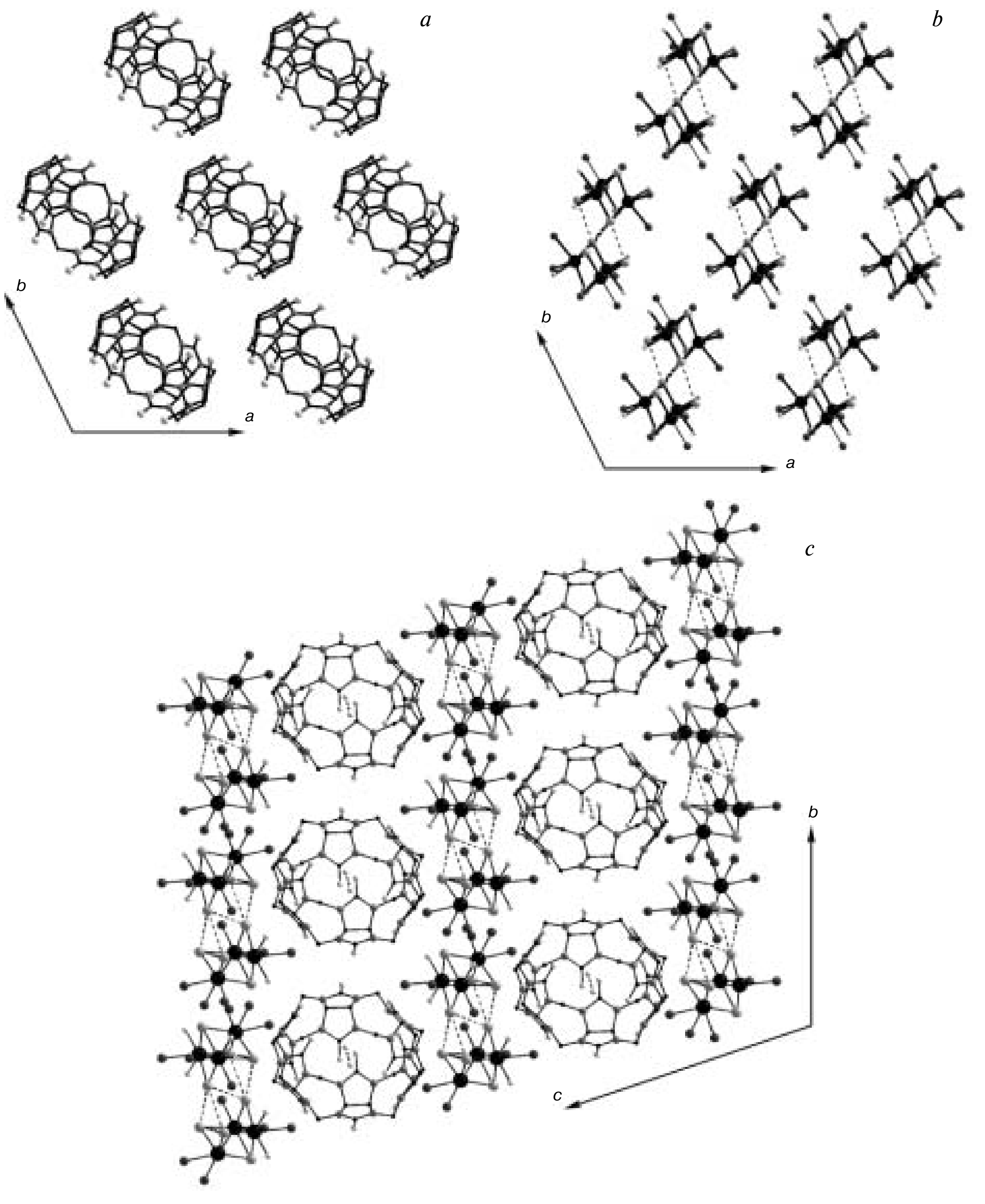

Fig. 10. Structure of the supramolecular adduct $(H_3O)_2\{[Mo_3Se_4Cl_5(H_2O)_4]_2(C_{36}H_{36}N_{24}O_{12})\} \cdot 15H_2O$ (**8**): a layer of the cucurbituril molecules (*a*); a layer of the dimers of the $[Mo_3Se_4Cl_5(H_2O)_4]^-$ clusters (*b*); the packing of the layers (*c*).

rise to heterometallic cuboidal complexes (see Fig. 1) in which nonbonded Q...Q interactions cannot occur. Nevertheless, six coordinated water molecules in *cis* positions with respect to the μ_3-Q atom, which is bound only to the Mo or W atoms, are complementary to six O atoms of the portal of cucurbituril. Hence, cuboidal heterometallic

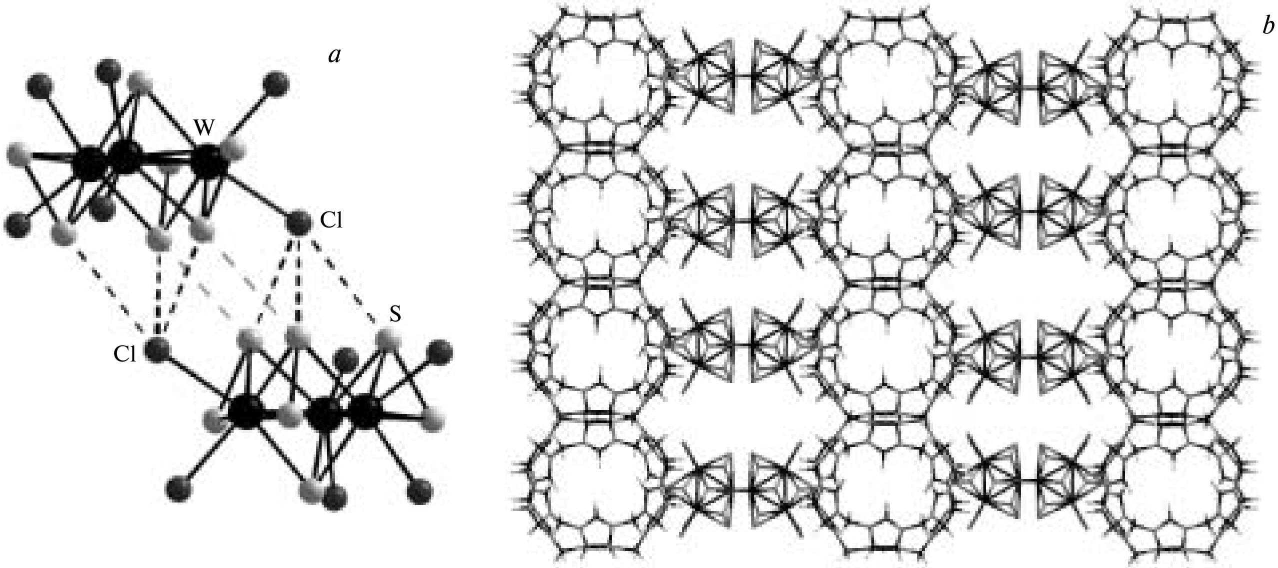

Fig. 11. Structure of the supramolecular adduct $(H_3O)_4\{[W_3S_7Cl_6]_2(C_{36}H_{36}N_{24}O_{12})\}\cdot 8H_2O$ (**9**): the structure of the dimer of the $[W_3S_7Cl_6]^{2-}$ clusters (*a*); the structure of the supramolecular ensemble (*b*).

aqua complexes also form supramolecular adducts with cucurbituril of the type of a "barrel with one lid" or a "barrel with two lids." This section of the review deals with the characteristic features of the crystal structures of compounds formed by heterometallic cuboidal aqua complexes and cucurbituril.

The $\{[Mo_3(PdCl)Se_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}Cl\cdot 7H_2O$ complex (11) (see Ref. 36). Complex **11** was prepared by crystallization from dilute (~1 mmol L^{-1}) solutions of cucurbituril and the molybdenum-palladium cluster in 2 *M* hydrochloric acid. The structure of the supramolecular cluster—cucurbituril adduct $\{[Mo_3(PdCl)Se_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}^+$ is shown in Fig. 12, *a*. According to the stoichiometry of the product, only one portal of cucurbituril is closed by the $[Mo_3(PdCl)Se_4(H_2O)_7Cl_2]^+$ cluster cation. Six water molecules of the cation in *cis* positions with respect to the μ_3-bridging Se atom, which links only the Mo atoms, are

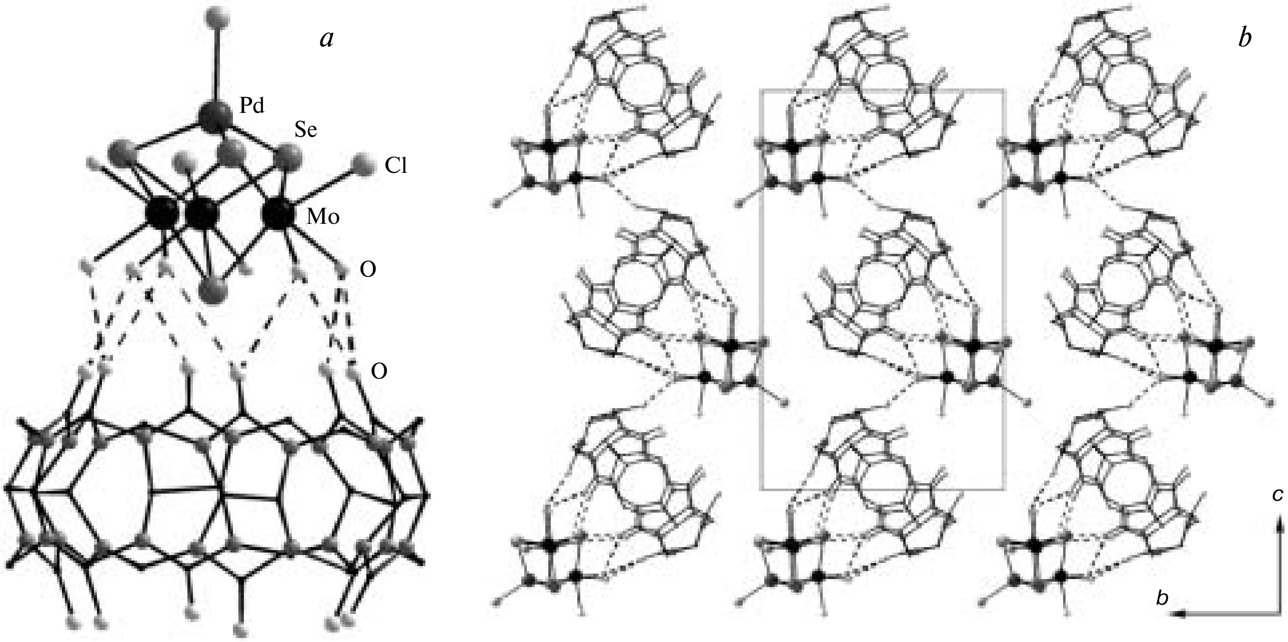

Fig. 12. Structure of the supramolecular adduct $\{[Mo_3(PdCl)Se_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}Cl\cdot 7H_2O$ (**11**): the structure of the $\{[Mo_3(PdCl)Se_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}^+$ supramolecule (*a*); the packing of the supramolecular adducts (*b*).

involved in hydrogen bonding. The O...O distances are in the range of 2.76—3.04 Å. The μ_3-Se atom is directed inside the cavity formed by the O atoms of the carbonyl groups of cucurbituril.

In the crystal packing, the supramolecules are linked in chains through additional hydrogen bonds. The supramolecular adducts are linked in zigzag chains along the *c* axis by hydrogen bonds between the water molecules in *cis* positions with respect to the μ_3-Se atoms and the O atoms of the cucurbituril molecules of the adjacent adducts (see Fig. 12, *b*). The short O...O distance between the supramolecular adducts (2.55 Å) is indicative of strong hydrogen bonding. The zigzag chains, in turn, are packed in layers parallel to the *bc* plane (see Fig. 12, *b*). The space between the supramolecules is occupied by Cl^- ions and water molecules.

The $\{[Mo_3(PdCl)S_4(H_2O)_6Cl_3](PyH\subset C_{36}H_{36}N_{24}O_{12})\}Cl \cdot 14H_2O$ complex (12) (see Ref. 37). The addition of cucurbituril to dilute (1—10 mmol L^{-1}) solutions of $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ in 3 *M* HCl in the presence of pyridine afforded the compound with composition $\{[Mo_3(PdCl)S_4(H_2O)_6Cl_3](PyH\subset C_{36}H_{36}N_{24}O_{12})\}Cl \cdot 14H_2O$ in high yield. The cluster : cucurbituril ratio in complex **12** is 1 : 1. Attempts to prepare the supramolecular adduct with the cluster : cucurbituril ratio of 2 : 1 failed even when a large excess of the heterometallic cuboidal cluster was used.

The structure of the cluster—cucurbituril—pyridinium cation supramolecular adduct $\{[Mo_3(PdCl)S_4(H_2O)_6Cl_3](PyH\subset C_{36}H_{36}N_{24}O_{12})\}^+$ is shown in Fig. 13, *a*. According to the results of X-ray diffraction study, the inner cavity of the cucurbituril molecule is occupied by the pyridinium cation resulting in distortions of the structures of both the guest and host molecules, like in other above-considered compounds containing PyH^+ in the cavity (**2**, **4**, and **6**). According to the stoichiometry of the product, only one portal of cucurbituril is coordinated by the outer-sphere $[Mo_3(PdCl)S_4(H_2O)_6Cl_3]$ ligand through a system of complementary hydrogen bonds. The O...O distances are in the range of 2.76—3.04 Å.

The crystals of compound **12** are stabilized by an extensive hydrogen bond network involving the supramolecules and water molecules of solvation. The supramolecular adducts with composition heterocube : cucurbituril = 1 : 1 are linked in dimers. The latter, in turn, are packed in herringbone-like pseudohexagonal layers parallel to the *bc* plane (see Fig. 13, *b*).

A comparison of the structures of the supramolecular adducts of the palladium cubes with cucurbituril (**11** and **12**) shows that the incorporation of the pyridinium cation into the cavity of cucurbituril in compound **12** does not lead to substantial changes in the structures of the supramolecular adducts and both the cluster : cucurbituril ratio and the total charge of the supramolecule (+1) remain unaltered. However, the crystal packing undergoes substantial changes. In the crystals of **11**, the supramolecules are linked in zigzag chains (see Fig. 12, *b*), whereas the addition of pyridine (compound **12**) gives rise to dimers forming a layered structure (see Fig. 13, *b*).

The $\{[W_3(InCl_3)S_4(H_2O)_9]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 28H_2O$ complex (13) (see Ref. 38). The addition of cucurbituril to a solution of the heterometallic cluster complex $[W_3(InCl_3)S_4(H_2O)_9]^{2+}$ in a 2 *M* HCl solution afforded dark-blue needle-like single crystals. According to the results of X-ray diffraction analysis, compound **13** occurs as the supramolecular adduct with the cluster : cucurbituril ratio of 2 : 1. The structure of the supramolecule is shown in Fig. 14, *a*. According to the stoichiometry of the product, each portal of cucurbituril is closed by the $[W_3(InCl_3)S_4(H_2O)_9]^{2+}$ cluster cation through hydrogen bonds involving six water molecules of the cation. The O...O distances are in the range of 2.586—2.895 Å.

The crystal packing of compound **13** has large (~7 Å) channels (see Fig. 14, *b*) extended along the *a* axis. These channels are occupied by water molecules of solvation and Cl^- counterions, which accounts for a large hydration number and provides an extensive hydrogen bond network in the structure.

The $\{[Mo_3(PdP(OH)_3)S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_2 \cdot 20H_2O$ (14) and $\{[Mo_3(PdAs(OH)_3)S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_2 \cdot 19H_2O$ complexes (15) (see Ref. 39). Isostructural compounds **14** and **15** were prepared by the addition of cucurbituril to hydrochloric acid solutions of the palladium cluster and H_3PO_3 or H_3AsO_3, respectively. The structural supramolecular units of these compounds are the cucurbituril molecules in which both portals are closed by the cationic cluster complexes $[Mo_3(PdX(OH)_3)S_4(H_2O)_6Cl_3]^+$ (X = P or As); *d*(O...O) = 2.81—2.85 (X = P) and 2.75—2.87 Å (X = As). The size of the supramolecule is ~30 Å (Fig. 15, *a*). According to the results of X-ray diffraction analysis, the cavity of the cucurbituril molecule contains water molecules (two water molecules in phosphorus compound **14** and one water molecule in arsenic derivative **15**). The supramolecules are packed in the CO_2 structural type. The centers of the supramolecular adducts form a face-centered cubic lattice, the supramolecules themselves are located on four mutually coplanar threefold axes in the cubic cells (see Fig. 15, *b*).

The $\{[Mo_3(Pd(PhSO_2))S_4(H_2O)_8Cl][Mo_3(Pd(PhSO_2))S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}Cl_3 \cdot 11H_2O$ complex (16) (see Ref. 28). Compound **16** was prepared by the addition of cucurbituril to a hydrochloric solution of the palladium cluster complex and sodium benzene sulfinate. The structure is composed of two independent supramolecular adducts with similar geometric parameters. Each supramolecule can be described as a barrel (cucurbituril) closed by two cluster lids (Fig. 16). The O atoms of the carbonyl groups of the cucurbituril

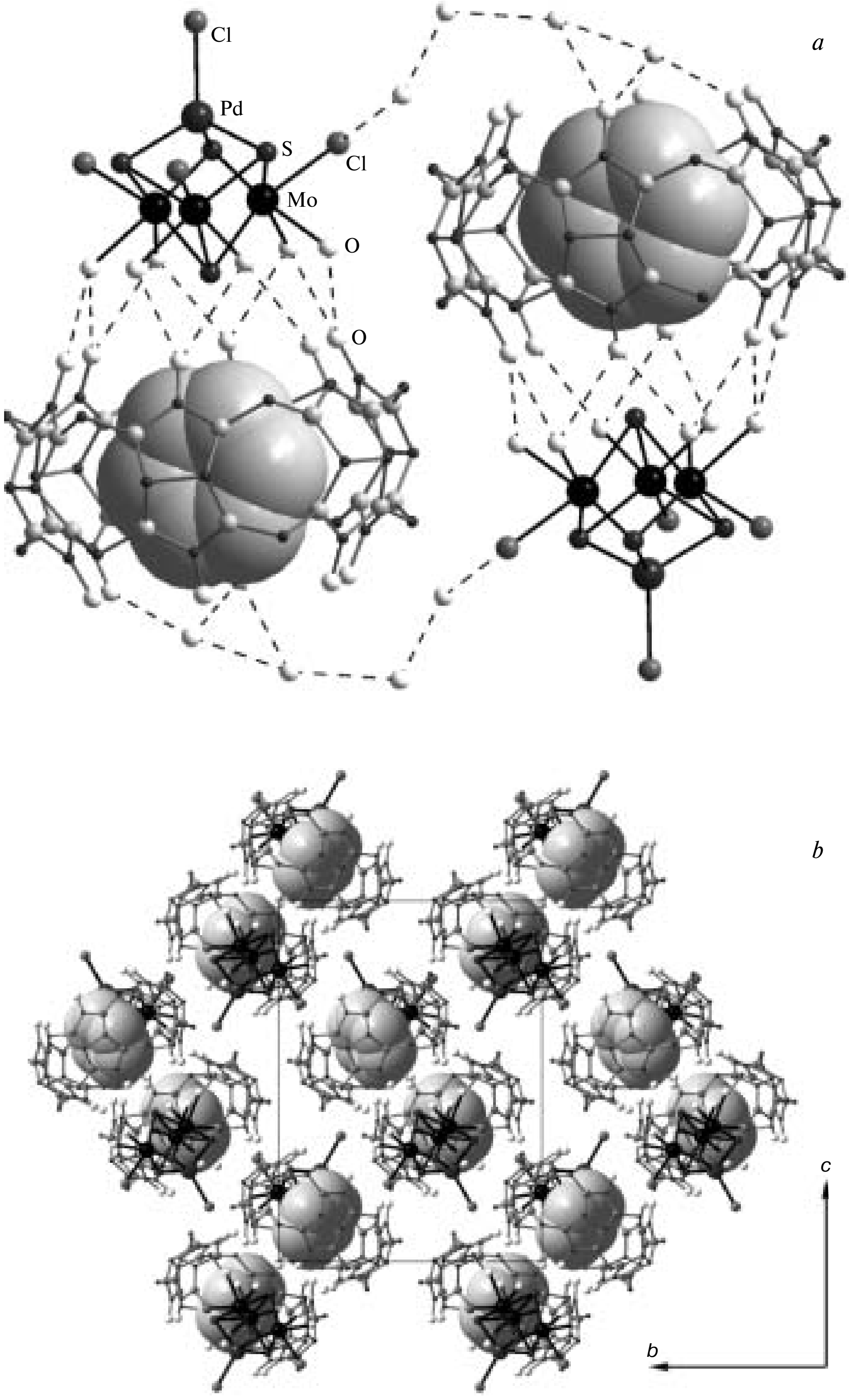

Fig. 13. Structure of the supramolecular adduct $\{[Mo_3(PdCl)S_4(H_2O)_6Cl_3](PyH\subset C_{36}H_{36}N_{24}O_{12})\}Cl \cdot 14H_2O$ (**12**): the structure of the $\{[Mo_3(PdCl)S_4(H_2O)_6Cl_3](PyH\subset C_{36}H_{36}N_{24}O_{12})\}^+$ supramolecule (*a*) (dimer of the supramolecules and selected water molecules of solvation are shown); the packing of the dimers of the supramolecules (*b*).

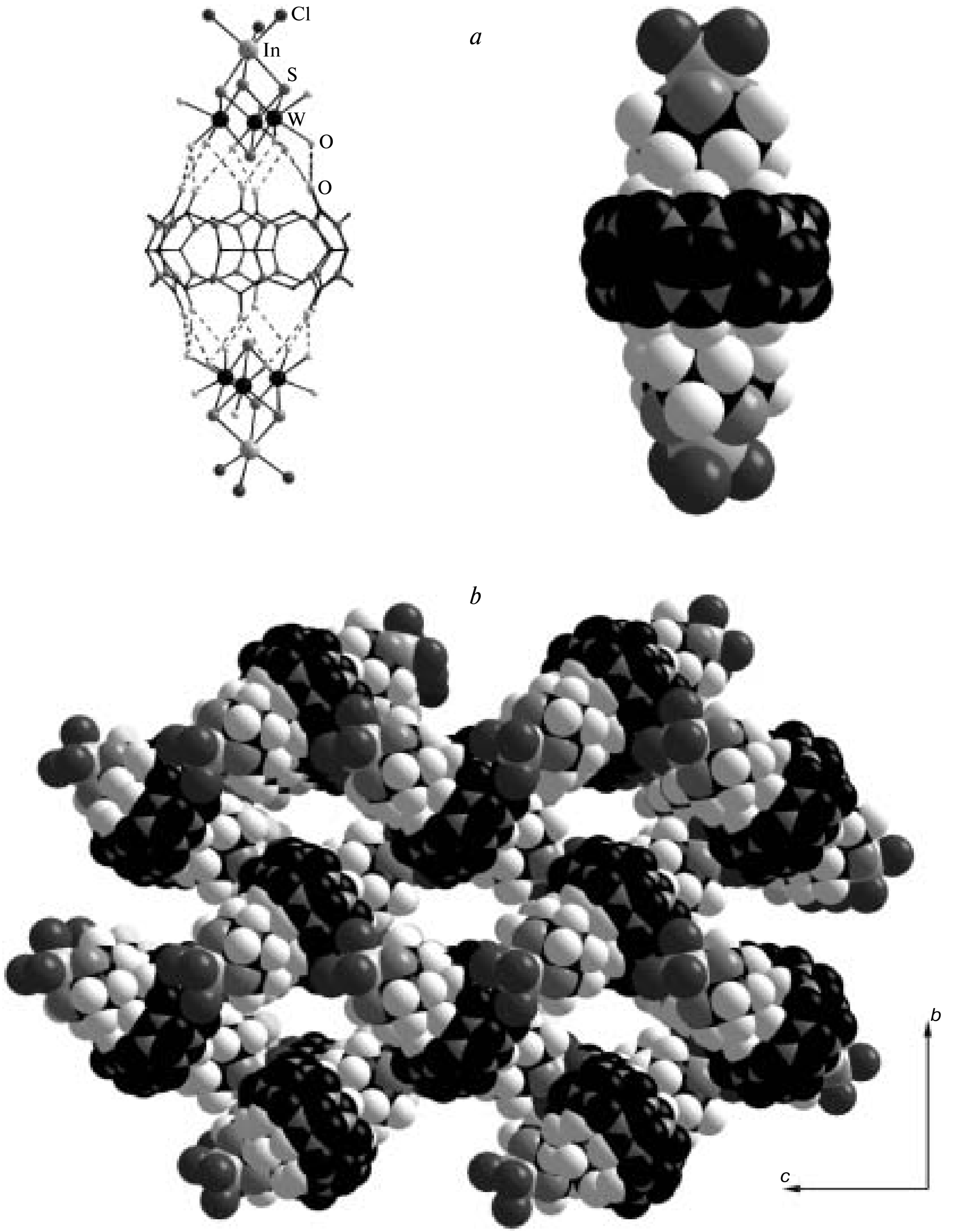

Fig. 14. Structure of the supramolecular adduct $\{[W_3(InCl_3)S_4(H_2O)_9]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 28H_2O$ (**13**): a schematic structure (ball-stick model and a model of van der Waals spheres) of the $\{[W_3(InCl_3)S_4(H_2O)_9]_2(C_{36}H_{36}N_{24}O_{12})\}^{4+}$ supramolecule (*a*); the packing of the supramolecules (*b*).

molecules are involved in hydrogen bonds with the cluster lids, the O...O distances varying over a wide range (2.566—3.065 Å). The supramolecules differ by the coordination environment about the Mo atoms. In the cluster lids of one of the supramolecular adducts, two Mo atoms are coordinated by two water molecules and one Cl^- ligand, and the third Mo atom is coordinated by three water molecules. In another adduct, one Mo atom is co-

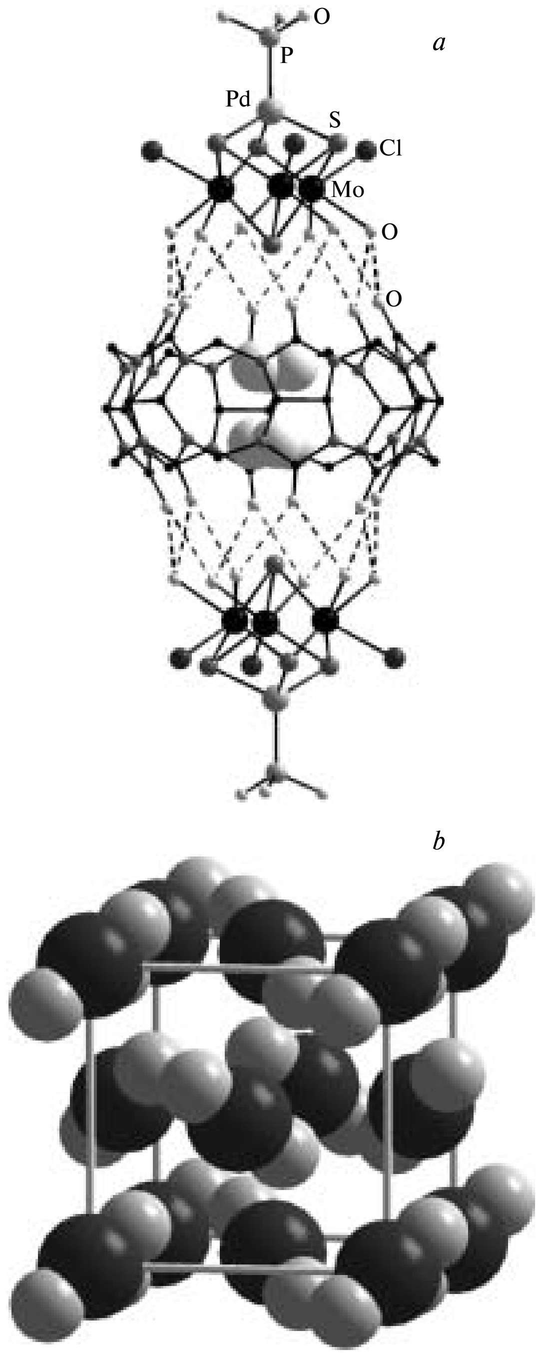

Fig. 15. Structure of the supramolecular adduct $\{[Mo_3(PdP(OH)_3)S_4(H_2O)_6Cl_3]_2(C_{36}H_{36}N_{24}O_{12})\}Cl_2 \cdot 20H_2O$ (**14**): the structure of the $\{[Mo_3(PdP(OH)_3)S_4(H_2O)_6Cl_3]_2(2H_2O \subset C_{36}H_{36}N_{24}O_{12})\}^{2+}$ supramolecule (*a*); the packing of the supramolecules in the cubic unit cell (*b*) (cucurbituril molecules and $[Mo_3(PdP(OH)_3)S_4(H_2O)_6Cl_3]^+$ cluster complexes are shown by large black and gray spheres, respectively).

ordinated by two water molecules and one Cl^- ligand, whereas two Mo atoms are coordinated by three water molecules.

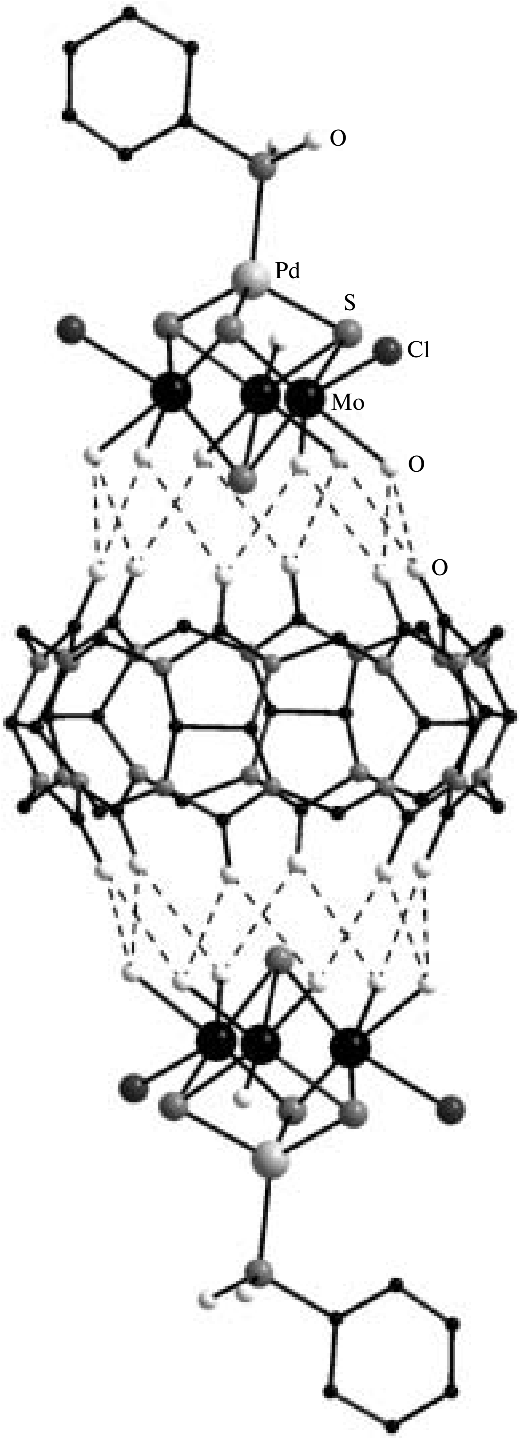

Fig. 16. Structure of the $\{[Mo_3(Pd(PhSO_2))S_4(H_2O)_8Cl][Mo_3(Pd(PhSO_2))S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}^{3+}$ supramolecule in compound **16**.

The $\{[M_6HgQ_8(H_2O)_{14}Cl_4](C_{36}H_{36}N_{24}O_{12})\}Cl_4 \cdot 14H_2O$ complexes (M = Mo, Q = S (**17**); M = Mo, Q = Se (**18**); M = W, Q = Se (**19**)) (see Ref. 30). Isostructural compounds **17**—**19** were prepared by the addition of cucurbituril to hydrochloric solutions (4 mol L^{-1}) of the corresponding heterometallic mercury cluster. In these compounds, the heterometallic double cube $[M_6HgQ_8(H_2O)_{14}Cl_4]^{4+}$ is linked to two cucurbituril molecules by hydrogen bonds (d(O...O) = 2.67—2.74 Å), and each cucurbituril molecule, in turn, is linked to two heterometallic clusters. The crystal structures of complexes **17—19** consist of supramolecular chains built from alternating mercury cluster complexes and cucurbituril molecules (Fig. 17, *b*). Therefore, the molecules are linked in these chains by hydrogen bonds and Hg atoms that bind the adjacent triangular $[M_3Q_4(H_2O)_7Cl_2]^{2+}$ clusters to each other.

The most remarkable feature of compounds **17—19** is the fact that they are isostructural with the above-described compounds **5** and **7** (see Fig. 17, *a*) in which the

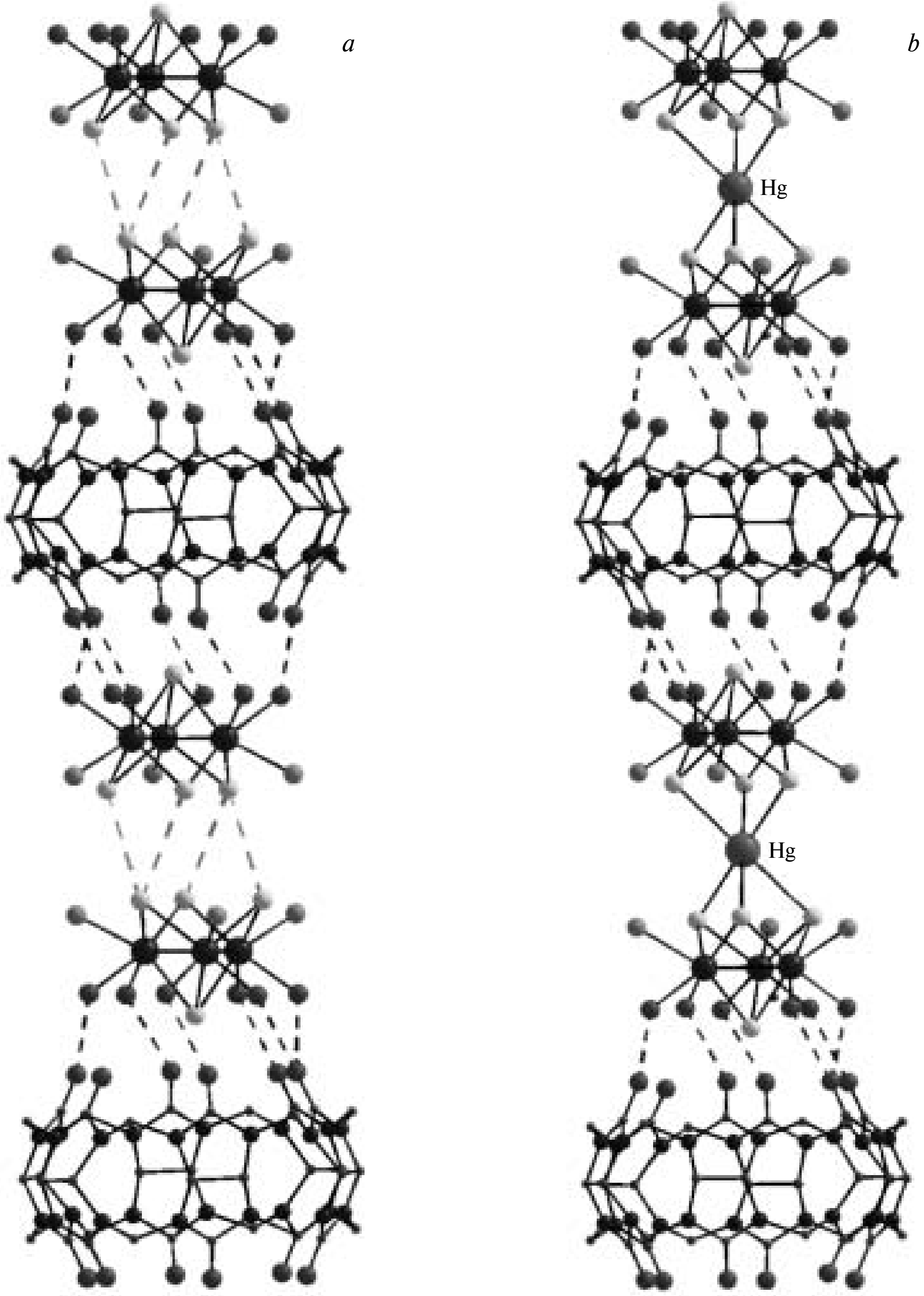

Fig. 17. Structures of the supramolecular polymeric chains in compounds **5**, **7** (*a*), and **17—19** (*b*).

adjacent triangular clusters are linked by nonbonded Q...Q interactions, like in layered dichalcogenides of early transition metals (MQ_2) belonging to an important class of inorganic compounds. In the structures of **5** and **7**, the adjacent triangular chalcogenide clusters M_3Q_4 serve as models of a fragment of the van der Waals gap in layered MQ_2. An important property of the latter compounds is that they can include small molecules or atoms between the layers to form intercalates. In compounds **17—19**, the Hg atoms are located between the chalcogenide clusters M_3Q_4. Therefore, isostructural compounds **5** and **7**, on the one hand, and compounds **17** and **18**, on the other hand, are related as a matrix and an intercalate. This result shows that the supramolecular chemistry of small chalcogenide clusters unexpectedly intersects with the chemistry of layered compounds. In both cases, nonbonded Q...Q interactions play an important structure-forming role.

Conclusion

To summarize, a new structural type of supramolecular compounds was synthesized. These compounds are built from molybdenum and tungsten cluster aqua complexes and macrocyclic cavitand cucurbituril. In these nanosized compounds, six water molecules of the triangular aqua complexes or their heterometallic cuboidal derivatives, which are coordinated to molybdenum or tungsten atoms, are complementary to six O atoms of the portals of cucurbituril. The geometric and functional compatibility is responsible for the formation of strong hydrolytically stable supramolecular compounds with composition cucurbituril : aqua complex = 1 : 1 (structural type "barrel with one lid") or 1 : 2 ("barrel with two lids"). The nonbonded μ_2-Q...μ_2-Q interactions play an important structure-forming role in supramolecular compounds of cucurbituril with triangular Mo and W chalcogenide aqua complexes giving rise to one-dimensional supramolecular compounds. Supramolecular compounds stabilized by nonbonded chalcogen—chalcogen interactions can serve as models of an important class of inorganic materials, *viz.*, layered transition metal dichalcogenides. The compositions and structures of supramolecular adducts depend on the nature of the aqua complex, the concentration of hydrochloric acid, and inclusion of a guest molecule in the inner cavity of cucurbituril.

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