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Coordination Chemistry of Polyniobates and Tantalates

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Abstract—Recent results on the synthesis of polynuclear niobium and tantalum oxohydroxo complexes, investigation of their reactivity, and specific features of the characterization of these compounds are reviewed.

Keywords: polyoxometallates, niobium, tantalum, coordination of organometallic fragments, hydrothermal synthesis

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INTRODUCTION

The chemistry of polynuclear oxo complexes of transition metals (polyoxometallates) is one of the most important parts of the modern chemical science. This class of compounds is distinctive due to an unusual diversity of structural types and properties. Catalytic activity, anticancer and antiviral activities, molecular magnetism, and other properties predetermined interest in polyoxometallates from both fundamental and applied points of view [1–5]. The most attention of researchers was historically concentrated on the investigation of the chemistry of molybdenum and tungsten polyoxoanions. One of the analytical methods for molybdenum determination in solutions is the formation of yellow $[PMo_{12}O_{40}]^{3-}$ in an acidic medium.

Polyoxo complexes of Group V metals (V, Nb, and Ta) form two large families of inorganic compounds exhibiting more distinctions rather than similarities in spite of their apparent similarity [6–15]. Vanadium(V) exists in an aqueous solution in a wide range of pH as a very stable decanuclear anion $[V_{10}O_{28}]^{6-}$ (the search over the Cambridge Structural Database gives more than 150 structurally characterized salts of this anion with various organic cations). The structural rearrangement of this anion is observed only in the presence of PO_4^{3-} as a template at very low pH to form the "two-capped" anion $[PV_{14}O_{42}]^{9-}$ of the Keggin type [16–20] in parallel with the decomposition of the polyoxoanions to mononuclear complexes containing $\{VO_2\}^+$. Vanadium(IV) (but not Nb(IV) or Ta(IV)) can be aggregated in acidic aqueous solutions around anionic templates (for example, Cl^-, NCS^-, etc.) to form a new class of polynuclear inorganic compounds with unique magnetic properties [21, 22]. The chemistry of polyoxoniobates and tantalates is significantly poorly studied and was restricted for a long time by alkali metal salts with hexanuclear anions of the Lindqvist type $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$. This is reasoned by the fact that the complexes exist only in medium- and strong-alkaline media and form amorphous jelly-like precipitates upon the addition of the most part of alkali-earth and transition metal salts. The first steps in the development of this chemical trend were made by Spinner, Pope, and Stucky at the period from the late 1960s to the early 1980s [23–29]. The authors found the condensation of $[Nb_6O_{19}]^{8-}$ to a more complicated structures (for example, decaniobate $[Nb_{10}O_{28}]^{6-}$) and discovered the ability of hexaniobate to act as a tridentate ligand for the coordination of some transition metals. Free hexavanadate $[V_6O_{19}]^{8-}$ is unknown because, most likely, of the unusually high charge density of this anion (in the chemistry of polyoxometallates, charge density I is the value obtained by the division of the anion charge into the number of non-hydrogen atoms in this anion). Among all known polyoxometallates, $[M_6O_{19}]^{8-}$ has the highest density (0.32) [14]. Evidently, $[V_6O_{19}]^{8-}$ will have the maximum charge density, which seems to be thermodynamically unfavorable. This anion was stabilized only upon the coordination of four positively charged organometallic fragments $\{Cp^*Rh\}^{2+}$ ($Cp^* = \eta^5$-$C_5(CH_3)_5^-$) [30, 31]. At the same time, analogs of decavanadate, namely, decaniobate $[Nb_{10}O_{28}]^{6-}$ [32, 33] and decatantalate $[Ta_{10}O_{28}]^{6-}$ synthesized in 2013 [34], exist but at very high pH.

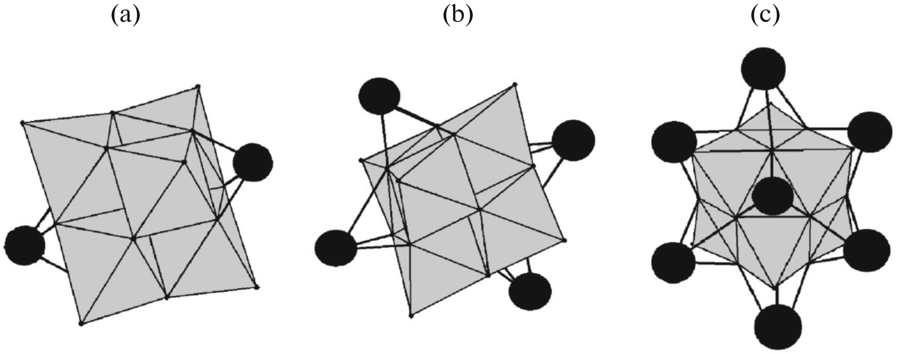

Fig. 1. Binding of the alkali metal with $[Nb_6O_{19}]^{8-}$; an increase in the number of coordinated metal ions with an increase in the metal radius is shown: (a) $\{A_2[Nb_6O_{19}]\}^{6-}$ (A = Li, Na), (b) $\{A_4[Nb_6O_{19}]\}^{4-}$ (A = K), and (c) $\{A_8[Nb_6O_{19}]\}$ (A = Rb, Cs).

The $[Nb_6O_{19}]^{8-}$—alkali metal system in the solid phase is a classical example for an increase in the degree of ionic dissociation on going from the top to down along the periodic table, when large weakly hydrated ions form associates not via water molecules but directly [14, 35]. It is shown by different methods that two Li^+ cations, two Na^+ cations, and four K^+ cations coordinate to each $[Nb_6O_{19}]^{8-}$, whereas Rb^+ and Cs^+ occupy all eight accessible sites (Fig. 1). The solubility of the $[Nb_6O_{19}]^{8-}$ salts with alkali metals increases in the order Li < Na < K < Rb/Cs [36]. This is a unique distinctive feature of niobates and tantalates, because cesium salts of usual polyoxometallates are almost insoluble. It was shown by the small-angle X-ray scattering (SAXS) method that the Lindqvist anions exist as neutral associates $\{A_8[Nb_6O_{19}]\}$ in a solution of AOH (A = Rb, Cs) [37], whereas in a solution of Me_4NOH they exist as isolated $[Nb_6O_{19}]^{8-}$ anions. In the case of hexatantalates, similar anomalies of solubility are observed, but the solubility of the $[Ta_6O_{19}]^{8-}$ salts is lower on the whole [38].

Hexaniobate has a high affinity to protonation because of the high charge density, resulting in an increase in the pH of the solution. It is shown that buffer solutions of hexaniobate contain $[H_3Nb_6O_{19}]^{5-}$ (pH 8), $[H_2Nb_6O_{19}]^{6-}$ (pH 10), $[HNb_6O_{19}]^{7-}$ (pH 12), and $[Nb_6O_{19}]^{8-}$ (pH 14) [39]. Hexatantalate can also exist as three protonated forms $[HTa_6O_{19}]^{7-}$, $[H_2Ta_6O_{19}]^{6-}$, and $[H_3Ta_6O_{19}]^{5-}$ [40–42]. Even in a solution of NBu_4OH this anion exists as $[H_2Ta_6O_{19}]^{6-}$ [43].

The binding of $[M_6O_{19}]^{8-}$ with alkali metals in solutions does not prevent the coordination of transition metals. On the contrary, $[M_6O_{19}]^{8-}$ are excellent ligands due to the high charge density. It was shown that this coordination mode of $[Nb_6O_{19}]^{8-}$ can stabilize Mn(IV) and Ni(IV) [23–29]. It has recently been found that Co(III) also forms complexes $[M(Nb_6O_{19})_2]^{n-}$ of a similar ("sandwich") type in which two anions of the Lindqvist structure (each anion acts as a tridentate ligand) are coordinated to the transition metal atom [44].

COORDINATION OF TRANSITION METALS

Since it is necessary to work with polyoxoniobates and tantalates at pH not lower than 10, rigid restraints should be imposed on the preparation conditions of the complexes with transition metals, the most part of which forms insoluble precipitates of hydroxides under the conditions discussed. The second problem is the fast aggregation of these complexes in solutions resulting finally in the formation of gels. For example, cobalt salts can be dissolved in a solution of potassium polyoxoniobate, but jelly-like blue (Co^{2+}) or green (Co^{3+}) precipitates are formed with time. Therefore, we chose the starting compounds (anionic oxo complexes or hydroxo complexes) suitable for the above conditions and optimized the synthesis conditions.

The reaction of $K_7[HNb_6O_{19}] \cdot 13H_2O$ with $KMnO_4$ at 180°C in an alkaline medium affords a brown precipitate and an orange solution, the slow evaporation of which leads to the crystallization of complex $Cs_9H_3[Mn(Nb_6O_{19})_2] \cdot 20H_2O$ as orange crystals. The crystalline product is stable in air and does not lose water during several months. The IR spectrum contains characteristic bands of the Nb=O (861 cm^{-1}) and Nb—O—Nb (530, 433 cm^{-1}) vibrations [45, 46]. Since niobates and tantalates are characterized by the phenomenon of anomalous solubility, i.e., an increase in the solubility with an increase in the cation size [36], it is not surprising that $Cs_9H_3[Mn(Nb_6O_{19})_2] \cdot 20H_2O$ is highly soluble in water. The major structural unit of this complex is the "sandwich-like" polyoxoanion $[Mn(Nb_6O_{19})_2]^{12-}$ with the point symmetry group D_{3d} (Fig. 2). The oxygen atoms of the triangular faces $\{Nb_3O_3\}$ of two $[Nb_6O_{19}]^{8-}$ anions coordinate the Mn(IV) atom exist-

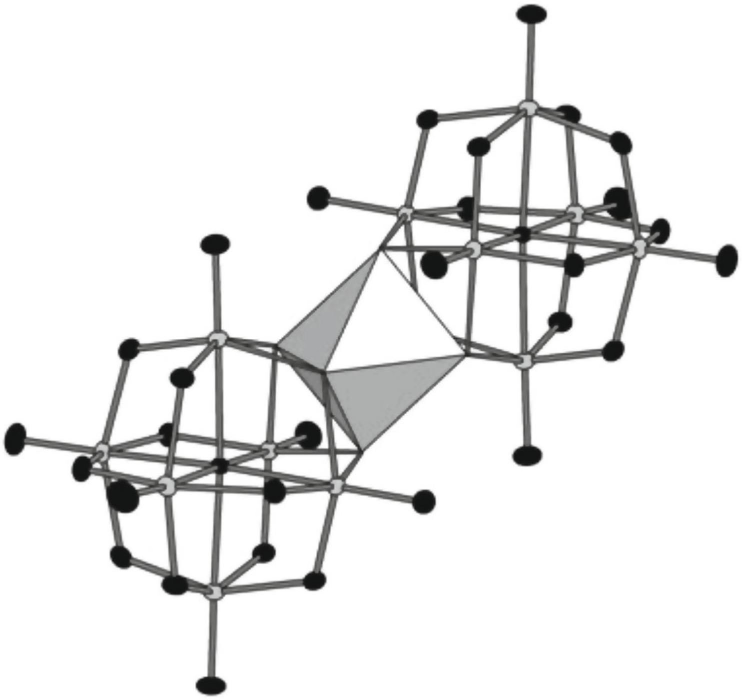

Fig. 2. Structure of the $[Mn^{IV}(Nb_6O_{19})_2]^{12-}$ anion in the crystal structure of complex $Cs_9[H_3Mn(Nb_6O_{19})_2] \cdot 20H_2O$.

ing in the distorted octahedral environment (Mn(1)–O(18) 1.915(4), Mn(1)–O(19) 1.898(4), Mn(1)–O(9) 1.924(4) Å). In the known structure $Na_{12}[Mn(Nb_6O_{19})_2] \cdot 50H_2O$ [25], the Mn–O distances are 1.87 ± 0.01 Å, which is similar to the Mn–O bond lengths in two crystalline modifications of MnO_2 (1.87–1.94 Å) [47] and in $Na_7H_4[Mn^{IV}(IO_6)_3] \cdot 17H_2O$ (1.90 Å) [48]. The independent part of the unit cell contains six sites of the cesium atoms, two of which are occupied by 1/4. All Cs–O bonds are longer than 3 Å. Thus, only nine Cs^+ cations fall onto one anion, due to which $[Mn(Nb_6O_{19})_2]^{12-}$ should be triply protonated. The absence of any redox processes during experiment was shown by cyclic voltammetry, indicating a very slow kinetics of electron transfer. Attempts to chemically oxidize the manganese ion by ozone or bromine do not change the absorption spectra. However, the complex is reduced by Sn^{2+}, resulting in the disappearance of the characteristic orange color. According to the data of mass spectrometry, after the reaction the solution contains only free hexaniobate, possibly indicating that the complex decomposed upon reduction. As the pH of the solution increases, the hexaniobate framework is rearranged to lose one vertex, which is occupied by the manganese atom. As a result, heteropolyanion $[Mn^{IV}(Nb_5O_{16})_2]^{10-}$ was isolated and structurally characterized in the form of salt $Cs_{10}[Mn^{IV}(Nb_5O_{16})_2] \cdot 12H_2O$ (Fig. 3). This manganoniobate has previously been obtained in a methanol solution only [49]. At 90–100°C hexaniobate can capture Mn(IV) generated in situ by the oxidation of Mn(II) with hydrogen peroxide in an alkaline solution. This route turned out to be convenient for the preparation of a new salt of $Na_8K_4[Mn(Nb_6O_{19})_2] \cdot 18H_2O$. Attempts to apply the approaches described above to the synthesis of tantalum complexes with Mn(IV) were unsuccessful, because the products are unstable in aqueous solutions and are rapidly transformed into insoluble jelly-like precipitates.

The possibility of coordination of $[Nb_6O_{19}]^{8-}$ to Pt(IV) was demonstrated under the conditions of hydrothermal synthesis [50]. The heteropolyanion with a basically new type of coordination to the Lindquist-type anion was obtained at the 1 : 1 reactant ratio: dimeric anionic complex $[(Nb_6O_{19})(Pt(OH)_2)]_2^{12-}$, which was structurally characterized in the $Cs_2K_{10}[(Nb_6O_{19})(Pt(OH)_2)]_2 \cdot 13H_2O$ composition (Fig. 4). The formation of this product is observed in a narrow temperature range (130–150°C), and no platinum-containing products are formed as the temperature decreases. The “sandwich-type” complex $Na_2K_{10}[Pt(Nb_6O_{19})_2] \cdot 18H_2O$ was isolated and characterized with an increase in the amount of hexaniobate to the 2 : 1 molar ratio. This complex is formed in a range of 150–170°C, whereas PtO_2 is formed at a higher temperature, and a mixture of 2 : 1 and 1 : 1 complexes is formed at a lower temperature.

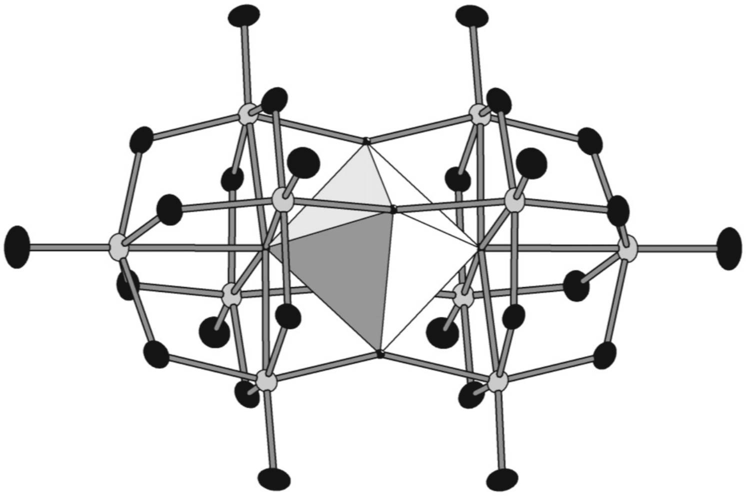

Fig. 3. Structure of $[\mathrm{Mn}^{\mathrm{IV}}(\mathrm{Nb}_5\mathrm{O}_{16})_2]^{10-}$ in the crystal structure of $\mathrm{Cs}_{10}[\mathrm{Mn}^{\mathrm{IV}}(\mathrm{Nb}_5\mathrm{O}_{16})_2] \cdot 12\mathrm{H}_2\mathrm{O}$ (oxygen atoms are shown by black, and niobium atoms are gray).

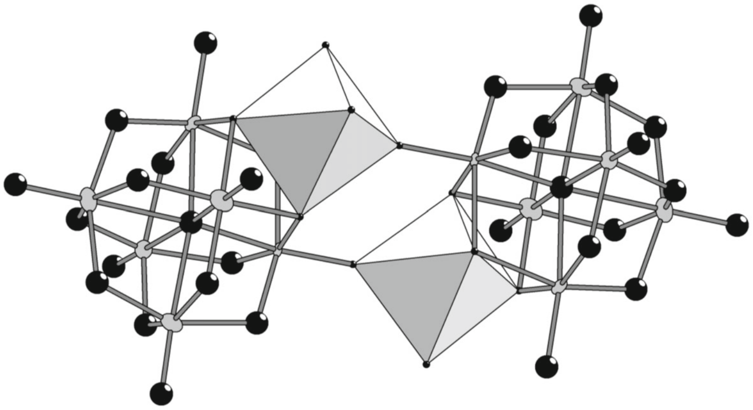

Fig. 4. Structure of $[(\mathrm{Nb}_6\mathrm{O}_{19})(\mathrm{Pt(OH)}_2)]_2^{12-}$ in the crystal structure of $\mathrm{Cs}_2\mathrm{K}_{10}[(\mathrm{Nb}_6\mathrm{O}_{19})(\mathrm{Pt(OH)}_2)]_2 \cdot 13\mathrm{H}_2\mathrm{O}$ (oxygen atoms are shown by black, and niobium atoms are gray).

Thus, Pt(IV) is the fourth element along with Mn(IV), Ni(IV), and Co(III) that forms “sandwich-type” complexes with hexaniobate.

It can be assumed that Te(VI) tending to the octahedral mode also supplements this list. However, the reaction of telluric acid ($\mathrm{H}_6\mathrm{TeO}_6$) with potassium hexaniobate in a molar ratio of 1 : 1 at 100°C gave the hexanuclear anion $[(\mathrm{OH})\mathrm{TeNb}_5\mathrm{O}_{18}]^{6-}$ isolated and characterized as potassium and sodium salts. The direct substitution of the niobium atom by tellurium with the retention of the general structure of the Lindquist type is a new reaction in the chemistry of polyoxoniobates, which makes it possible to modify polyoxoanions by the introduction of tellurium atoms into the framework. The formation of the $[(\mathrm{OH})\mathrm{TeNb}_5\mathrm{O}_{18}]^{6-}$ anion was detected for the first time [51] for the reaction of niobium oxide with telluric acid in methanol under drastic conditions. We showed that $[(\mathrm{OH})\mathrm{TeNb}_5\mathrm{O}_{18}]^{6-}$ with sources of cationic organometallic fragments of noble metals ($[\mathrm{Cp^*RhCl}_2]_2$, $[(\mathrm{C}_6\mathrm{H}_6)\mathrm{RuCl}_2]_2$) formed complexes $[\{\mathrm{Cp^*Rh}\}\mathrm{Nb}_5\mathrm{O}_{18}\{\mathrm{Te(OH)}\}]^{5-}$ and $[\{\mathrm{Cp^*Rh}\}_2\mathrm{Nb}_5\mathrm{O}_{18}\text{-}\{\mathrm{Te(OH)}\}]^{3-}$ or $[\{(\mathrm{C}_6\mathrm{H}_6)\mathrm{Ru}\}\mathrm{Nb}_5\mathrm{O}_{18}\{\mathrm{Te(OH)}\}]^{5-}$ and $[\{(\mathrm{C}_6\mathrm{H}_6)\mathrm{Ru}\}_2\mathrm{Nb}_5\mathrm{O}_{18}\{\mathrm{Te(OH)}\}]^{3-}$ [52]. It can be concluded that the binding between $[(\mathrm{OH})\mathrm{TeNb}_5\mathrm{O}_{18}]^{6-}$ and the organometallic fragment is weaker than that of $[\mathrm{Nb}_6\mathrm{O}_{19}]^{8-}$ because of a decrease in *I*.

COORDINATION OF ORGANOMETALLIC FRAGMENTS

The noble metal complexes immobilized on the polyoxometallate surface that find use in catalysis were described [53, 54]. The synthesis of the family of

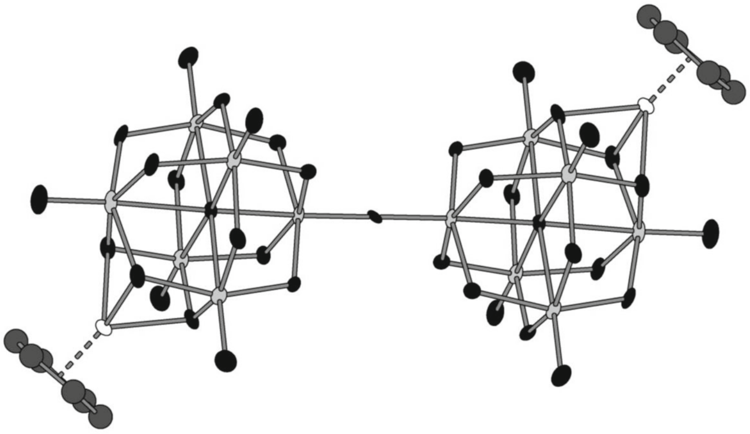

Fig. 5. Structure of the $[\{(C_6H_6)RuTa_6O_{18}\}_2(\mu\text{-}O)]^{10-}$ anion in the crystal structure of $Na_{10}[\{(C_6H_6)RuTa_6O_{18}\}_2(\mu\text{-}O)] \cdot 39.4H_2O$.

hybrid organometallic complexes by the coordination of $\{(p\text{-cym})Ru\}^{2+}$ (*p*-cym is cymene, from 1 to 4 equivalents consequently) to $[Nb_6O_{19}]^{8-}$ was reported in 2007 [55]. We found that the reaction between $[(C_6H_6)RuCl_2]_2$ and $Na_8[Ta_6O_{19}]$ resulted in the formation of two new hybrid complexes $Na_{10}[\{(C_6H_6)RuTa_6O_{18}\}_2(\mu\text{-}O)] \cdot 39.4H_2O$ (ratio 1 : 1, Fig. 5) and $Na_4[trans\text{-}\{(C_6H_6)Ru\}_2Ta_6O_{19}] \cdot 20H_2O$ (ratio 2 : 1, Fig. 6), but a higher molar ratio was not achieved [56]. In both cases, the $\{(C_6H_6)Ru\}^{2+}$ fragments of the C_{3v} symmetry are coordinated to the $\{Ta_3(\mu_2\text{-}O)_3\}$ faces. In a solution the dimeric anions $[\{(C_6H_6)RuTa_6O_{18}\}_2(\mu\text{-}O)]^{10-}$ dissociate completely to form monomeric anions $[(C_6H_6)RuTa_6O_{19}]^{6-}$.

The reactions between $[M_6O_{19}]^{8-}$ (M = Nb, Ta) and $[Cp^*RhCl_2]_2$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) taken in the ratio $[M_6O_{19}]^{8-}$: $\{Cp^*Rh\}$ = 1 : 2 afford *trans*-$[\{Cp^*Rh\}_2M_6O_{19}]^{4-}$, which were isolated in the form of $K_4[\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 17H_2O$ and $Cs_4[\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 18H_2O$ [57]. To study the behavior of these complexes in solutions, we applied the ^1H NMR DOSY procedure for the first time in the chemistry of Group V polyoxometallates. This procedure made it possible to estimate the diffusion coefficients of the complexes in an aqueous solution, their radii, and molecular weights. The absence of *cis–trans* isomerism in a solution was found for both complexes by the temperature dependence of the ^1H NMR spectra, indicating a strong coordination of the organometallic fragments to the polyoxometallate.

The oxidation of $[\{(C_6H_6)Ru\}_2Nb_6O_{19}]^{4-}$ gives a dark brown solution forming a gel dissolved upon the addition of an alkali. However, the crystalline product cannot be isolated from this solution. It was shown by light scattering that this colloidal solution contained particles about 100 nm in diameter. It is most probable that these are ruthenium oxide particles to the surface of which hexaniobate anions are bound. The study of these systems seems interesting from the viewpoint of the electrocatalytic oxidation of water. At the present time, $[Ru_4^{IV}(\mu\text{-}O)_4(\mu\text{-}OH)_2(H_2O)_4(\gamma\text{-}SiW_{10}O_{36})_2]^{10-}$ is the most efficient catalyst of this process among the polyoxometallates containing noble metals [58]. The

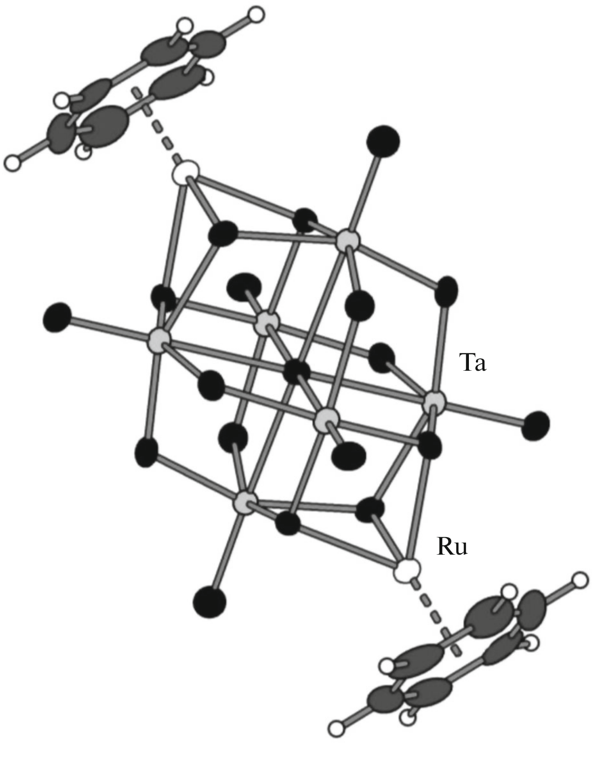

Fig. 6. Structure of the $[trans\text{-}\{(C_6H_6)Ru\}_2Ta_6O_{19}]^{4-}$ anion in the crystal structure of complex $Na_4[trans\text{-}\{(C_6H_6)Ru\}_2Ta_6O_{19}] \cdot 20H_2O$.

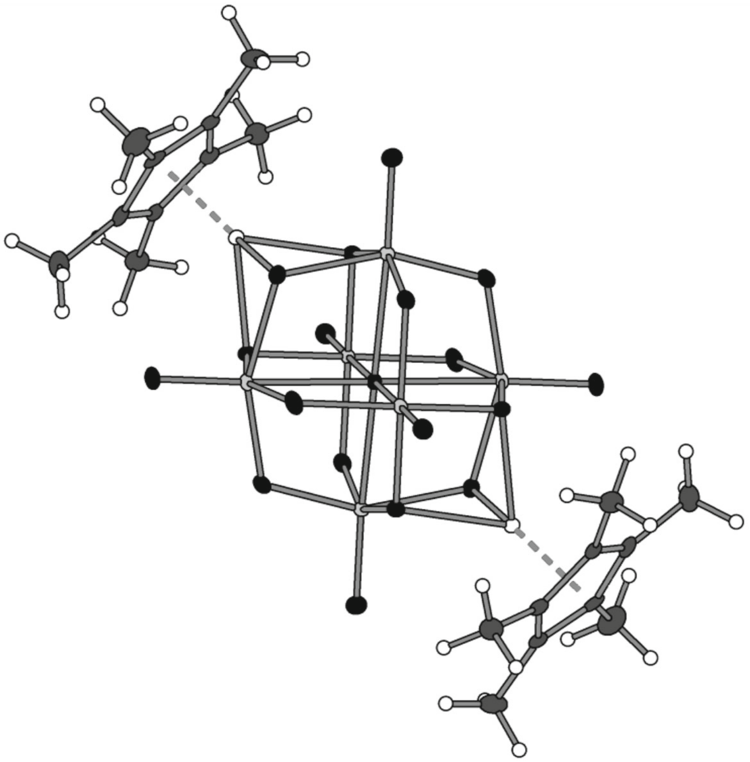

Fig. 7. General structure of the [*trans*-$\{Cp^*M'\}_2M_6O_{19}]^{4-}$ anion (M = Nb, Ta; M' = Rh, Ir).

most efficient catalysts of the photo- and electrooxidation of water are IrO_2 nanoparticles supported on niobium or tantalum oxide [59]. Therefore, we synthesized the $[M_6O_{19}]^{8-}$ complex with the coordinated $\{Cp^*Ir\}^{2+}$ fragments.

The reactions of hexametallates of Nb and Ta with $[Cp^*IrCl_2]_2$ in the molar ratio $[M_6O_{19}]^{8-} : \{Cp^*Ir\}^{2+} = 1 : 2$ with slight heating for 3 days afforded the products A_4[*trans*-$\{Cp^*Ir\}_2M_6O_{19}] \cdot xH_2O$ (A = Na, M = Nb, $x = 22$; A = K, M = Nb, $x = 22$; A = Na, M = Ta, $x = 24$) (Fig. 7) [60]. Different products were isolated at the molar ratio $[M_6O_{19}]^{8-} : \{Cp^*Ir\}^{2+} = 1 : 1$ for Nb and Ta under similar conditions: $Na_6[\{Cp^*Ir\}Ta_6O_{19}] \cdot 27H_2O$ is formed in the case of tantalum, and a mixture of 1 : 1 and 1 : 2 complexes with the predomination of the former (about 90%) is formed in the case of niobium. During crystallization the 1 : 1 complex forms dimer $[\{Cp^*IrNb_6O_{18}\}_2(O)]^{10-}$, which is similar in structure to $[\{(C_6H_6)RuTa_6O_{18}\}_2(O)]^{10-}$ [56]. This dimer was isolated in the composition of complex $Na_8[H_2\{Cp^*IrNb_6O_{18}\}_2(O)] \cdot 47H_2O$. Thus, it can be concluded that the formation of dimers of this type of the $[M_6O_{19}]^{8-}$ complexes with the $\{(C_6H_6)M\}^{2+}$ and $\{Cp^*M\}^{2+}$ fragments (M = Ru, Rh, Ir) is typical, although this dimerization was never observed for free hexaniobate and tantalate. The electrochemical behavior of Na_4[*trans*-$\{Cp^*Ir\}_2Nb_6O_{19}] \cdot 22H_2O$ was studied by cyclic voltammetry. In the presence of Na_4[*trans*-$\{Cp^*Ir\}_2Nb_6O_{19}] \cdot 22H_2O$, the catalytic current related to water oxidation increased sharply. Probably, the loss of the organic ligand, aquation of iridium, and formation of iridium(IV) oxide particles at the electrode surface are observed during oxidation. To check this possibility, Na_4[*trans*-$\{Cp^*Ir\}_2Nb_6O_{19}] \cdot 22H_2O$ was oxidized by sodium persulfate to give a dark green solution containing, according to the data of electronic absorption spectroscopy and photon-correlation spectroscopy, iridium dioxide particles about 80 nm in diameter. A comparison of the electrochemical activities of solutions of $[Cp^*_2Ir_2(OH)_3]NO_3$ and Na_4[*trans*-$\{Cp^*Ir\}_2Nb_6O_{19}] \cdot 22H_2O$ containing equivalent amounts of iridium shows that the catalytic effect is higher for hexaniobate.

HIGH-TEMPERATURE REARRANGEMENT OF HEXANIOBATE ANION

The high-temperature rearrangement of the hexaniobate anion in the presence of $Si(OEt)_4$ with the formation of $[SiNb_{12}O_{40}]^{16-}$ and $[Si_4Nb_{16}O_{56}]^{16-}$ became the starting point of the chemistry of heteropolyniobates [61]. In continuation of these works, we developed a new method for the synthesis of $[Si_4Nb_{16}O_{56}]^{16-}$ (Fig. 8) and isolation of this anion in the form of $NaK_8H_6[Na@Nb_{16}Si_4O_{56}] \cdot 26H_2O$ using

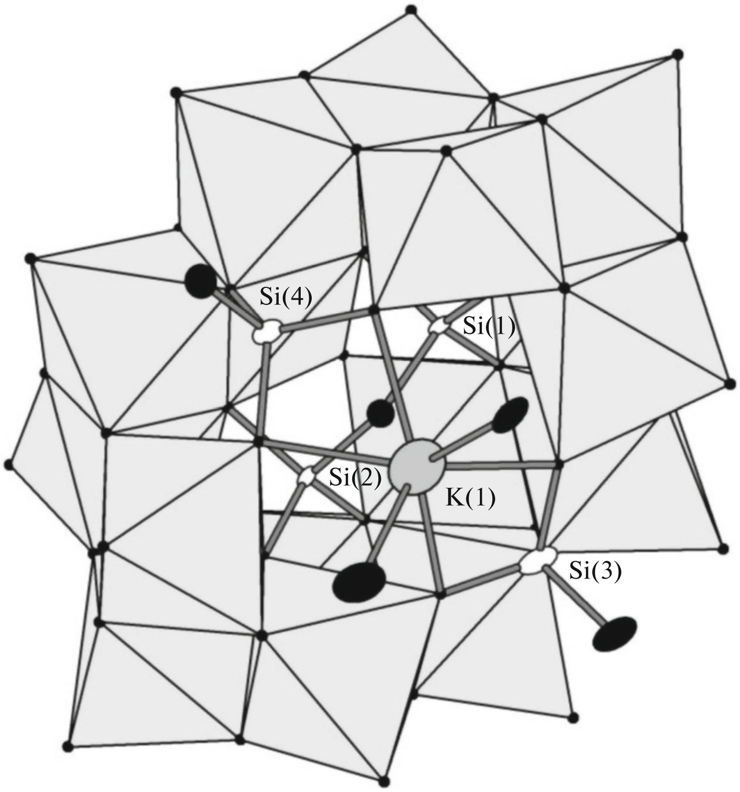

Fig. 8. Structure of the $[Si_4Nb_{16}O_{56}]^{16-}$ lacunary anion (potassium cation occupies the lacuna) in the crystal structure of complex $K_{13}H_2[K@Nb_{16}Si_4O_{56}] \cdot 28H_2O$.

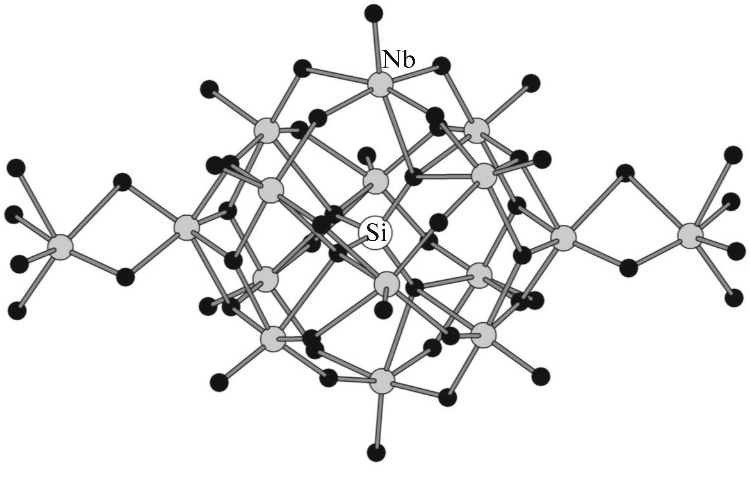

Fig. 9. Infinite chains of the $[SiNb_{12}O_{40}]^{16-}$ anions linked by the $[Nb_2O_2]^{6+}$ fragments in the crystal structure of complex $K_{10}[Nb_2O_2][SiNb_{12}O_{40}] \cdot 16H_2O$.

Na_2SiO_3 and in the form of $K_{13}H_2[K@Nb_{16}Si_4O_{56}] \cdot 28H_2O$ using $Ph_2Si(OH)_2$ as silicon sources in the reaction with hexaniobate. When the reaction time increases, $[Si_4Nb_{16}O_{56}]^{16-}$ is rearranged into infinite chains of Keggin anions linked through the bridges $Nb_2O_2^{6+}$. This product was isolated and structurally characterized in the form of $K_{10}(Nb_2O_2)[SiNb_{12}O_{40}] \cdot 16H_2O$ (Fig. 9).

The maintenance of $K_7H[Nb_6O_{19}] \cdot 13H_2O$ at 200°C for 20 h leads to a set of isopolyniobates with the

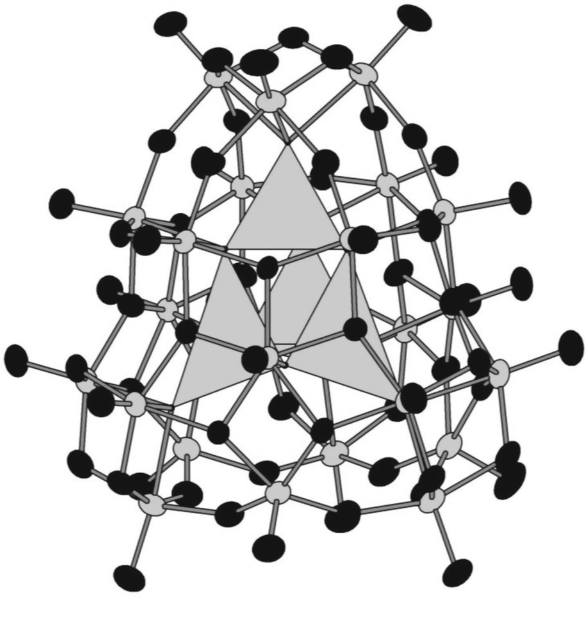

Fig. 10. Structure of the $[V_4Nb_{24}O_{72}]^{12-}$ anion (vanadium atoms occupy tetrahedral cavities inside the anion).

metallic cage $\{Nb_{10}\}$, $\{Nb_{20}\}$, and $\{Nb_{27}\}$ [62]. The addition of dibenzyl dithiocarbamate to the reaction mixture resulted in the formation of complexes containing $[HNb_{27}O_{76}]^{16-}$ and $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$. Their main structural feature is the pentagonal $\{(Nb)Nb_5\}$ fragment, which is more typical of the chemistry of molybdenum and tungsten. For example, these fragments are observed in various keplerates or uranyl complexes [63, 64].

We studied the thermally induced rearrangement of hexaniobate in the presence of vanadate. Several products are formed due to the maintenance of an aqueous solution of $K_7H[Nb_6O_{19}] \cdot 13H_2O$ and $NaVO_3 \cdot 2H_2O$ at 220°C. Among these products, complex $[K@V_4Nb_{24}O_{76}]^{11-}$ having no analogs was isolated and structurally characterized. This complex contains the pentagonal building block $\{(Nb)Nb_5\}$, which was stabilized by the vanadium(V) cations included into the tetrahedral cavities (Fig. 10). The comparison with the earlier mentioned isopolyniobates of similar structures [62] allows one to conclude that the structures have tetrahedral cavities. In our case, the cavities are occupied by vanadium, whereas niobium occupies these sites in the case of $[HNb_{27}O_{76}]^{16-}$ and $[H_{10}Nb_{31}O_{93}(CO_3)]^{23-}$ [62]. Thus, the simultaneous presence of the ion with the tetrahedral geometry of the oxygen environment is an important point for the stabilization of the pentagonal fragment $\{(Nb)Nb_5\}$.

Unlike the potassium salt, the thermolysis of sodium hexaniobate in the presence of vanadate affords the product of basically another structure $Na_9H_4[VNb_{14}O_{42}(CO_3)_2] \cdot 34H_2O$ (Fig. 11) [65] containing the Keggin-type anion with two additional fragments $\{NbO(CO_3)\}^+$ (coordination number of Nb 7, bidentate carbonate, four oxide ligands from the anion and terminal oxygen atom). Anions of similar type are known for vanadium, for example, $[PV_{14}O_{42}]^{9-}$ [15, 16], as well as mixed anions $[PM_xV_{12-x}O_{40}(VO)_2]^{n-}$ (M = Mo, W) [66]. In the case of vanadium, the chemistry of these complexes is restricted by acidic media, whereas polyoxometallates of niobium with the Keggin structure exist in basic media only.

The study of the stability of $[VNb_{14}O_{42}(CO_3)_2]^{13-}$ at different pH by the ^{51}V NMR method and mass spectrometry made it possible to monitor the evolution of the anion from "two-capped" $\{VNb_{14}\}$ to the free Keggin anion $\{VNb_{12}\}$ through the intermediate formation of oligomeric chains $\{[Nb_2O_2][VNb_{12}O_{40}]\}_n$. The peaks from $[VNb_{12}O_{40} + xH^+ + yNa^+]^{2-}$ and $[VNb_{14}O_{42}(CO_3)_2 + xH^+ + yNa^+]^{2-}$ are observed in the mass spectrum of an aqueous solution of $Na_9H_4[VNb_{14}O_{42}(CO_3)_2] \cdot 34H_2O$ at a high dilution. The signals of only these two complex species were observed in the ^{51}V NMR spectrum at pH < 11.6. No signals from $[VNb_{12}O_{40} + xH^+ + yNa^+]^{2-}$ were observed at pH > 11.6, while instead we observed a sharp signal at –492 ppm from $[VNb_{13}O_{41}(CO_3)]^{14-}$ and a broad signal at –495 ppm from the dimer $[Nb_2O_2][VNb_{13}O_{41}(CO_3)]_2^{22-}$.

The reaction of $[VNb_{14}O_{42}(CO_3)_2]^{13-}$ with $[(C_6H_6)RuCl_2]_2$ gave the complex containing the Keggin anion with four coordinated organometallic fragments $Na_6H[\{(C_6H_6)Ru\}_4VNb_{12}O_{40}] \cdot 41.5H_2O$ (Fig. 12). The major product of the reaction of $K_{10}[Nb_2O_2][SiNb_{12}O_{40}] \cdot 16H_2O$ with $[(C_6H_6)RuCl_2]_2$ is also $[\{(C_6H_6)Ru\}_4SiNb_{12}O_{40}]^{8-}$, which is the Keggin-type anion with four coordinated organometallic fragments. A similar behavior is not characteristic of the Keggin anions formed by the Group VI elements (Mo and W). In the case of niobium, this coordination mode becomes possible due to a high negative charge (increase in *I*) for the anion. It follows from the structure determined for the vanadium complex that the organometallic fragments are coordinated, in three cases, to the triangular faces $\{Nb_3O_3\}$, as in the case of hexametallates [56], whereas the fourth fragment is coordinated to the quadrilateral face. It is very interesting, because one free triangular face remains in the anion. Presently it is impossible to explain what compels the fourth organometallic fragment to be coordinated in such a way. The existence in a solution of two types of particles with a radius of 8 and 10 Å was shown by the ^1H NMR DOSY method, indicating the decoordination of one $\{(C_6H_6)Ru\}^{2+}$ fragment in a solution. Thus, the general regularity for two types of Keggin anions with the $\{SiO_4\}$ and $\{VO_4\}$ central fragments

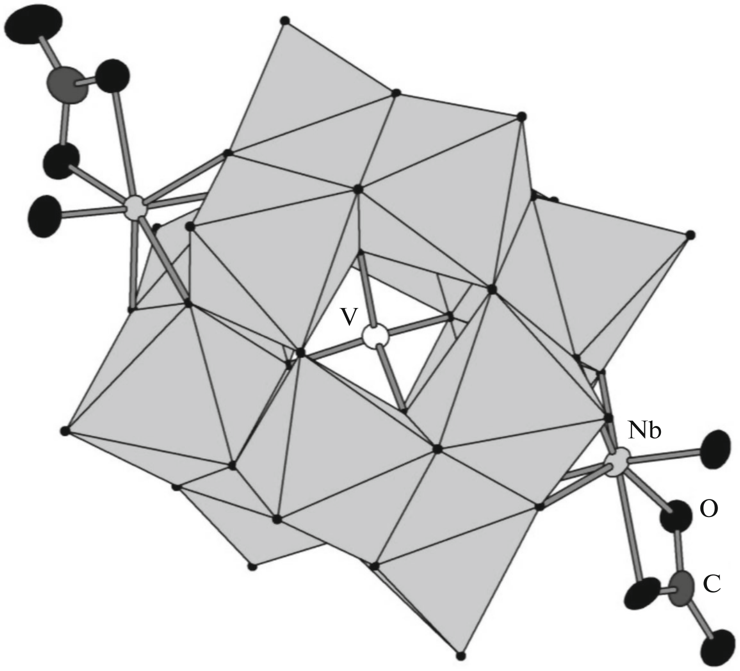

Fig. 11. Structure of the two-capped α-Keggin-type $[VNb_{14}O_{42}(CO_3)_2]^{13-}$ anion in the crystal structure of $Na_9H_4[VNb_{14}O_{42}(CO_3)_2] \cdot 34H_2O$.

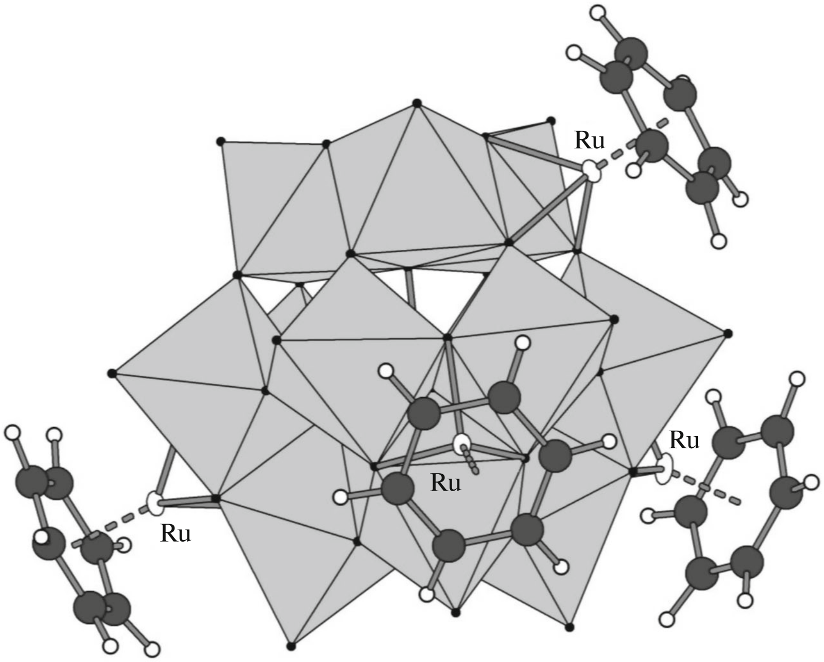

Fig. 12. Structure of the hybrid α-Keggin-type anion with four metallic fragments $\{(C_6H_6)Ru\}^{2+}$ in the crystal structure of complex $Na_6H[\{(C_6H_6)Ru\}_4VNb_{12}O_{40}] \cdot 41.5H_2O$.

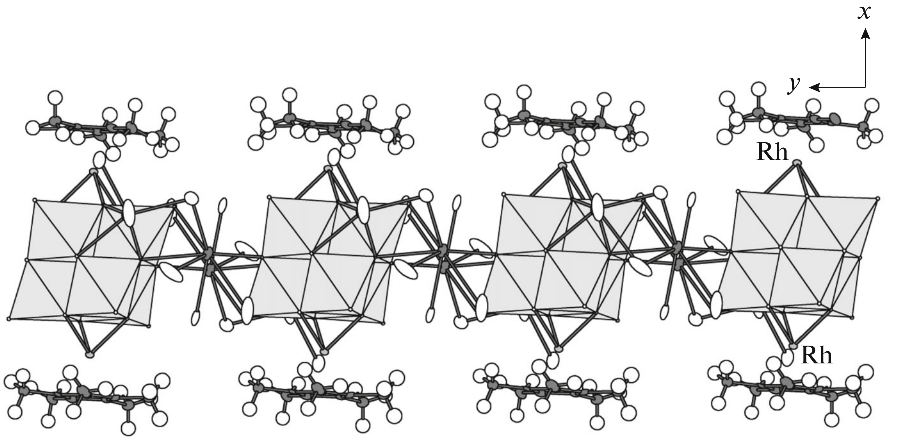

Fig. 13. Layer of K^+ cations and [*trans*-$\{Cp^*Rh\}_2Nb_6O_{19}]^{4-}$ anions in the crystal structure of complex K_4[*trans*-$\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 20H_2O$.

is the coordination of four $\{(C_6H_6)Ru\}^{2+}$ fragments to form anions $[\{(C_6H_6)Ru\}_4XNb_{12}O_{40}]^{n-}$.

UNIQUE SOLUBILITY OF HYBRID COMPLEXES IN METHANOL

The coordination of organometallic fragments to hexaniobates and tantalates should result in their solubility in organic solvents, as it takes place in the case of molybdenum and tungsten [53, 54]. However, among all organic solvents, the hybrid anions $[\{Cp^*M'\}_xM_6O_{19}]^{n-}$ and $[\{(C_6H_6)Ru\}_xM_6O_{19}]^{n-}$ (M' = Rh, Ir; $x = 1, 2$; $n = 6, 4$) can be dissolved only in methanol [67]. In spite of the presence of two Cp* ligands, they are insoluble in acetonitrile or dichloromethane and even in ethanol! This behavior can be explained by a combination of several factors: specific crystal structures of all the complexes, a strong bond of the alkali metal ions with polyoxometallates, solvation effects, and the possibility of the reaction with methanol.

All crystal structures of the hybrid anions $[\{Cp^*M'\}_xM_6O_{19}]^{n-}$ and $[\{(C_6H_6)Ru\}_xM_6O_{19}]^{n-}$ (M' = Rh, Ir; $x = 1, 2$; $n = 6, 4$) demonstrate the layered type of crystal packing in which the layers are composed of anions, alkali metal cations, and water molecules. These layers are connected to each other by $\pi-\pi$ interactions (Fig. 13). Possibly, at the first stage of dissolution, the solvent penetrates between the layers followed by the substitution of water molecules in the coordination spheres of the alkali metal cations. However, this could take place in both ethanol and acetonitrile. It is most likely that an important role also belongs to the dielectric permeability of the solvent, which is noticeably higher for methanol than that for ethanol (31.2 vs. 25.0, and only 14.1 for acetonitrile). In addition, the formation of the methoxide complexes was observed in methanol solutions of all these hybrid complexes (the formation formally proceeds via the replacement of oxide ligands (from one to three) in the polyoxometallate anion by methoxide ligands). The question why this does not occur in the case of ethanol or isopropanol remains yet unanswered. However, the formation of the methoxo complexes is reversible, since the oxo complexes are again isolated upon crystallization but in the form of solvates with methanol in the composition of the following compounds: $Na_4[\{(C_6H_6)Ru\}_2Nb_6O_{19}] \cdot 14.125MeOH \cdot 2H_2O$, $K_4[\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 4MeOH \cdot 10H_2O$, and $K_4[\{Cp^*Ir\}_2Nb_6O_{19}] \cdot 10MeOH \cdot 4H_2O$. In the structures of these compounds, the most part of methanol molecules is coordinated to the alkali metal ion. Thus, we found the specific solubility of the hybrid anions in methanol accompanied by the reversible solvolysis with the formation of the methoxo complexes.

To conclude, the chemistry of polynuclear niobium and tantalum oxohydroxo complexes became considerably richer within the last 15 years, passing the way from hexanuclear anions of the Lindqvist type to anions containing pentagonal building blocks or anionic associates containing up to the 96 niobium atoms in the structure [68]. In this cycle of works, new methods were developed for the inclusion of heterometals into the polyoxoniobate structures, including those with the formation of novel structural types. Owing to the coordination of organometallic fragments, the reversible dimerization of anions with the Lindqvist-type structure in aqueous solutions has been found for the first time. The organometallic fragments are convenient markers for studying polyoxoniobates and tantalates in solutions by the NMR method. The possibility of the high-temperature rearrangement of hexaniobates in the presence of vanadium(V) to form new types of polyoxoanions was shown. The ability of the polyniobates with the Keggin-type structure to act as ligands was shown for the first time.

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