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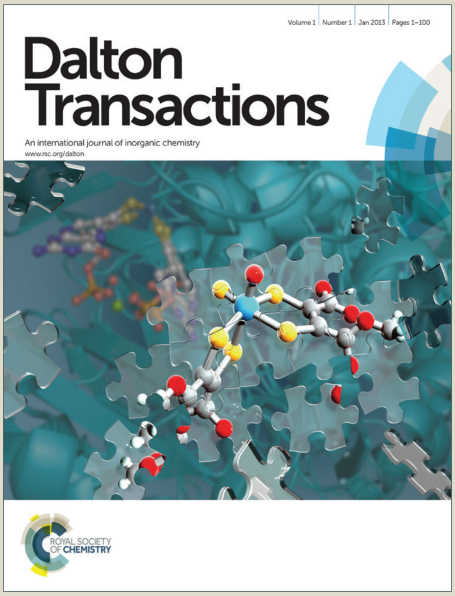

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Grafting $\{Cp^*Rh\}^{2+}$ on the surface of Nb and Ta Lindqvist-type POM

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New hybrid POM based on Lindqvist-type polyoxometalates $[M_6O_{19}]^{8-}$ (M = Nb, Ta) and organometallic fragment $\{Cp^*Rh\}^{2+}$ have been isolated and characterized. X-ray quality crystals of $K_4[(Cp^*Rh)_2Nb_6O_{19}]\cdot 20H_2O$ (**1**) and $Cs_4[(Cp^*Rh)_2Ta_6O_{19}]\cdot 18H_2O$ (**2**) were obtained from solutions with $\{Cp^*Rh\}$:$[M_6O_{19}]^{8-}$ stoichiometry 2:1. Solution behavior of hybrid polyoxoanions was studied with ESI-MS and ^1H DOSY NMR. For the poorly investigated chemistry of polyoxotantalates complex **2** is the first complex bearing a grafted organometallic fragment. The formation of 1:1 complexes was detected by ESI-MS techniques.

Introduction

Chemistry of polyoxometalates (POM) is an actively depeloping area of modern coordination chemistry. A relatively new but already important branch of this chemistry is study of coordination of noble metals to POM.[1,2] Another emerging line of research is chemistry of polyoxoniobates and tantalates, which offer many chemical challenges like use pentagonal building blocks[3], nanosized catalysts for water splitting[4] etc. Coordination of organometallic fragments, such as $\{(p\text{-}cym)Ru\}^{2+}$ or $\{Cp^*Rh\}^{2+}$, to POM adds extra possibilities for the synthesis of hybrid complexes. This development reflects not only academic interest in such compounds, being a logical development of POM chemistry in general, but also is driven by the well-known catalytic properties of noble-metal complexes.[5] This point of view has a good endorsement in the chemistry of organometallic/oxide complexes of vanadium or mixed tungsten-vanadium or niobium-tungsten POM complexes.

In particular, $\{Cp^*Rh\}^{2+}$ is an excellent building block for grafting on POM, regardless of their charge and geometry. The hexavanadate complex $[\{Cp^*Rh\}_4(V_6O_{19})]$ was prepared from $[Cp^*RhCl_2]_2$ and $NaVO_3$.[6,7] The compound is stable in non-aqueous solvents and in water, but at pH<4 loses the organometallic moiety. This compound is a nice example of stabilization of a non-existing POM structure (free hexavanadate, $[V_6O_{19}]^{8-}$ has not been detected) by coordination. The stabilization is probably due to almost complete shielding the POM core by the bulky Cp* rings, and charge compensation. Liberation of $[Cp^*Rh(H_2O)_3]^{2+}$ groups can be followed by coordination of $[Cp^*Ir(H_2O)_3]^{2+}$ ones, and this generates the whole range of mixed rhodium–iridium-vanadium oxo-clusters $[\{Cp^*Rh\}_{4-n}\{Cp^*Ir\}_n(V_6O_{19})]$.[6,8,9] These Rh/V hexavanadates show catalytic activity.[5,10,11]

The three possible diastereoisomers of *cis*-$[\{Cp^*Rh\}Nb_2W_4O_{19}]^{2-}$ were obtained by reaction of $(Bu_4N)_4[\textit{cis}\text{-}Nb_2W_4O_{19}]$ with $[Cp^*Rh(MeCN)_3]^{2+}$ which yielded all three isomeric forms in a 1:1:1 ratio.[12]

Grafting $\{Cp^*Rh\}^{2+}$ onto a trisubstituted Nb-substituted silicon-tungsten Keggin-type polyanion gives 1:1 $[\{Cp^*Rh\}SiNb_3W_9O_{40}]^{5-}$ complex, in which the $\{Cp^*Rh\}^{2+}$ unit is attached to the μ_2-oxygen atoms flanking the NbW_2 site [13,14], while the V_3 site is preferred in the case of the vanadium analogue, $[\{Cp^*Rh\}(H_2PV_3W_9O_{40})]^{6-}$. The Nb-containing compound is stable in MeCN, in contrast to the vanadium analogues $[\{Cp^*Rh\}_2P_2V_3W_{15}O_{62}]^{5-}$ and $[\{Cp^*Rh\}P_2V_2W_{16}O_{62}]^{6-}$.[15] $[\{Cp^*Rh\}_2P_2V_3W_{15}O_{62}]^{5-}$ [16] and $[\{Cp^*Rh\}P_2V_2W_{16}O_{62}]^{6-}$ [17] were also reported. The organometallic rhodium fragments $\{Cp^*Rh\}^{2+}$ and $\{codRh\}^{+}$ were grafted onto Dawson-type $[P_2Nb_3W_{15}O_{62}]^{9-}$ anion with the formation of $[\{Cp^*Rh\}P_2Nb_3W_{15}O_{62}]^{7-}$ and $[(codRh)P_2Nb_3W_{15}O_{62}]^{8-}$.[18-20] The latter complex catalyzes oxidation of cyclohexene with O_2.[21]

No reports on coordination of $\{Cp^*Rh\}^{2+}$ to hexaniobate or hexatantalate exist, to the best of our knowledge. The reaction of isolobal $\{(p\text{-}cym)Ru\}^{2+}$ with $[Nb_6O_{19}]^{8-}$ gives a set of coordination species $[\{(p\text{-}cym)Ru\}_xNb_6O_{19}]^{(8-2x)-}$ (x up to 4).[22]

In this paper we report synthesis, crystal structures and characterization in solution of two new hybrid complexes of niobium and tantalum Lindqvist-type anions, $[M_6O_{19}]^{8-}$, with organometallic $\{Cp^*Rh\}^{2+}$ fragments.

Results and discussion

Organometallic fragments like $\{Cp^*Rh\}^{2+}$ and $\{(p\text{-}cym)Ru\}^{2+}$ are excellent building blocks for combining with POMs into hybrid complexes. They have predictable coordination geometry and can be used both for grafting on pre-existent POM species without changing their structure and for coordination-induced formation of new POM frameworks. The latter is the case with highly labile polymolybdates and polytungstates. The resulting complexes are also labile and can be converted into other species. Thus reaction of Na_2MoO_4 with $[Cp^*RhCl_2]_2$ leads to the formation of $[\{Cp^*Rh\}_4Mo_4O_{16}]$.[23] This can be converted by refluxing in MeOH into $[\{Cp^*Rh\}_2Mo_3O_9(OMe)_4]$. In organic solvents the latter species condense into $[\{Cp^*Rh\}_4Mo_6O_{22}]$ with a quadruple cubane structure.[24] Another hexanuclear complex, $[\{Cp^*Rh\}_2Mo_6O_{20}(OMe)_2]^{2-}$, was obtained by reaction of $[Cp^*RhCl_2]_2$ and $(Bu_4N)_2Mo_2O_7$ in methanol.[25] Such complexes may be relevant for catalysis.[5,26] Yet another complex, $[\{Cp^*Rh\}_8(Mo^{V}{}_{12}O_{36})(Mo^{VI}O_4)]^{2+}$, was obtained from MoO_3 and $[\{Cp^*Rh\}_2(OH)_3]Cl$ under hydrothermal conditions, when most of Mo^{VI} was reduced to Mo^{V}.[27] Reaction of $[Cp^*Rh(MeOH)_3]^{2+}$ (generated *in situ* from reaction of $AgNO_3$ and $[Cp^*RhCl_2]_2$ in methanol) with the nitrosyl derivative of an open Lindqvist anion $[Mo_5O_{13}(OMe)_4(NO)]^{3-}$ yields $[\{Cp^*Rh(H_2O)\}\{Mo_5O_{13}(OMe)_4(NO)\}]^{-}$.[28,29]

It is also possible to produce selectively two isomers of $[\{Cp^*Rh\}_4W_4O_{16}]$ by varying the temperature of the reaction synthesis in the $\{Cp^*Rh\}^{2+}/WO_4{}^{2-}$ system.[30]

A mixture of the $[\{p\text{-}cym\}RuCl_2]_2$ and $[Cp^*RhCl_2]_2$ with Na_2MoO_4 in water yielded new POM with two different noble metals: $[\{(p\text{-}cym)Ru\}\{Cp^*Rh\}_3Mo_4O_{16}]$ and $[\{(p\text{-}cym)Ru)_2\{Cp^*Rh\}_2Mo_4O_{16}]$.[31]

We have found in the present study that heating of $[Cp^*RhCl_2]_2$ with $K_7H[Nb_6O_{19}]\cdot 13H_2O$ or $Cs_8[Ta_6O_{19}]\cdot 14H_2O$ in water at 80-90 °C for 8 hours gives yellow-orange solutions. The molar ratio of $\{Cp^*Rh\}^{3+}$ and $[M_6O_{19}]^{8-}$ in both cases was 2:1. Vapor diffusion of acetone into the reaction solutions yielded orange X-ray quality crystals of **1** and **2**, respectively. IR spectroscopy and analytical data confirm the presence of Cp* ligands in the solid products, the ratio of $\{Cp^*Rh\}$:M_6O_{19} being 2:1 in both cases.

Crystal structures of both complexes contain hybrid anions *trans*-$[\{Cp^*Rh\}_2M_6O_{19}]^{4-}$ (fig. 1) with the typical Lindqvist-type oxide metal core (metal octahedron with one μ_6-, twelve μ_2- and six terminal oxygen ligands) decorated at an opposite pair of triangular $\{M_3O_3\}$ faces with organometallic fragments $\{Cp^*Rh\}^{2+}$. In both cases exclusively trans-isomers crystallize, which was confirmed by x-ray powder diffraction patterns of the products (see fig. S1, S2 in SI).

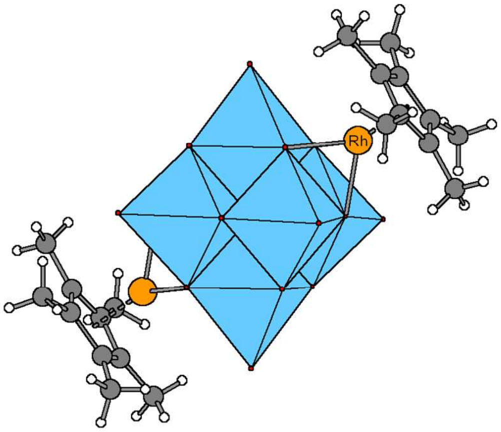

Fig. 1. Structure of *trans*-$[\{Cp^*Rh\}_2M_6O_{19}]^{4-}$, Rh is orange, $\{MO_6\}$ octahedrons are in light blue, C atoms are grey, H atoms are white.

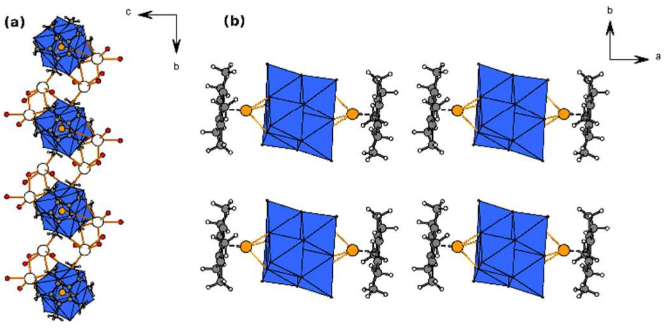

Fig. 2. (a) Crystal packing of **1** showing the connectivity between K^+ cations (white) and the Linqvist entity; (b) π-π interactions between the aromatic C_5 rings of two adjacent Linqvist entities in **1**.

Averaged Rh-O distances are 2.149(5) Å in **1** and 2.138(8) Å in **2**. For comparison, in $[Cp^*Rh(H_2O)_3](OTf)_2$ the Rh-O distance is 2.156(8) Å [32], in $[Cp^*{}_2Rh_2(OH)_3]\cdot 11H_2O$ - 2.109 Å.[33] This value is also close to 2.11 Å found both in $[\{Cp^*Rh\}_4V_6O_{19}]\cdot 3CH_3CN\cdot H_2O$ and in $[\{Cp^*Rh\}_3\{Cp^*Ir\}V_6O_{19}]\cdot 3CH_3CN\cdot H_2O$, which feature the same type of coordination of the $\{Cp^*Rh\}^{2+}$ unit.[8] The shortest Rh-O bond in this series (2.026 Å) is observed in $(NBu_4)_7[\{Cp^*Rh\}P_2W_{15}Nb_3O_{62}]$, where the $\{Cp^*Rh\}$ moiety is bound to the three Nb-O-Nb bridging oxygen atoms in the Dawson-type polyoxoanion.[19]

The crystal structure of **1** has layer-type packing ([011] orientation of layers) due to the presence of hydrophilic polyoxometalate part and hydrophobic Cp* ligands. (fig. 2b). The layers are combined together through π-π interactions of the aromatic C_5 rings. Two K^+ cations are coordinated to triangular $\{M_3O_3\}$ faces in *cis* positions relative to the organometallic $\{Cp^*Rh\}^{3+}$ fragments (K1 has CN = 8, $d(K1\text{-}O)_{av}$ = 2.918(6) Å, K2 has CN = 7, $d(K2\text{-}O)_{av}$ = 2.830(8) Å). The K^+ cations are connected into dimers by water molecules (fig. 2a). Such dimers are combined together through additional water molecules. High solubility of **1** in water can be explained by the relatively small number of K^+ cations (two), coordinated to *trans*-$[\{Cp^*Rh\}_2M_6O_{19}]^{4-}$ anion, in agreement with the explanation of the abnormal solubility trends in the alkali metal salts of polyniobates and polytantalates put forward by M. Nyman.[34]

The crystal structure of **2** also has a layer-type packing, but this time with [110] orientation of the layers (fig. S3, SI), due to the co-existence of hydrophilic polyoxometalate part and hydrophobic Cp* ligands. The cesium cations are coordinated to POM in the same way as K^+ in **1,** and also form dimers orientated along the layers (Cs1 with CN = 8, $d(Cs1\text{-}O)_{av}$ = 3.13(1) Å, Cs2 with CN = 9, $d(Cs2\text{-}O)_{av}$ = 3.11(1) Å) (fig. S4, SI). The symmetry of the unit cells of **1** and **2** are not the same due to the presence of more bulky Cs^+ cations in the crystal structure of complex **2**.

Both complexes produce basic solutions when dissolved in water. Dissolution of 10 mg of **1** or **2** in 2 ml of water gives the pH value of 8.8, which is lower comparing to that produced by alkali metal salts of $[M_6O_{19}]^{8-}$ (M = Nb, Ta) solutions of equal concentration (10.5-11.0). In order to explain the behavior of **1** and **2** in water ESI-MS experiments have been done. The ESI(-) mass spectrum of aqueous solutions of compound **1** (Figure 3a) displays the peak of $[(Cp^*Rh)_2Nb_6O_{19} + 2H]^{2-}$ dianion (m/z 669.7) as the main peak, accompanied by a minor signal due to the singly-charged $[(Cp^*Rh)_2Nb_6O_{19} + 3H]^-$ (m/z 1340.5). The ESI(-) mass spectrum of aqueous solutions of **2** is very much alike to that observed for **1** (fig. 3b), and displays expected signals from the protonated adducts of the $[(Cp^*Rh)_2Ta_6O_{19}]^{4-}$ anion as dominant species, namely $[(Cp^*Rh)_2Ta_6O_{19} + 2H]^{2-}$ and $[(Cp^*Rh)_2Ta_6O_{19} + 3H]^-$ at m/z 933.8 and 1868.6, respectively.

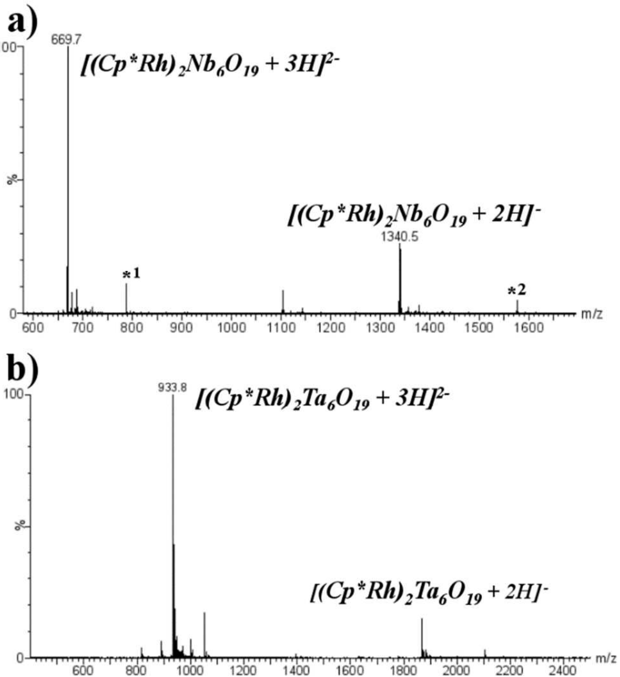

Fig. 3. ESI(-) mass spectra of aqueous solutions recorded at Uc = 10 V of the reaction mixture after the synthesis of **1** (a) and **2** (b). $*^1$ and $*^2$ correspond to $[(Cp^*Rh)_3Nb_6O_{19}]^{2-}$ and $[(Cp^*Rh)_3Nb_6O_{19} + H]^-$, respectively.

It means that in the water solution both anions $[(Cp^*Rh)_2M_6O_{19}]^{2-}$ produce two identical protonation forms $[(Cp^*Rh)_2M_6O_{19} + 2H]^{2-}$ and $[(Cp^*Rh)_2M_6O_{19} + 3H]^{2-}$. This protonation indicates the basic nature of the $[\{Cp^*Rh\}_2M_6O_{19}]^{4-}$ anions and is responsible for pH increase.

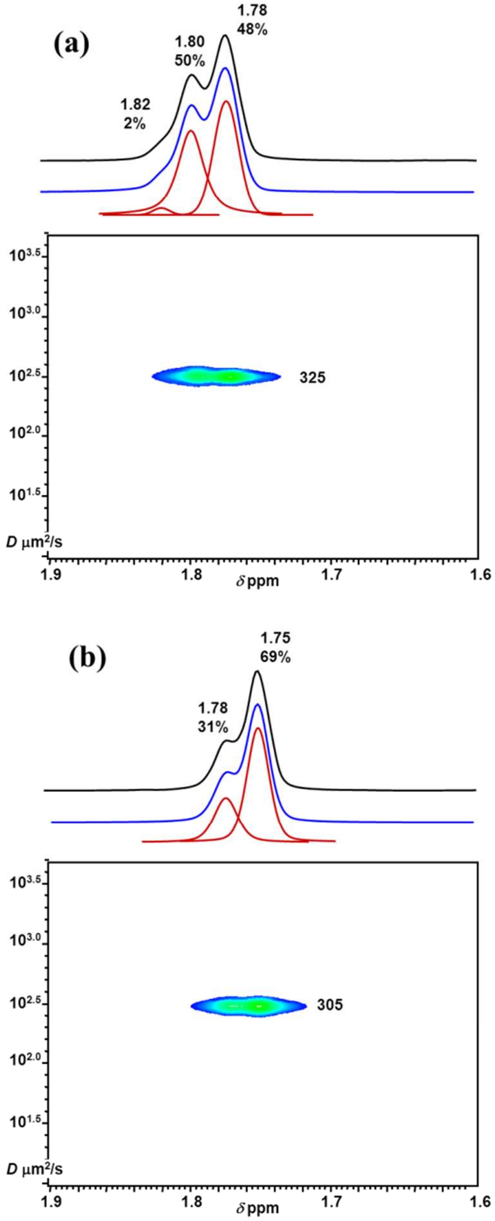

Fig. 4. ^{1}H NMR (up) and 2D ^{1}H DOSY NMR (bottom) spectra of the reaction mixture after the synthesis of **1** (a) and **2** (b) in D_2O. The experimental spectra are given in black, the simulated spectra in blue and the deconvoluted spectra in red.

In attempt to check if other species were present in solution, NMR studies of the reaction mixtures after the isolation of **1** and **2** were done. $[Cp^*{}_2Rh_2(OH)_3]^+$ has a signal in ^{1}H NMR (D_2O) at 1.61 ppm, which was absent in our reaction mixture. The signal at 1.50 ppm attributable to $[Cp^*Rh(H_2O)_3]^+$ was also absent in our reaction mixtures. In the case of **1**, ^{1}H NMR spectrum shows two main singlets located at 1.80(s) and 1.78(s) ppm in 50:48 ratio, whereas a minor signal representing about 2% of total intensity is located at 1.82 ppm (Fig. 4a).

In ^{13}C NMR spectra two sets of signals from coordinated Cp* ligands 8.48 (s), 8.43 (s); 93.75 (d, ^2J = 10 Hz), 93.56 (d, ^2J = 10 Hz) are observed (Fig. 5a). The ^{1}H

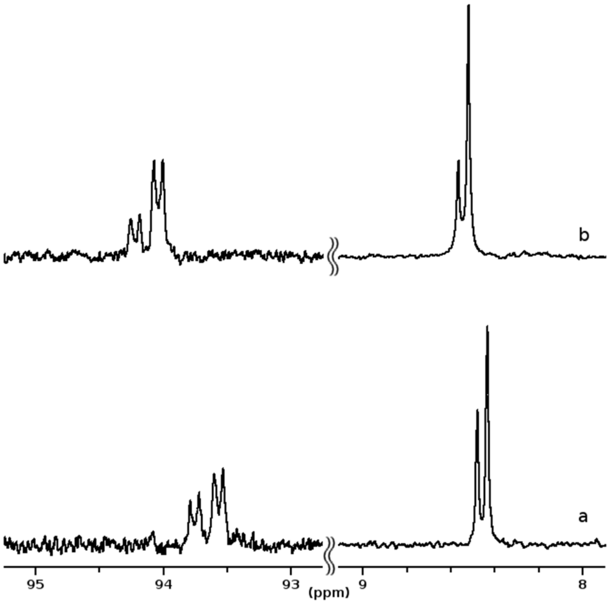

Fig. 5. ^{13}C NMR Spectra of **1** (a) and **2** (b) in D_2O.

DOSY NMR technique is a powerful tool for identifying inorganic clusters in aqueous medium.[35] A ^{1}H DOSY NMR experiment performed on the reaction mixture from the synthesis of **1** in D_2O (Fig. 4a) has yielded the same self-diffusion coefficients D = 325 ± 10 μm²·s^{-1} for the two main signals found at 1.80 and 1.78 ppm, whereas the intensity of the minor peak at 1.82 ppm was too low for any accurate determination of the D value. These identical values evidence that both species possess similar hydrodynamic radii in solution and the Stokes-Einstein relation applied to the latter give hydrodynamic radii of 0.675 nm which are compatible with the radii expected for the solvated *trans* and *cis* isomers (this notation implies that the {Cp*Rh} units are attached at the opposite (*trans*) or adjacent (*cis*) faces of the $\{M_6O_{19}\}$ superoctahedron. of the monomeric species $[(Cp^*Rh)_2Nb_6O_{19}]^{4-}$. The minor peak located at 1.82 ppm could result from another minor isomer or a $[(Cp^*Rh)_3Nb_6O_{19}]^{2-}$ identified by ESI-MS as a minor species (m/z 787.7), as protonated $[(Cp^*Rh)_3Nb_6O_{19} + H]^-$ adduct at m/z 1576.5 from the analysis of the reaction mixture. In the case of pure **1** only two signals at 1.82 and 1.78 ppm were detected with the same diffusion coefficients. We can cite the NMR characteristics of $[Cp^*RhMoO_4]_4{\cdot}2H_2O$ in $CDCl_3$, which are related to our case: ^{1}H NMR ($CDCl_3$) 1.75 s; ^{13}C NMR 9.33 s, 90.15 d ($J^2_{Rh\text{-}C}$ = 8.8 Hz).[36]

To confirm the suggestion about possible *cis-trans* isomerization in the solution ^{1}H-NMR temperature dependent experiments have been carried out. The complex **1** (10 mg) was solved in 1 ml of D_2O at 1°C. ^{1}H NMR spectrum at 1 ºC shows two signals with relative intensities 0.35:0.65. Heating this solution to 80 ºC and doing NMR scans after each 10 degrees finally gives 0.45:0.55 ratio, that did not change after keeping of the solution for 1 hour at 80 ºC. However, after dissolution of pure trans isomer (as confirmed by XRPD) the equilibrium between cis – trans is unlikely to immediately produce (at 0 ºC) a comparable amount, in the 0.35:0.65 ratio, of the isomers. We rather believe that in the solution we have non-equivalent protons due to the hindering of free rotation of the methyl groups in the bulky Cp* in order to avoid to close contacts of H atoms of the CH_3 groups with terminal oxygen atoms coordinated to niobium (Fig. 6).

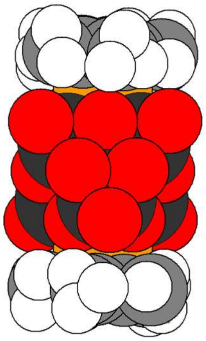

Fig. 6. View of *trans*-$[\{Cp^*Rh\}_2M_6O_{19}]^{4-}$ (M = Nb (**1**), Ta (**2**)). The atoms are shown according to their van-der-Waals radii.

In the case of hexatantalate (**2**) the NMR studies also show the presence of two main signals: in ^{1}H NMR 1.78 (s) and 1.75 (s) ppm (fig. 4a) with intensity ratio of 31:69, and in ^{13}C NMR: 8.6 (s), 8.57 (s), 94.25 (d, ^2J = 10 Hz), 94.07 (d, ^2J = 10 Hz) ppm (fig. 5b). The same value of the self-diffusion coefficients, D = 305 ± 10 μm²·s^{-1}, was found for both signals by ^{1}H DOSY. This value give a hydrodynamic radius of 0.720 nm, which is consistent with the values expected for the solvated *trans*-$[\{Cp^*Rh\}_2Ta_6O_{19}]^{4-}$. VT- ^{1}H NMR experiments for this solution lead to the same conclusions as for complex **1**, indicating non-equivalence of protons in the CH_3 groups as the reason for splitting signals in NMR, and not the *cis-trans* isomerization.

The reactions of $[M_6O_{19}]^{8-}$ salts with $[Cp^*RhCl_2]_2$ at the 1:1 molar ratio were with ESI-MS spectrometry. The components were reacted in 1:1 ratio under the same conditions as were used in preparation of the 1:2 complexes. Attempts to obtain single crystals from these reaction mixtures failed. Acetone vapor diffusion produced poorly diffracting yellow solids. These solids were extracted with MeOH yielding yellow solutions. In the case of Nb complexes signals from ($[\{Cp^*Rh\}Nb_6O_{19}H_5]^-$, m/z 1104; $[\{Cp^*Rh\}Nb_6O_{17}(OMe)_2H_3]^-$, m/z 1132; $[\{Cp^*Rh\}Nb_6O_{18}(OMe)H_4]^-$, m/z 1118; plus corresponding signals from various {H+K+M} associates) as well as from 1:2 species ($[\{Cp^*Rh\}_2Nb_6O_{19}H_3]^-$, m/z 1340; $[\{Cp^*Rh\}_2Nb_6O_{18}(OMe)H_2]^-$, m/z 1354; $[\{Cp^*Rh\}Nb_6O_{16}(OMe)_3H_3]^-$, m/z 1382; and the signals from the {H+K+M} associates) were detected. In the case of hexatantalate only signals from 1:1 complex were detected, namely, ($[\{Cp^*Rh\}Ta_6O_{18}(OMe)H_3]^{2-}$ m/z 824; $[\{Cp^*Rh\}Ta_6O_{18}(OMe)H_4]^-$ m/z 1646). Attempts at isolation of these methoxide complexes are under way.

Experimental

General procedures

Starting $K_7H[Nb_6O_{19}]\cdot 13H_2O$ and $Cs_8[Ta_6O_{19}]\cdot 14H_2O$ were synthesized as described in the literature.[37,38] $[Cp^*RhCl_2]_2$ was obtained from $RhCl_3\cdot 3H_2O$ with Cp*H by the standard procedure.[39] Other reagents were of commercial quality and used as purchased.

IR spectra (4000 – 400 cm^{-1}) were recorded on an IFS-85 Bruker spectrometer and presented in SI (fig. S5).

EDX measurements were performed on a JEOL JSM 5800LV apparatus.

Electrospray ionization (ESI) mass spectra

Electrospray ionization (ESI) mass spectra were recorded on a QTOF Premier (quadrupole-T-wave-time-of-flight) instrument. The temperature of the source block was set to 100 ºC and the desolvation temperature to 200 ºC. A capillary voltage of 3.3 kV was used in the negative scan mode and the cone voltage was set to 10 V to control the extent of fragmentation of the identified species. Mass calibration was performed using a solution of sodium iodide in isopropanol:water (50:50) from m/z 50 to 3000. Sample solutions ca. 5×10^{-5} M in water were infused via syringe pump directly connected to the ESI source at a flow rate of 10 μL/min. The observed isotopic pattern of each compound perfectly matched the theoretical isotope pattern calculated from their elemental composition using the MassLynx 4.1 program.

NMR experiments

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance 400 and 500 spectrometers respectively with inner references in D_2O at room temperature. Translational diffusion measurements were performed using Bruker's 'ledbpgs2s' stimulated echo DOSY pulse sequence including bipolar and spoil gradients. Apparent diffusion coefficients were obtained using an adapted algorithm based on the inverse Laplace transform and maximum entropy.

X-ray crystallography

Crystallographic data and refinement details are given in Table S1. The diffraction data were collected on a Bruker Apex Duo diffractometer with MoKα radiation (λ = 0.71073 Å) by doing φ and ω scans of narrow (0.5°) frames at 100 K. Structures of **1** and **2** were solved by direct methods and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation with SHELXTL programs set.[40] Absorption corrections were applied empirically with SADABS program.[41] All non-hydrogen atoms of main structural units were refined anisotropically. Positions of all cations in both structures are fully occupied, that prevent protonation of hybrid polyoxoanions. Further details may be obtained from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC 1016219-1016220. Copies of this information may be obtained free of charge from http://www.ccdc.cam.ac.uk.

K_4[*trans*-$\{Cp^*Rh\}_2Nb_6O_{19}]\cdot 20H_2O$ (1): 0.050 g (0.036 mmol) of $K_7H[Nb_6O_{19}]\cdot 13H_2O$ was dissolved in 4 ml of H_2O under stirring and heating at 80 °C. 0.023 g (0.037 mmol) of $[Cp^*RhCl_2]_2$ was then added to a clear solution of hexaniobate, and the reaction mixture was stirred for 8 hours at 80 °C, leading to complete dissolution of $[Cp^*RhCl_2]_2$. Vapor diffusion of acetone into resulting orange solution yielded a crop of yellow-orange crystals of **1**. Yield 80%. The pH of solution obtained from dissolution of 10 mg in 2 ml H_2O is 8.8. Elemental analysis Calculated $C_{20}H_{70}K_4Nb_6O_{39}Rh_2$ C, H (%): 12.9; 3.8. Found C, H (%): 12.3; 3.3. IR (KBr pellet, cm^{-1}): 3343(s), 2911(m), 1626(m), 1465(m), 1375(m), 1081(w), 1024(w), 853(s), 777(s), 659(s), 550(s), 497(s), 407(s). EDX atomic ratios calculated for **1** (found): Nb/Rh = 3.00 (2.85), K/Rh = 2.00 (1.85). ^1H NMR (δ, ppm): 1.7 (s), 1.68 (s); ^{13}C NMR (δ, ppm): 8.48 (s), 8.43 (s), 93.75 (d, ^2J = 10 Hz), 93.56 (d, ^2J = 10 Hz).

Cs_4[*trans*-$\{Cp^*Rh\}_2Ta_6O_{19}]\cdot 18H_2O$ (2) was obtained in a similar way from 0.1 g (0.037 mmol) $Cs_8[Ta_6O_{19}]\cdot 14H_2O$ and 0.023 g (0.037 mmol) of $[Cp^*RhCl_2]_2$. Yield 70%. The pH of solution obtained from dissolution of 10 mg in 2 ml H_2O is 8.8. Elemental analysis Calculated $C_{20}H_{66}Cs_4O_{37}Rh_2Ta_6$ C, H (%): 8.8; 2.4. Found C, H (%): 9.2; 2.1. IR (KBr pellet, cm^{-1}): 3366(s), 3232(s), 2932(m), 1653(w), 1465(w), 1379(w), 1079(w), 1026(w), 854(s), 780(s), 679(s), 531(m), 511(m), 471(m), 431(m). EDX atomic ratios calculated for 2 (found): Ta/Rh = 3.00 (3.11), Cs/Rh = 2.00 (2.01). ^1H NMR (δ, ppm): 1.77 (s), 1.75 (s); ^{13}C NMR (δ, ppm): 8.6 (s), 8.57 (s), 94.25 (d, ^2J = 10 Hz), 94.07 (d, ^2J = 10 Hz).

Conclusions

The chemistry of polyoxoniobates and tantalates is a relatively new field in the polyoxometalate science. In particular, little is known about coordination chemistry of $[Ta_6O_{19}]^{8-}$. This work has yielded two new hybrid POMs based on Lindqvist-type $[M_6O_{19}]^{8-}$ (M = Nb, Ta) and organometallic fragment

$\{Cp^*Rh\}^{2+}$. $K_4[trans\text{-}\{Cp^*Rh\}_2Nb_6O_{19}]\cdot 20H_2O$ (**1**) and $Cs_4[trans\text{-}\{Cp^*Rh\}_2Ta_6O_{19}]\cdot 18H_2O$ (**2**) were isolated and characterized in solid state and in solution. According to ESI-MS experiments $[\{Cp^*Rh\}_2M_6O_{19}]^{4-}$ anions are the dominant forms. Their protonation accounts for the basicity of aqueous solutions of **1** and **2**. ^1H DOSY and VT-NMR data show the presence of *trans*-isomer in solution for both complexes, and reveal hindered rotation of the CH_3 groups of the Cp* rings.

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Notes and references

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Electronic Supplementary Information (ESI) available: X-ray powder patters (Figures S1 and S2), crystal packing of compound 2 (Figures S3 and S4); IR spectra of compounds 1 and 2 (Figure S5). See DOI: 10.1039/b000000x/

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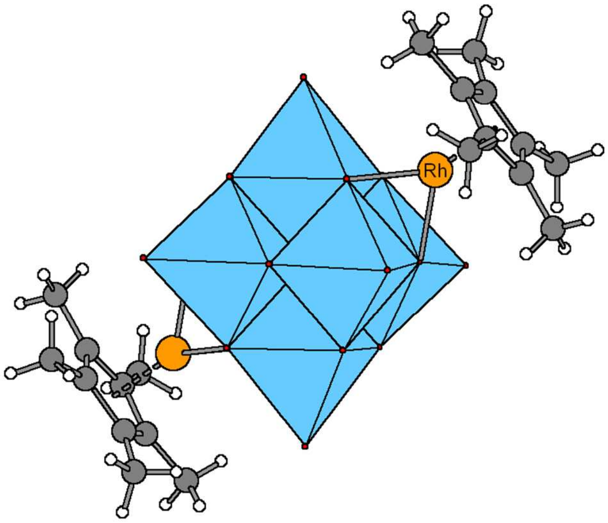

Structure of a new hybrid organometallic-POM complex [trans-{Cp*Rh}2M6O19]4- (M = Nb, Ta)