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Unique solubility of polyoxoniobate salts in methanol: coordination to cations and POM methylation

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Sodium salts of hybrid organometallic POM complexes consisting of $[M_6O_{19}]^{8-}$ ($M = Nb, Ta$) and half-sandwich fragments $\{Cp^*M\}^{2+}$ ($Cp^* = \eta^5-C_5(CH_3)_5$; $M = Rh, Ir$) and $\{(C_6H_6)Ru\}^{2+}$ dissolve only in one organic solvent – in methanol. From methanolic solutions crystals of $Na_4[trans-\{(C_6H_6)Ru\}_2Nb_6O_{19}] \cdot 14.125MeOH \cdot 2H_2O$ (**1**), $K_4[trans-\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 4MeOH \cdot 10H_2O$ (**2**) and $K_4[trans-\{Cp^*Ir\}_2Nb_6O_{19}] \cdot 10MeOH \cdot 4H_2O$ (**3**) were isolated and characterized by X-ray analysis. Methoxo species $\{[LM']_2M_6O_{19-n}(OCH_3)_n\}$ ($n = 1-3$) were detected in solution by ESI-MS and NMR, and they account only for about half the total speciation in the solution. DFT calculations were used to calculate ^{13}C NMR chemical shifts in the methoxo complexes and to assess their relative stability. Reasons for the preferred solubility in methanol are discussed.

Introduction

The chemistry of polyoxoniobates and tantalates is routinely confined to strongly alkaline aqueous solutions, but a remarkably rich chemistry is displayed even under these restrictions.¹ Non-aqueous chemistry of Nb and Ta polyoxometalates is by far less studied. Hydrated Nb_2O_5 can be solubilized in methanol under solventothermal conditions in the presence of Me_4NOH as a base.² It also reacts with different organic bases in acetonitrile. In this way $[Nb_{10}O_{28}]^{6-}$,³ $[Nb_{20}O_{54}]^{8-}$ ⁴ as well as recently reported $[Ta_{10}O_{28}]^{6-}$ ⁵ were prepared. The main reason of the strong bias in favor of choosing water as solvent is the high charge of the polyoniobates, which requires large amounts of counter cations, typically alkali metal cations. This leads to high lattice energies, which can be counterbalanced only by a solvent with high dielectric constant and donor/acceptor number, preferably with water. Hydrogen bonds also play an important part in stabilizing the highly charged polyanions, and those are again best provided by water. Can hydrated alkali metal salts of highly charged polyoxometalates be dissolved and handled in organic solvents? One can expect that coordination of a positively charged organometallic moiety such as $\{Cp^*M\}^{2+}$ ($M = Rh, Ir$) or $\{(arene)Ru\}^{2+}$ (arene is benzene and its derivatives) to $[Nb_6O_{19}]^{8-}$ would reduce the overall negative charge and simultaneously increase the hydrophobicity of the hybrid complex, thus enabling solubility in organic solvents. Indeed,

A. Proust et al. reported that neutral complex $\{[(p-cym)Ru]_4Nb_6O_{19}\}$ ($p-cym = 1-Methyl-4-(1-methylethyl)benzene$) was soluble in CH_3OH , and negative ion mode electrospray mass-spectrum of methanolic solutions detected formation of the methoxocomplexes $\{[(p-cym)Ru]_2Nb_6O_{16}(OCH_3)_3\}^-$ and $\{[(p-cym)Ru]_3Nb_6O_{18}(OCH_3)_2\}^-$, arising from de-complexation of one or two $\{(p-cym)Ru\}^{2+}$ fragments and formation of $Nb-OCH_3$ bonds.⁶ This solvolytic behavior in methanol is strongly reminiscent of the reactivity of $[Nb_2W_4O_{19}]^{4-}$ towards CH_3OH , and of $[P_2W_{15}V_3O_{62}]^{9-}$ with $CH_3C(CH_2OH)_3$.^{7,8} In the present study we found that sodium salts of $\{[(C_6H_6)Ru]_2Nb_6O_{19}\}^{4-}$, $\{[Cp^*Rh]_2Nb_6O_{19}\}^{4-}$ and $\{[Cp^*Ir]_2Nb_6O_{19}\}^{4-}$ are soluble in methanol, but not in ethanol or other organic solvents. Both the solvolysis of the anion and solvation of the alkali metal cation are the driving force in our case: the methoxo species $\{[LM']_2M_6O_{19-n}(OCH_3)_n\}$ ($n = 1-3$) are detected by ESI-MS and NMR, and they account for about half the total speciation of the hybrid complexes in methanol. From these solutions crystals of $Na_4\{[(C_6H_6)Ru]_2Nb_6O_{19}\} \cdot 14.125MeOH \cdot 2H_2O$ (**1**), $K_4[trans-\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 4MeOH \cdot 10H_2O$ (**2**) and $K_4[trans-\{Cp^*Ir\}_2Nb_6O_{19}] \cdot 10MeOH \cdot 4H_2O$ (**3**) were isolated in high yields, which bear no $Nb-OCH_3$ groups, but show direct coordination of CH_3OH to Na^+ instead. These observations are presented and discussed in detail below.

Results and discussion

ESI-MS experiments

First indications of the formation of methoxocomplexes were obtained from ESI-MS experiments. Reactions of $[M_6O_{19}]^{8-}$ ($M = Nb$ and Ta) salts with $[Cp^*RhCl_2]_2$ at the Rh/M_6 2:1 ratio in water yielded solids containing the $\{[Cp^*Rh]_2M_6O_{19}\}^{4-}$ anions.

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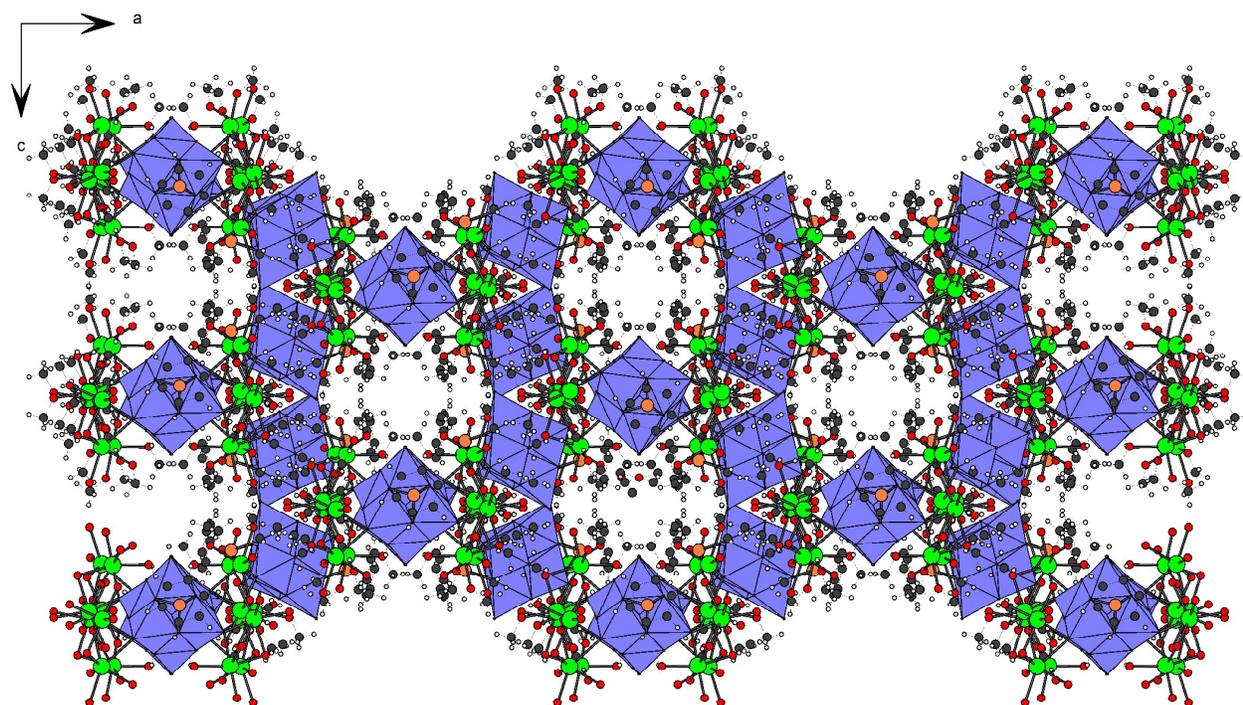


Fig. 1. Infinite channels occupied only with disordered methanol molecules (removed for clarity) in the crystal packing of **1**. Lindqvist anions are shown in blue polyhedra, sodium cations are colored in green.

When their ESI(-) mass spectra were investigated using methanol as solvent, signals attributed to methoxo species were readily identified on the basis of their m/z value as well as their isotopic distribution. In particular signals from the 2 : 1 species $[\{(\text{Cp}^*\text{Rh})_2\text{Nb}_6\text{O}_{19}\text{H}_3\}]^-$ (m/z 1340), $[\{(\text{Cp}^*\text{Rh})_2\text{Nb}_6\text{O}_{18}(\text{OCH}_3)\text{H}_2\}]^-$, (m/z 1354) and $[\{(\text{Cp}^*\text{Rh})_2\text{Ta}_6\text{O}_{19}\text{H}_3\}]^-$, (m/z 1868); $[\{(\text{Cp}^*\text{Rh})_2\text{Ta}_6\text{O}_{18}(\text{OCH}_3)\text{H}_2\}]^-$ (m/z 1882) were identified. Table S1 collects the m/z values for the methoxo species identified. Signals from 1:1 adducts, namely $[\{(\text{Cp}^*\text{Rh})\text{Nb}_6\text{O}_{19}\text{H}_5\}]^-$, (m/z 1104), $[\{(\text{Cp}^*\text{Rh})\text{Nb}_6\text{O}_{17}(\text{OCH}_3)_2\text{H}_3\}]^-$ (m/z 1132), $[\{(\text{Cp}^*\text{Rh})\text{Nb}_6\text{O}_{18}(\text{OCH}_3)\text{H}_4\}]^-$ (m/z 1118) and $[\{(\text{Cp}^*\text{Rh})\text{Ta}_6\text{O}_{18}(\text{OCH}_3)\text{H}_3\}]^{2-}$ (m/z 824), and $[\{(\text{Cp}^*\text{Rh})\text{Ta}_6\text{O}_{18}(\text{OCH}_3)\text{H}_4\}]^-$ (m/z 1646),⁹ were also observed in their respective ESI mass spectra in methanol. We also found that sodium salts of 2:1 and 1:1 complexes $\text{Na}_4[\{(\text{Cp}^*\text{Ir})_2\text{Nb}_6\text{O}_{19}\} \cdot 22\text{H}_2\text{O}]$ and $\text{Na}_6[\{(\text{Cp}^*\text{Ir})\text{Ta}_6\text{O}_{19}\} \cdot 27\text{H}_2\text{O}]$ were soluble in CH_3OH , and signals from the corresponding anions

as well as from their mono- and dimethylated derivatives $[\{(\text{Cp}^*\text{Ir})_2\text{Nb}_6\text{O}_{18}(\text{OCH}_3)\text{H}\}]^{2-}$ (m/z 765) and $[\{(\text{Cp}^*\text{Ir})_2\text{Nb}_6\text{O}_{17}(\text{OCH}_3)\text{H}_2\}]^-$ (m/z 1532) were detected (see for example Fig. S1, S2) in these solutions.¹⁰ Methoxo complexes were also detected in the ESI-MS spectra of $[\{(\text{Cp}^*\text{Ir})_2\text{TeNb}_5\text{O}_{19}\}]^{3-}$ and $[\{(\text{Cp}^*\text{Ir})\text{TeNb}_5\text{O}_{19}\}]^{5-}$.¹¹ This indicates the proclivity of the Lindqvist POMs to form methoxo species upon dissolving in methanol.

Since in all cases formation of methylated hybrid anions was detected by ESI-MS experiments in freshly prepared methanolic solutions, it would appear that they rapidly form in solution in significant amounts, up to a certain equilibrium point between the starting oxo and methoxo species. However, we are aware that the large methanol excess employed for sample preparation for ESI-MS analysis (sample concentration ca. 5×10^{-5} M in CH_3OH) might exaggerate the propensity of the oxo or hydroxo groups to be replaced by methoxo; in addition, the appearance of the signals due to

methoxo species may be due to secondary processes operative only in the gas phase under experimental conditions. Therefore we tried to isolate methoxocomplexes directly from methanolic solutions and demonstrate their formation in solution by X-ray crystallography and NMR techniques, respectively.

X-ray structures

The reaction of sodium hexaniobate with $[(C_6H_6)RuCl_2]_2$ proceeds slowly upon dissolution of the ruthenium complex in water solution of hexaniobate, which typically takes 1-2 hours to completion depending on the loads and temperature, and then the yellow solution is heated and stirred for 12 h. The product is precipitated with acetone (slow diffusion gives yellow crystals; quick addition – yellow precipitate). Recrystallization from CH_3OH yields large yellow plates of $Na_4\{[(C_6H_6)Ru]_2Nb_6O_{19}\} \cdot 14.125MeOH \cdot 2H_2O$ (**1**), whose structure was determined. The phase purity of the product was confirmed by XRPD.

The crystal structure of **1** consists of $trans-[(C_6H_6)Ru]_2Nb_6O_{19}^{4-}$ hybrid anions and sodium cations, which aggregate into $[(MeOH)_3Na(\mu-MeOH)Na(H_2O)(MeOH)_2]^{2+}$ dimers; hence the formula of **1** is better rendered as $[(MeOH)_3Na(\mu-MeOH)Na(H_2O)(MeOH)_2]_2\{[(C_6H_6)Ru]_2Nb_6O_{19}\} \cdot 2.125MeOH$. The cationic dimers unite the anions into a 3D framework (Fig. 1). This is the first example of breaking the standard layered structural motif common to all previously known hybrid complexes bearing two coordinated C_6H_6 or Cp^* fragments.^{6,9} The formation of the 3D framework (the building block is presented in Fig. S3) creates infinite channels running along [010] and [100] crystallographic directions, which are filled with disordered methanol molecules (2.125 molecules per formula unit from XRD refinement) (Fig. S4). The methanol molecules that are coordinated to the cations form strong hydrogen bonds with bridging oxo ligands ($d(MeOH \cdots \mu_2-O)$ are 2.645 and 2.701 Å) of the hybrid POM. Moreover, one solvate water molecule forms a weaker hydrogen bond with μ_2-O ($H_2O \cdots O$ distance is 2.821 Å).

$trans-K_4\{[Cp^*Rh]_2Nb_6O_{19}\} \cdot 20H_2O^9$ and $trans-K_4\{[Cp^*Ir]_2Nb_6O_{19}\} \cdot 22H_2O^{10}$ also dissolve in methanol, but crystalline samples could not be obtained by straightforward evaporation of the solvent. In one of the crystallization attempts we added a few milligrams of dibenzo-18-crown-6 to the methanolic solutions, which then were left at 2 °C. Yellow single crystal plates were obtained in both cases, but curiously enough, no crown ether molecules entered the structure, the formulae of the products being $trans-K_4\{[Cp^*Rh]_2Nb_6O_{19}\} \cdot 4MeOH \cdot 10H_2O$ (**2**) and $trans-K_4\{[Cp^*Ir]_2Nb_6O_{19}\} \cdot 10MeOH \cdot 4H_2O$ (**3**). Possibly the crown ether binds excess water, forming associates with strong hydrogen bonds, which remain in solution, but this hydration shifts equilibrium and facilitates formation of **2** and **3**. They two salts are obviously not isostructural, and **2** crystallizes in $P2_1/c$ space group while **3** adopts $P-1$ group. This difference is due to the different values in the content of methanol and water molecules. However, whatever the differences, in both

structures the hybrid anions $trans-[(Cp^*M)_2Nb_6O_{19}]^{4-}$ are combined with the cationic part (there are infinite chains of the cations connected with solvate methanol, water molecules and oxygen ligands of the anions, Fig. S5, S6) into the layers spreading along [011] ($M = Rh$) or [110] ($M = Ir$) crystallographic directions (Fig. S7, S8). Both in **2** and **3** additional K^+ cations coordinate free $\{Nb_3O_3\}$ faces of the anions. In **2** such cations have CN 7 (with three oxo ligands from anion face, three water molecules and one methanol, Fig. S9), in **3** K^+ has CN 8 (three oxo ligands from anion face, three water molecules and two methanol molecules, Fig. S10, left). Methanol molecules, coordinated to the cations, form hydrogen bonds with POM both in **2** and **3**. In **2** only the methanol molecules that are located in the positions near to the anion produce hydrogen bonds ($d(Nb=O \cdots HOCH_3)$ is 2.761 Å) stronger than water molecules ($d(Nb=O \cdots H_2O)$ is 2.900 Å) (Fig. S9). This effect is more significant in the case of **3**, which has more CH_3OH molecules in the structure. All methanol molecules are oriented in a way to afford hydrogen bonding with the anion ($d(O \cdots O) = 2.717-2.748$ Å) (Fig. S10, right). Details of XRD experiments and refinement are summarized in Table S2.

Qualitative experiments have shown that also Cs^+ (Ta), K^+ (Nb), Na^+ (Ta, Nb) salts for $[(Cp^*M)_2M_6O_{19}]^{4-}$ complexes ($M = Rh, Ir$), and K^+ (Nb), Na^+ (Nb, Ta) salts for $[(C_6H_6)Ru]_2M_6O_{19}^{6-}$ complexes are soluble in methanol. Attempts to get crystals from these solutions failed. The crystal packing of all starting materials consists of the layers formed by the hybrid anions and solvated cations which stack together only through $\pi-\pi$ interactions between the aromatic rings of the organic ligands. Methanol can penetrate between such layers and replace water in the coordination spheres of the cations, while CH_3CN or CH_2Cl_2 cannot do this.

¹³C and ¹H NMR experiments

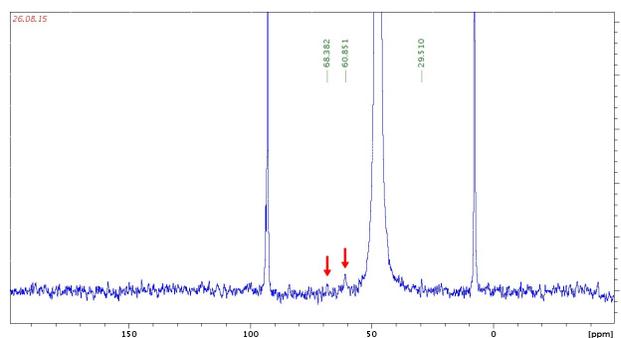


Fig. 2. ¹³C NMR spectrum of d^4 -MeOH solution of **2**.

The compounds **1-3** were isolated in high yields. This means either means that methoxocomplexes are present only in solution in a rapidly shifting equilibrium so that they dissociate upon crystallization, or they are kinetically stable, but only as a minor component of the complicated equilibria. In order to check this hypothesis we studied methanolic solutions of **2** and

3 by NMR. In the ^{13}C NMR spectra of **2** and **3** in CD_3OD there appear two signals at 68 and 61 ppm for the Rh complex (Fig. 2), and 61 and 56 ppm for the Ir complex (Fig. 3), in addition to the signals from Cp^* ligands.

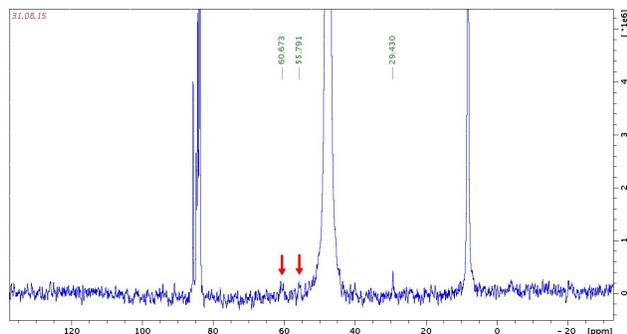


Fig. 3. ^{13}C NMR spectrum of **3** in CD_3OD .

Table 1. ^1H NMR data for **1-3** in CD_3OD .

Complex	$\delta(\text{term})^*$	$\delta(\text{bridged})^*$
1	3.530, 3.520, 3.504, 3.491, 3.468	4.284
2	3.670	4.002, 3.987, 4.553, 4.537, 4.528
3	3.678, 3.630	4.347, 4.334, 4.307, 4.294, 4.260

* assigned from ref. 14.

Since free methanol gives ^{13}C NMR resonance at 49.5 ppm, these signals can be assigned to coordinated CH_3O^- . Indeed, Errington et al. reported for $(\text{Bu}_4\text{N})_2[(\text{MeO})\text{NbW}_5\text{O}_{18}]$ in CD_3CN $\delta_{\text{CH}_3\text{O}}$ at 65.91 ppm.¹² Similar chemical shifts for various methoxy species were reported elsewhere.¹³ Karaliota et al. even discriminated between terminal $\text{Nb}-\text{OCH}_3$ and bridging $\text{Nb}-(\mu-\text{OCH}_3)-\text{Nb}$ modes, assuming δ 67 ppm for the bridging and 60-64 ppm for terminal methoxy ligand for solutions of NbCl_5 in methanol.¹⁴ Thus ^{13}C NMR gives evidence for formation of methoxocomplexes in methanolic solutions of **2** and **3**. In order to confirm this assignment we carried out DFT calculation of ^{13}C chemical shifts taking methylated isomers of $[(\text{Cp}^*\text{Ir})_2\text{Nb}_6\text{O}_{18}(\text{OCH}_3)]^{3-}$ as models, which yielded δ_{CH_3} 60.6 ppm and 63.4 ppm for terminal and bridging methoxide, respectively. These results show that the difference between chemical shifts of the terminal and bridged methoxy ligand is meaningful and agrees with Karaliota's assignment. According to ^{13}C NMR, we have complexes with both terminal (upfield) and bridging (downfield) CH_3O^- ligand in solution. Three isomers are possible, as shown in Fig. 4. The formation of the new species in CH_3OH solutions can be also deduced from new signals from Cp^* which appear at 93.70 and 94.23 ppm as

broad resonances, together with signals from starting $\text{trans}-[(\text{Cp}^*\text{Rh})_2\text{Nb}_6\text{O}_{19}]^{4-}$ at 92.91 and 92.68 ppm.

The methyl group proton (^1H NMR) resonances which appear in solutions of NbCl_5 in CH_3OH fall in three series around 4.5 ppm, 4.2-3.8 ppm, and 3.3 ppm regions, and are due to bridging, terminal methoxides, and to free methanol, respectively.^{14,15} ^1H NMR of **1** in MeOH gives δ = 3.530, 3.520, 3.504, 3.491, 3.468 ppm for terminal coordination and δ = 4.284 ppm for bridging coordination, but in ^{13}C NMR we observed only one signal at 61 ppm. For complex **2** ^1H NMR also shows formation of terminal MeO^- species (δ = 3.67 ppm), but peaks from bridging ligands also appear at 4.53-4.55 ppm. The Cp^* signals from $\text{trans}-[(\text{Cp}^*\text{Rh})_2\text{Nb}_6\text{O}_{19}]^{4-}$ appear at 1.90 and 1.87 ppm, together with new signals at 1.92 and 1.94 ppm. The latter two signals can be assigned to the signals from Cp^* groups in CH_3O^- complexes. The signal intensity at 3.67 ppm is 5 % of that of the two signals with δ = 1.90 and 1.87 ppm, hence the corresponding Cp^* signal must have 10-fold intensity, which in turn corresponds to that of the peak with δ = 1.92 ppm. In the same way, the integral intensity of the signals from bridging CH_3O group (from various isomers at 4.53-4.55 ppm) is only 1 %, which correlates with the intensity of the Cp^* peak at 1.94 ppm (10 %). Total intensity of the Cp^* signals from the methoxocomplexes is 60 % of that of $\text{trans}-[(\text{Cp}^*\text{Rh})_2\text{Nb}_6\text{O}_{19}]^{4-}$ which indicates a high degree of methylation (37.5 %), in qualitative agreement with the ESI data. Methanolic solution of **3** demonstrates signals from terminal (3.68 ppm) and bridging (4.35, 4.33, 4.32, 4.30, 4.29, 4.26 ppm). The signals from Cp^* appear 1.83, 1.81 ppm (for $\text{trans}-[(\text{Cp}^*\text{Ir})_2\text{Nb}_6\text{O}_{19}]^{4-}$) and 1.85-1.87 ppm (for methylated POMs). The signal at 1.85 ppm can be assigned to the isomers with terminal CH_3O group (10 % of the intensity of the Cp^* groups from starting $\text{trans}-[(\text{Cp}^*\text{Ir})_2\text{Nb}_6\text{O}_{19}]^{4-}$), and that of 1.87 ppm – to the isomers with bridging methoxide (100 % of the intensity). This corresponds to the total methylation of ca. 53 % of the starting complex. The formation of the new species in CH_3OH solutions can be also deduced from new signals from Cp^* which appear at 84.75 and 85.65 ppm as broad resonances, together with the signals from starting $\text{trans}-[(\text{Cp}^*\text{Ir})_2\text{Nb}_6\text{O}_{19}]^{4-}$ at 83.67 and 83.64 ppm. Observed signals in ^1H NMR for all complexes are summarized in Table 1. Also both for Rh and Ir there is a signal with δ = 29.4 ppm (^1H NMR δ =3.37 ppm) that appeared also in the work¹⁴ and was assigned by the authors to CH_3Cl . But we assign it as acetone trace (30 ppm, <http://nmrshiftdb.nmr.uni-koeln.de/>).

The conclusion from this part of work is that the formation of the methoxocomplexes does take place in methanolic solutions and contributes to enhanced solubility of $\text{Na}_4[(\text{C}_6\text{H}_6)\text{Ru}]_2\text{Nb}_6\text{O}_{19}$ and $\text{K}_4[(\text{Cp}^*\text{M})_2\text{Nb}_6\text{O}_{19}]$ (M = Rh, Ir) in methanol as result of specific solvolysis.

DFT calculations

In order to gain more insight into the formation of the methoxy complexes DFT calculations were carried out (atomic numbering is presented at Fig. 4). Calculation of the charge distribution on the terminal oxoligands of the free Lindqvist anion $[\text{Nb}_6\text{O}_{19}]^{8-}$ shows equal Hirshfeld charges of -0.754 (see

Table S3). Coordination of a $\{\text{Cp}^*\text{Ir}\}^{2+}$ fragment leads, as expected, to an overall decrease in the negative charge for all terminal oxygens, but the terminal oxo ligands at the free face

opposite to $\{\text{Cp}^*\text{IrNb}_3\text{O}_3\}$ retain more negative charge, -0.620 vs -0.565 (Table S3).

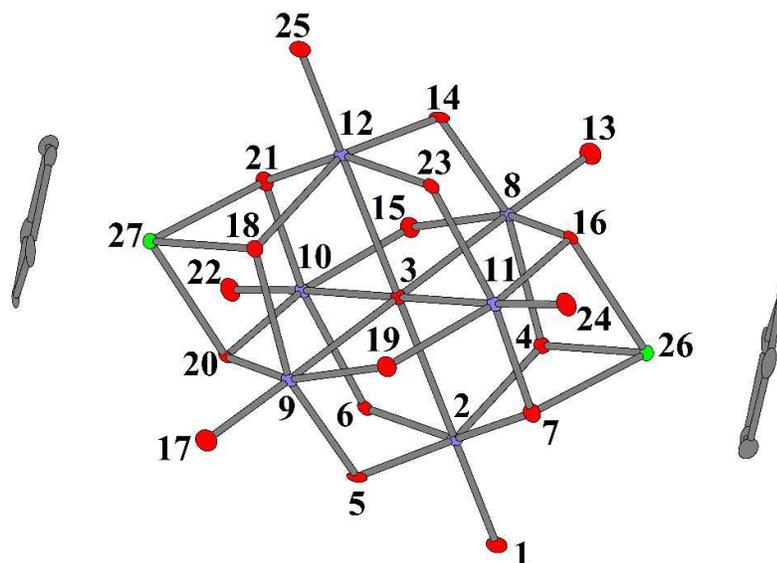


Fig. 4. Atomic numbering scheme used in DFT calculations for $\text{trans}-\{[\text{Cp}^*\text{Ir}]_2\text{Nb}_6\text{O}_{18}(\text{OCH}_3)\}^{3-}$. Isomer I: CH_3 group added to terminal oxygen atoms (any of six equivalent atoms O1, O24, O13, O17, O22, O12). Isomer II: CH_3 group added to any of six equivalent bridging atoms in the “equatorial belt” (O14, O15, O23, O5, O6, O19). Isomer III: CH_3 group added to any of six capping oxygens (O4, O7, O16, O18, O20, O21).

This means that the coordination of $\{\text{Cp}^*\text{Ir}\}^{2+}$ “polarizes” the Lindquist structure in such a way that more negatively charged oxygen atoms belong to the face opposite to the $\{\text{Cp}^*\text{IrNb}_3\text{O}_3\}$ group. This perhaps explains preferential formation of the *trans*-isomers observed for bicapped $[\{\text{XM}\}_2\text{M}_6\text{O}_{19}]^{4-}$ species.⁹⁻¹¹

Capping of $[\text{Nb}_6\text{O}_{19}]^{8-}$ with half-sandwich moieties also significantly increases the positive charge at the Nb atoms (by almost 0.2 e). This may lead to stabilization of an intermediate with CN 7, where a CH_3OH molecule is coordinated to Nb; in fact there are examples of POM with seven-coordinated Nb.¹⁶ Following this, we can envision proton transfer of one of terminal or bridging oxides, following by substitution of CH_3O^- for OH^- . We have calculated total energies and Hirshfeld charges for various isomers of monomethylated $\text{trans}-\{[\text{Cp}^*\text{Ir}]_2\text{Nb}_6\text{O}_{18}(\text{OCH}_3)\}^{3-}$. The formation of single possible terminal methoxocomplex by methylation of one of the six equivalent terminal Nb=O groups (Fig. 4, Isomer I) is slightly favored over the bridging isomer where methylation occur either at six equivalent Nb-O-Nb groups (isomer II). The isomer with capping $\mu_3\text{-OCH}_3$ (Isomer III) is the least favored (Table S3).

This is in agreement with Errington’s isolation of $(\text{Bu}_4\text{N})_2[(\text{MeO})\text{NbW}_5\text{O}_{18}]$ with terminal Nb-OCH₃ group,¹² but does not exclude the presence of methoxo-bridged isomers in equilibrium, as can be seen from NMR spectra in our case.

To conclude, exclusive solubility of the hybrid organometallic-POM complexes salts with alkali metal cations in methanol is

due to the formation of the methoxocomplexes (as detected in solutions) and solvation of Na^+ and K^+ (as is seen in the crystals of the solids which were isolated from such solutions), and hydrophobic interactions with Cp^* and C_6H_6 moieties. This, *prima facie*, does not explain lack of solubility in ethanol, which is a better donor (being more basic). But CH_3OH strongly differs from $\text{C}_2\text{H}_5\text{OH}$ in having significantly larger value of dielectric constant (ϵ), 31 vs. 24.

Thus methanol is better suited for dismantling the crystal lattice of these ionic compounds due to sufficiently high ϵ value. The packing in the crystals of hydrates such as $\text{trans}-\text{K}_4\{[\text{Cp}^*\text{Rh}]_2\text{Nb}_6\text{O}_{19}\}\cdot 20\text{H}_2\text{O}^9$ and $\text{trans}-\text{K}_4\{[\text{Cp}^*\text{Ir}]_2\text{Nb}_6\text{O}_{19}\}\cdot 22\text{H}_2\text{O}^{10}$ consists of the layers formed by hybrid anions and solvated cations which stacks together only through π - π interactions between organic ligands. Methanol can penetrate between such layers and replace water in the coordination spheres of the cations.

Experimental

General procedures

Starting $\text{Na}_7\text{H}[\text{Nb}_6\text{O}_{19}]\cdot 15\text{H}_2\text{O}$ was synthesized as described in the literature.¹⁷ $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ was obtained from the reaction of $\text{RuCl}_3\cdot x\text{H}_2\text{O}$ (Krastsvetmet) with 1,3-cyclohexadiene (Sigma Aldrich) by the standard procedure.¹⁸ $\text{K}_4[\text{trans}-\{\text{Cp}^*\text{Rh}\}_2\text{Nb}_6\text{O}_{19}]\cdot 20\text{H}_2\text{O}$ and $\text{K}_4[\text{trans}-\{\text{Cp}^*\text{Ir}\}_2\text{Nb}_6\text{O}_{19}]\cdot 22\text{H}_2\text{O}$ were prepared as described in literature.^{9,10} Other reagents

were of commercial quality and used as purchased. Methanol was purified according to standard methodology. IR spectra (4000 – 400 cm^{-1}) were recorded on an IFS-85 Bruker spectrometer.

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 °C and the desolvation temperature to 200 °C. 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 with a solution of sodium iodide in isopropanol:water (50:50) in the mass range from m/z 50 to 3000. Sample solutions ca. 5×10^{-5} M in water or methanol were infused via a syringe pump directly connected to the ESI source at a flow rate of 10 $\mu\text{L}/\text{min}$. 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 III 500 spectrometer with inner references in CD_3OD at different temperatures.

DFT calculations

The measured crystal structures of $\text{Na}_7\text{H}[\text{Nb}_6\text{O}_{19}] \cdot 14\text{H}_2\text{O}$ ¹⁹ and $\text{K}_4[\text{trans}\text{-}\{\text{Cp}^*\text{Ir}\}_2\text{Nb}_6\text{O}_{19}] \cdot 22\text{H}_2\text{O}$ ¹⁰ were used as the initial input for the geometry optimization of the anions. The converged molecular structures changed a little from the geometries found in crystal. The structures with coordinated MeO ligand were constructed *in silico*. Quantum chemical calculations were carried out with the Amsterdam Density Functional (ADF2013.01.c) program (ADF2013, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, <http://www.scm.com>). The calculations were performed with an all-electron Slater type TZ2P basis set. As with the geometry optimization, the VWN (Local Density Approximation) and Becke-Perdew (Generalized Gradient Approximation) functionals were used. Relativistic corrections were introduced by both scalar and spin-orbit relativistic zeroth order regular approximation (ZORA).

A Hirshfeld population analysis and NMR spectra were performed according to the corresponding modules of ADF program.

X-ray crystallography

Crystallographic data and refinement details are given in Table S2. The diffraction data were collected on a Bruker Apex Duo (for **1**) and Bruker X8 Apex (for **2** and **3**) diffractometers with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) by doing ϕ and ω scans of narrow (0.5°) frames at 100 K. Structures were solved by direct methods and refined by full-matrix least-squares treatment against $|F|^2$ in anisotropic approximation in SHELX 2014/7 with ShelXle program.²⁰ Absorption corrections were applied empirically with SADABS program.²¹ All non-hydrogen atoms of

main structural units were refined anisotropically. Positions of all cations in both structures were fully occupied, which excluded models with protonated polyoxoanions. Further details may be obtained from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC 1423580-1423582. Copies of this information may be obtained free of charge from <http://www.ccdc.cam.ac.uk>.

Na₄trans-[(C₆H₆)Ru]₂Nb₆O₁₉]-14.125MeOH-2H₂O (1): 0.4 g (0.3 mmol) of $\text{Na}_7\text{H}[\text{Nb}_6\text{O}_{19}] \cdot 15\text{H}_2\text{O}$ was dissolved upon heating (80-90 °C) and stirring in 8 ml of distilled water. To the clear solution 0.154 g (0.3 mmol) of crude $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ was added. The mixture was kept at 80 °C overnight upon stirring producing clear yellow-orange solution. After cooling crude product (0.480 g) was precipitated by addition of 20 ml of acetone and isolated by filtration. Then product was dissolved in 10 ml of freshly distilled methanol under stirring and heating at 50 °C. If some insoluble material appeared it was filtered off and discarded. Slow evaporation of the clear solution gives nice rhombohedral orange crystals of **1**, which were characterized with XRD. After the filtration crystals were washed with cold methanol (2x by 5 ml) and carefully dried *in vacuo*. Solid material is very hygroscopic and absorbs water during keeping in air. Yield 80%. TGA: weight loss corresponds c.a. 12 CH_3OH . Analysis Calc. for $\text{Na}_4\text{C}_{12}\text{H}_{12}\text{Ru}_2\text{Nb}_6\text{O}_{19}(\text{CH}_3\text{OH})_2(\text{H}_2\text{O})_2$ C, H (%); 11.91, 1.71; found C, H (%): 11.53; 1.55. IR (KBr, cm^{-1}) 3400 (s), 2922(m), 2853(m), 1628(m), 1431(m), 1139(w), 1012(sh), 867(s), 766(sh), 622(s), 609(sh), 530(s), 465(s).

K₄trans-[(Cp*Rh)₂Nb₆O₁₉]-4MeOH-10H₂O (2): 0.1 g (0.05 mmol) of $\text{K}_4\text{trans}\text{-}[(\text{Cp}^*\text{Rh})_2\text{Nb}_6\text{O}_{19}] \cdot 20\text{H}_2\text{O}$ was dissolved in 5 ml of freshly distilled methanol upon gentle heating (c.a. 50 °C). To the clear solution 30 mg of dibenzo-18-crown-6 were added, after that the solution was allowed to evaporate slowly in air at 2 °C. Large yellow rhombohedral crystals of **2** were collected overnight. Drying the sample *in vacuo* gives a sample without methanol molecules. Solid material is very hygroscopic and absorbs water during keeping in air. Yield 80%. Analysis Calc. for $\text{K}_4\text{C}_{20}\text{H}_{50}\text{Rh}_2\text{Nb}_6\text{O}_{29}$ C, H (%); 14.31, 3.04; found C, H (%): 14.02; 2.84. IR (KBr, cm^{-1}): 3455(s), 3358(s), 2922(m), 1651 (m), 1459(m), 1387(m), 1190(m), 1085(m), 1023(m), 852(s), 782(s), 656(s), 606(s), 549(s), 506(m), 411(s).

K₄trans-[(Cp*Ir)₂Nb₆O₁₉]-10MeOH-4H₂O (3): Complex **3** was prepared by the same way as **2**. Drying the sample *in vacuo* causes loss of approximately eight methanol molecules. Solid material is very hygroscopic and absorbs water during keeping in air. Yield 80%. Analysis Calc. for $\text{K}_4\text{C}_{22}\text{H}_{46}\text{Ir}_2\text{Nb}_6\text{O}_{25}$ C, H (%); 14.61, 2.52; found C, H (%): 14.22; 2.13. IR (KBr, cm^{-1}): 3372(s), 2915(m), 2834(m), 1621(m), 1435(m), 1382(m), 1080(w), 1024(m), 875(s), 850(s), 776(s), 670(s), 611(s), 524(s), 500(s), 409(s).

Conclusions

Hybrid complex $A_4\{LM'\}_2M_6O_{19}$ ($\{LM'\} = \{Cp^*Rh\}^{2+}, \{Cp^*Ir\}^{2+}, \{(C_6H_6)Ru\}^{2+}$; $M = Nb, Ta$; $A = Na, K, Cs$) are soluble only in single organic solvent, namely, in CH_3OH . ESI-MS and NMR data of the methanolic solutions confirm the presence of methoxo complexes $[\{LM'\}_2M_6O_{19-n}(OCH_3)_n]$ ($n = 1-3$). NMR experiments show that about half of the starting $[\{LM'\}_2M_6O_{19}]^{4-}$ is present as methylated derivatives. Crystallization of the solutions of $Na_4trans-\{[(C_6H_6)Ru]_2Nb_6O_{19}\}$, $K_4trans-\{[Cp^*Rh]_2Nb_6O_{19}\}\cdot 20H_2O$ and $K_4trans-\{[Cp^*Ir]_2Nb_6O_{19}\}\cdot 22H_2O$ in methanol leads to isolation of $Na_4trans-\{[(C_6H_6)Ru]_2Nb_6O_{19}\}\cdot 14.125MeOH\cdot 2H_2O$ (**1**), $K_4trans-\{[Cp^*Rh]_2Nb_6O_{19}\}\cdot 4MeOH\cdot 10H_2O$ (**2**) and $K_4trans-\{[Cp^*Ir]_2Nb_6O_{19}\}\cdot 10MeOH\cdot 4H_2O$ (**3**) where direct coordination of CH_3OH to Na^+ or K^+ is observed. The crystal structure of **1** is the first example of a 3d framework built from dimeric $[(MeOH)_3Na(\mu-MeOH)Na(H_2O)(MeOH)_2]^{2+}$ cations and hybrid anions, which is typically new in the case of all known crystal structures of hybrid complexes. Its stability and sorption properties are under investigation. DFT calculations were used for comparison of ^{13}C NMR shifts of different positions of methoxo ligand in the $[\{Cp^*Ir\}Nb_6O_{18}(OCH_3)]^{5-}$ backbone. Comparison of the energies of $[\{Cp^*Ir\}Nb_6O_{18}(\mu-OCH_3)]^{5-}$ and $[\{Cp^*Ir\}Nb_6O_{18}(OCH_3)]^{5-}$ gives very close equal values suggesting that rapid exchange MeO^- ligand between different positions can be very fast in the solution.

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Unique solubility of polyoxoniobate salts in methanol: coordination to cations and POM methylation

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Hybrid complexes $A_4[LM'_2M_6O_{19}]$ ($\{LM'\} = \{Cp^*Rh\}^{2+}$, $\{Cp^*Ir\}^{2+}$, $\{(C_6H_6)Ru\}^{2+}$; $M = Nb, Ta$; $A = Na, K, Cs$) are soluble only in single organic solvent, namely, in CH_3OH . ESI-MS and NMR data of the methanolic solutions confirm the presence of methoxo complexes $[LM'_2M_6O_{19-n}(OMe)_n]$ ($n = 1-3$). From the solutions of $Na_4[trans-\{(C_6H_6)Ru\}_2Nb_6O_{19}]$, $K_4[trans-\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 20H_2O$ and $K_4trans-\{Cp^*Ir\}_2Nb_6O_{19} \cdot 22H_2O$ in methanol $Na_4trans-\{(C_6H_6)Ru\}_2Nb_6O_{19} \cdot 14.125MeOH \cdot 2H_2O$, $K_4trans-\{Cp^*Rh\}_2Nb_6O_{19} \cdot 4MeOH \cdot 10H_2O$, and $K_4trans-\{Cp^*Ir\}_2Nb_6O_{19} \cdot 10MeOH \cdot 4H_2O$ with direct coordination of CH_3OH to Na^+ or K^+ have been isolated.

