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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_2O_3]^6− (M = Nb, Ta) and half-sandwich fragments (CP^*M)^2+ (CP^* = η^2-C_5H_4) were found to dissolve only in methanol from as methanolic solutions crystals of Na_{trans-}[Cu(H_2O)_2]_{trans-}[Cu(H_2O)_2]_2·14.125MeOH·2H_2O (1), K_{trans-}[Cu(H_2O)_2]_{trans-}[Cu(H_2O)_2]_2·4MeOH·10H_2O (2) and K_{trans-}[Cu(H_2O)_2]_{trans-}[Cu(H_2O)_2]_2·10MeOH·4H_2O (3) were isolated and characterized by X-ray analysis. Methoxo species [(L^*M)_2]_{trans-}[Cu(H_2O)_2]_3 (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 13C 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_3 can be solubilized in methanol under solventothermal conditions in the presence of Me_2NOK as a base.2 It also reacts with different organic bases in acetonitrile. In this way [Nb_2O_3]^6−,3 [Nb_2O_2]^6−,3 as well as recently reported [Ta_2O_2]^6−,5 were prepared. The main reason of the strong bias in favor of choosing water as solvent is the high charge of the polyniobates, 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]^5+ (arene is benzene and its derivatives) to [Nb_2O_3]^6− would reduce the overall negative charge and simultaneously increase the hydrophobicity of the hybrid complex, thus enabling solubility in organic solvents. Indeed,

Results and discussion

ESI-MS experiments

First indications of the formation of methoxocomplexes were obtained from ESI-MS experiments. Reactions of [M_2O_3]^6− (M = Nb and Ta) with [CP^*RhCl]^2+ at the Rh/M_2 ratio in water yielded solids containing the [(CP^*Rh)_2M_2O_3]^4− anions.

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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 $\left[\langle\text{Cp}^*\text{Ir}\rangle_2\text{Nb}_6\text{O}_{19}\text{H}_3\rangle^-$ (m/z 1340), $\langle\text{Cp}^*\text{Rh}\rangle_2\text{Nb}_6\text{O}_{18}\text{H}_3\rangle^-$ (m/z 1354), and $\langle\text{Cp}^*\text{Rh}\rangle_2\text{Ta}_6\text{O}_{19}\text{H}_3\rangle^-$ (m/z 1882) were identified. Table S1 collects the m/z values for the methoxo species identified. Signals from 1:1 adducts, namely $\langle\text{Cp}^*\text{Rh}\rangle\text{Nb}_6\text{O}_{18}\text{H}_3\rangle^-$ (m/z 1104), $\langle\text{Cp}^*\text{Rh}\rangle\text{Nb}_6\text{O}_{17}\text{H}_3\rangle^-$ (m/z 1132), $\langle\text{Cp}^*\text{Rh}\rangle\text{Ta}_6\text{O}_{18}\text{H}_3\rangle^-$ (m/z 824), and $\langle\text{Cp}^*\text{Rh}\rangle\text{Ta}_6\text{O}_{18}\text{H}_3\rangle^-$ (m/z 1646), were also observed in their respective ESI mass spectra in methanol. We also found that sodium salts of 2:1 and 1:1 complexes $\left[\langle\text{Cp}^*\text{Ir}\rangle_2\text{Nb}_6\text{O}_{18}\text{H}_3\rangle\cdot 2\text{H}_2\text{O}\right]^-$ and $\langle\text{Cp}^*\text{Ir}\rangle_2\text{Ta}_6\text{O}_{18}\text{H}_3\rangle\cdot 2\text{H}_2\text{O}\rangle^-$ were soluble in CH$_3$OH, and signals from the corresponding anions as well as from their mono- and dimethylated derivatives $\langle\text{Cp}^*\text{Ir}\rangle_2\text{Nb}_6\text{O}_{18}\text{H}_3\rangle\cdot 2\text{H}_2\text{O}\rangle^-$ (m/z 765) and $\langle\text{Cp}^*\text{Ir}\rangle_2\text{Ta}_6\text{O}_{18}\text{H}_3\rangle\cdot 2\text{H}_2\text{O}\rangle^-$ (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 $\langle\text{Cp}^*\text{Ir}\rangle\text{TeNb}_5\text{O}_{19}\rangle^-$ and $\langle\text{Cp}^*\text{Ir}\rangle\text{TeNb}_5\text{O}_{19}\rangle^-$.$^{11}$ This indicates the proclivity of the Lindquist 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 x $10^{-5}$ M in CH$_3$OH) 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 \[
[(C_5H_5)RuCl_2]_2
\]
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_5H_5)Ru_2Nb_2O_19])·14.125MeOH·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-\[
[(C_5H_5)Ru_2Nb_2O_{19}]^{6-}
\]hybrid anions and sodium cations, which aggregate into \[
[(MeOH)Na(MeOH)]Na[M(Na(MeOH))MeOH]\]dimers; hence the formula of 1 is better rendered as \[
[(MeOH)Na(MeOH)]Na[H_2O](MeOH)\]dimers. 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_5H_5 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(OMeOH...μ-O) are 2.645 and 2.701 Å) of the hybrid POM. Moreover, one solvate water molecule forms a weaker hydrogen bond with μ-O (H_2O...O distance is 2.821 Å).\(^9\)

\[
\text{trans-K}_3[(\text{Cp}^{*}\text{Rh})_2\text{Nb}_2\text{O}_{19}]\cdot2\text{H}_2\text{O}
\]
and \[
\text{trans-K}_3[(\text{Cp}^{*}\text{Ir})_2\text{Nb}_2\text{O}_{19}]\cdot2\text{H}_2\text{O}
\]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 \[
\text{trans-K}_3[(\text{Cp}^{*}\text{Rh})_2\text{Nb}_2\text{O}_{19}]\cdot4\text{MeOH}\cdot1\text{H}_2\text{O}
\]and \[
\text{trans-K}_3[(\text{Cp}^{*}\text{Ir})_2\text{Nb}_2\text{O}_{19}]\cdot10\text{MeOH}\cdot4\text{H}_2\text{O}
\]. 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-\[
[(\text{Cp}^{*}\text{M})_2\text{Nb}_2\text{O}_{19}]^{6+}
\]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 \((\text{Nb}_2\text{O}_3)\) 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...HOC) is 2.761 Å) stronger than water molecules (d(Nb=O...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...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 \((\text{Cp}^{*}\text{M})_2\text{M}_2\text{O}_{18}\) complexes (M = Rh, Ir), and K\(^+\) (Nb), Na\(^+\) (Nb, Ta) salts for \((\text{C}_5\text{H}_5\text{H}_2\text{Ru}_2\text{M}_2\text{O}_{18}\) 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 π-π 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.

\(^{13}\)C and \(^1\)H NMR experiments

\[\text{Fig. 2.} \quad \text{\(^{13}\)C NMR spectrum of \text{d}^{6}\text{-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
In the $^{13}$C NMR spectra of 2 and 3 in CD$_3$OD 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$_3$OD.

**Table 1.** $^1$H NMR data for 1-3 in CD$_3$OD.

<table>
<thead>
<tr>
<th>Complex</th>
<th>δ(term)*</th>
<th>δ(bridded)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.530, 3.520, 3.504, 3.491, 3.468</td>
<td>4.284</td>
</tr>
<tr>
<td>2</td>
<td>3.670</td>
<td>4.002, 3.987, 4.553, 4.537, 4.528</td>
</tr>
</tbody>
</table>

* assigned from ref. 14.

Since free methanol gives $^{13}$C NMR resonance at 49.5 ppm, these signals can be assigned to coordinated CH$_3$O. Indeed, Errington et al. reported for $[\text{Bu}_4\text{N}]_2[(\text{MeO})\text{NbW}_{19}O_{84}]$ in CD$_3$CN δ$_{CH3}$ at 65.91 ppm. 12 Similar chemical shifts for various methoxy species were reported elsewhere. 13 Karaliota et al. even discriminated between terminal Nb-OCH$_3$ and bridging Nb-$\mu$-OCH$_2$-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 $[[\text{Cp}^*\text{Ir}]_2\text{Nb}_2\text{O}_{13}(\text{OCH}_3)]^{13+}$ as models, which yielded δ$_{CH3}$ 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$_3$O ligand in solution. Three isomers are possible, as shown in Fig. 4. The formation of the new species in CH$_3$OH 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 trans-[[Cp*Rh]$_2$Nb$_2$O$_{13}]^{5+}$ at 92.91 and 92.68 ppm.

The methyl group proton ($^1$H NMR) resonances which appear in solutions of NbCl$_5$ in CH$_3$OH fall in three series around 4.55 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 $^1$H 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 $^1$H 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 trans-[[Cp*Rh]$_2$Nb$_2$O$_{13}]^{4+}$ 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$_3$O 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$_3$O 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 trans-[[Cp*Rh]$_2$Nb$_2$O$_{13}]^{4+}$ 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 Cp* signals from 3 appear 1.83, 1.81 ppm (for trans-[[Cp*Ir]$_2$Nb$_2$O$_{13}]^{5+}$ and 1.85-1.87 ppm (for methylated POMs). The signal at 1.85 ppm can be assigned to the isomers with terminal CH$_3$O group (10 % of the intensity of the Cp* groups from starting trans-[[Cp*Ir]$_2$Nb$_2$O$_{13}]^{5+}$), 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$_3$OH 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 trans-[[Cp*Ir]$_2$Nb$_2$O$_{13}]^{5+}$ at 83.67 and 83.64 ppm. Observed signals in $^1$H NMR for all complexes are summarized in Table 1. Also both for Rh and Ir there is a signal with δ = 1.90 ppm ($^1$H NMR δ = 3.37 ppm) that appeared also in the work 14 and was assigned by the authors to CH$_3$O. 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 Na$_2[[\text{CpH}_2][\text{Ru}]_2\text{Nb}_2\text{O}_{13}]$ and K$_2[[\text{Cp*M}]_2\text{Nb}_2\text{O}_{13}]$ (M = Rh, Ir) in methanol as result of specific solvolysis.

**DFT calculations**

In order to gain more insight into the formation of the methoxocomplexes 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 [Nb$_2$O$_{13}$]$^{8-}$ shows equal Hirshfeld charges of -0.754 (see
Table S3). Coordination of a \{Cp*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 \{Cp*IrNb₃O₃\} retain more negative charge, -0.620 vs -0.565 (Table S3).

This means that the coordination of \{Cp*Ir\}²⁺ “polarizes” the Lindquist structure in such a way that more negatively charged oxygen atoms belong to the face opposite to the \{Cp*IrNb₃O₃\} group. This perhaps explains preferential formation of the \textit{trans}-isomers observed for bicapped \{XM\}⁺ species.⁹⁻¹¹

Capping of \{Nb₆O₁₈\}₆⁺ 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 CH₃OH 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 CH₃OH for OH. We have calculated total energies and Hirshfeld charges for various isomers of monomethylated \textit{trans}-\{Cp*Ir\}₂Nb₆O₁₈(OCH₃)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 occurs either at six equivalent Nb-O-Nb groups (isomer II). The isomer with capping μ₁-OCH₃ (Isomer III) is the least favored (Table S3).

This is in agreement with Errington’s isolation of \{(Bu₄N)₂(MeO)Nb₆W₂O₁₆\} with terminal Nb-OCH₃ group,¹² but does no 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 C₆H₆ moieties. This, \textit{prima facie}, does not explain lack of solubility in ethanol, which is a better donor (being more basic). But CH₃OH strongly differs from C₂H₅OH 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 \textit{trans}-K₄\{[(Cp*Rh)₂]Nb₆O₁₈\}·2CH₃OH and \textit{trans}-K₄\{[(Cp*Ir)₂]Nb₆O₁₈\}·2H₂O²⁰ 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.

\section*{Experimental}

\subsection*{General procedures}

Starting Na₃H[Nb₆O₁₈]·15H₂O was synthesized as described in the literature.¹⁷ \{[(C₆H₅)₃RuCl₂]_2 was obtained from the reaction of RuCl₃·xH₂O (Kratsvetmet) with 1,3-cyclohexadien (Sigma Aldrich) by the standard procedure.¹⁸ K₄\{[(Cp*Rh)₂]Nb₆O₁₈\}·20H₂O and K₄\{[(Cp*Ir)₂]Nb₆O₁₈\}·2H₂O were prepared as described in literature.¹⁹ 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 x 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 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**

\(^1\)H and \(^{13}\)C NMR spectra were recorded on a Bruker Avance III 500 spectrometer with inner references in CD\(_2\)OD at different temperatures.

**DFT calculations**

The measured crystal structures of Na\(_2\)H[Nb\(_6\)O\(_{19}\)]14H\(_2\)O\(^{19}\) and K\(_2\)trans-[Cp*Ir\(_2\)](C\(_6\)H\(_6\)O\(_2\))\(_2\)H\(_2\)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**

Crystalllographic 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 MoK\(_\alpha\) radiation (λ = 0.71073 Å) 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.

**Conclusions**

Na\(_2\)trans-[[C\(_6\)H\(_6\)]\(_2\)Ru\(_2\)]Na\(_6\)O\(_{19}\)]14.125MeOH·2H\(_2\)O (1): 0.4 g (0.3 mmol) of Na\(_2\)H[Nb\(_6\)O\(_{19}\)]15H\(_2\)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 [[C\(_6\)H\(_6\)]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\(_2\)OH. Analysis Calc. for Na\(_2\)C\(_6\)H\(_2\)Ru\(_2\)Na\(_6\)O\(_{19}\)((CH\(_3\))OH\(_2\))\(_2\)·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).

K\(_2\)trans-[[C\(_6\)Rh\(_2\)]Na\(_6\)O\(_{19}\)]4MeOH·10H\(_2\)O (2): 0.1 g (0.05 mmol) of K\(_2\)trans-[[C\(_6\)Rh\(_2\)]Na\(_6\)O\(_{19}\)]·20H\(_2\)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-krown-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 K\(_2\)C\(_6\)H\(_2\)Rh\(_2\)Na\(_6\)O\(_{19}\)·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).

K\(_2\)trans-[[Cp*Ir\(_2\)]Na\(_6\)O\(_{19}\)]·10MeOH·4H\(_2\)O (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 K\(_2\)C\(_6\)H\(_2\)Ir\(_2\)Na\(_6\)O\(_{19}\)·C, H (%): 14.61, 2.52; found C, H (%): 14.22. 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).
Hybrid complex $A_{4}[(LM')_{3}]_{2}M_{2}O_{13}$ ($[LM'] = \{Cp^*Rh\}^{2+}, \{Cp^*Ir\}^{2+}, \{(C_{2}H_{5})Ru\}^{2+}$; $M = \text{Nb}, Ta$; $A = \text{Na, K, Cs}$) are soluble only in single organic solvent, namely, in $\text{CH}_{3}\text{OH}$. ESI-MS and NMR data of the methanolic solutions confirm the presence of methoxo complexes $[LM']_{2}M_{2}O_{12}(\text{OCH}_{3})_{n}$ ($n = 1-3$). NMR experiments show that about half of the starting $[LM']_{2}M_{2}O_{12}^{2-}$ is present as methylaed derivatives. Crystallization of the solutions of $\text{Na}_{2}\text{trans-}[[\{(C_{2}H_{5})Ru\}_{2}\text{Nb}_{2}O_{13}]]$, $\text{K}_{2}\text{trans-}[[\{(Cp^*Rh)\text{Nb}_{2}O_{13}]]2\text{H}_{2}O$, and $\text{K}_{2}\text{trans-}[[\{(Cp^*Ir)\text{Nb}_{2}O_{13}]]2\text{H}_{2}O$ in methanol leads to isolation of $\text{Na}_{2}\text{trans-}[[\{(C_{2}H_{5})Ru\}_{2}\text{Nb}_{2}O_{13}]]14.125\text{MeOH}2\text{H}_{2}O$ (1), $\text{K}_{2}\text{trans-}[[\{(Cp^*Rh)\text{Nb}_{2}O_{13}]]4\text{MeOH}10\text{H}_{2}O$ (2) and $\text{K}_{2}\text{trans-}[[\{(Cp^*Ir)\text{Nb}_{2}O_{13}]]10\text{MeOH}4\text{H}_{2}O$ (3) where direct coordination of $\text{CH}_{3}\text{OH}$ to $\text{Na}^+$ or $\text{K}^+$ is observed. The crystal structure of 1 is the first example of a 3d framework built from dimeric $[[\text{MeOH}]\text{Na}^{+}\{(\mu-\text{MeOH})\text{Na}_{2}H_{2}O\}[[\text{MeOH}]]^{2+}$ 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 $[[\{(Cp^*Ir)\text{Nb}_{2}O_{13}]]$ backbone. Comparison of the energies of $[[\{(Cp^*Ir)\text{Nb}_{2}O_{13}]](\mu-\text{OCH}_{3})^{2-}$ and $[[\{(Cp^*Ir)\text{Nb}_{2}O_{13}]](\mu-\text{OCH}_{3})^{2-}$ 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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Notes and references


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

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Hybrid complexes $A_4[\{L'M\}'_2M_6O_{19}]$ ($\{L'M\}' = \{\text{Cp}^*\text{Rh}\}^{2+}$, $\{\text{Cp}^*\text{Ir}\}^{2+}$, $\{(\text{C}_6\text{H}_6)\text{Ru}\}^{2+}$; $M = \text{Nb, Ta}$; $A = \text{Na, K, Cs}$) are soluble only in single organic solvent, namely, in CH$_3$OH. ESI-MS and NMR data of the methanolic solutions confirm the presence of methoxo complexes $\{L'M\}'_2M_6O_{19-n}(\text{OMe})_n$ ($n = 1$-3). From the solutions of $\text{Na}_4[\text{trans-}\{(\text{C}_6\text{H}_6)\text{Ru}\}_2\text{Nb}_6\text{O}_{19}]$, $K_4[\text{trans-}\{\text{Cp}^*\text{Rh}\}_2\text{Nb}_6\text{O}_{19}]$·$20\text{H}_2\text{O}$ and $K_4[\text{trans-}\{\text{Cp}^*\text{Ir}\}_2\text{Nb}_6\text{O}_{19}]$·$22\text{H}_2\text{O}$ in methanol $\text{Na}_4[\text{trans-}\{(\text{C}_6\text{H}_6)\text{Ru}\}_2\text{Nb}_6\text{O}_{19}]$·$14.125\text{MeOH}$·$2\text{H}_2\text{O}$, $K_4[\text{trans-}\{\text{Cp}^*\text{Rh}\}_2\text{Nb}_6\text{O}_{19}]$·$4\text{MeOH}$·$10\text{H}_2\text{O}$, and $K_4[\text{trans-}\{\text{Cp}^*\text{Ir}\}_2\text{Nb}_6\text{O}_{19}]$·$10\text{MeOH}$·$4\text{H}_2\text{O}$ with direct coordination of CH$_3$OH to Na$^+$ or K$^+$ have been isolated.