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Na_4[*trans*-{Cp*Rh}$_2Ta_6O_{19}$] · $24H_2O$: Synthesis, Structure, Solution Studies[1]

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Abstract—Reaction of $[Cp^*RhCl_2]_2$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) with $Na_8[Ta_6O_{19}] \cdot 24.5H_2O$, taken in $\{Cp^*Rh\}^{2+}/[Ta_6O_{19}]^{8-}$ 2 : 1 molar ratio, in water leads to a new noble-metal-POM complex Na_4[*trans*-$\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 24H_2O$ (**I**), which was isolated and characterized by XRD (CIF file CCDC no. 1416810), elemental analysis, NMR and IR spectroscopy.

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INTRODUCTION

In aqueous solutions at pH 8–12 Nb and Ta in their highest oxidation states (V) form stable hexanuclear anionic oxo-complexes $[M_6O_{19}]^{8-}$ with so-called Lindqvist structure. Their stability in a high pH range coupled with high negative charge may be of interest when these complexes are used as tridentate non-flexible O-donors with fixed geometry. For example, $[M_6O_{19}]^{8-}$ can coordinate various transition [1–3] and noble [4] metals as well as cationic organometallic fragments [5–7]. The study of these complexes can provide insight in the processes which might occur at pH $\leqslant$ 8, when parent $[M_6O_{19}]^{8-}$ are unstable towards precipitating of hydrated M_2O_5. Since the number of experimental tools that can be used for solution studies of niobates and tantalates, is very limited (^{17}O NMR, mass-spectrometry [8], and small-angle X-ray scattering (SAXS) [9]), direct structural information is of utmost importance. Unfortunately, attempts to obtain single crystals from niobate and tantalate solutions under pH close to the stability limit yield only gels or amorphous precipitates. However, this problem can be circumvented by coordinating $\{(C_6H_6)Ru\}^{2+}$ or $\{Cp^*Rh\}^{2+}$ to $[M_6O_{19}]^{8-}$ [6, 7]. In this way it was possible to catch and structurally characterize a new dimeric oxo-bridged bis(Lindqvist) moiety $\{[Ta_6O_{18}]_2(\mu\text{-}O)\}^{14-}$, isolated as $Na_{10}\{[(C_6H_6)RuTa_6O_{18}]_2(\mu\text{-}O)\} \cdot 39.4H_2O$ [6].

In the present work we have studied reaction between $[Cp^*RhCl_2]_2$ ($Cp^* = \eta^5\text{-}C_5(CH_3)_5$) and $Na_8[Ta_6O_{19}] \cdot 24.5H_2O$ in $\{Cp^*Rh\}^{2+}/[Ta_6O_{19}]^{8-}$ 2 : 1 molar ratio in water, in continuation of our research aiming at elucidation of the influence of the nature of counter cation (here Na^+) on the composition and structure of the complexation products. We also report tantalate transfer between $[Cp_2^*Rh_2(OH)_3](NO_3)$ and in situ generated $[Mn(Ta_6O_{19})_2]^{12-}$.

EXPERIMENTAL

Starting materials and techniques: Starting $Na_8[Ta_6O_{19}] \cdot 24.5H_2O$ and $[Cp^*RhCl_2]_2$ were prepared according to the published procedures [10, 11]. All other reagents were of commercial quality and used as purchased (Sigma Aldrich). IR spectra were recorded on a Specord IR 75 spectrometer. NMR spectra of **I** in D_2O were recorded with a Bruker Avance 500 spectrometer at room temperature.

Preparation of $[Cp_2^*Rh_2(OH)_3](NO_3)$ (stock solution): 0.20 g (0.3 mmol) $[Cp^*RhCl_2]_2$ was dissolved in 20 mL of water by stirring at 80–90°C. To the resulting red-orange solution, 0.25 g (1.5 mmol) of $AgNO_3$ was added, and the mixture was further heated at 80°C for 2 h in the dark. Then the reaction mixture was allowed to cool down, and AgCl was removed by filtration, leaving orange solution of $[Cp_2^*Rh_2(OH)_3](NO_3)$ (c = 0.016 M, pH = 3) which was used in further experiments.

Synthesis of Na_4[*trans*-$\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 24H_2O$ (I): 0.10 g (50 μmol) of $Na_8[Ta_6O_{19}] \cdot 24.5H_2O$ was dissolved under stirring and heating at 80°C in 5 mL of water. Final pH was 12. The solution was put in a vial (V = 25 mL) with a tight screw-cap, and 0.03 g (50 μmol) of solid $[Cp^*RhCl_2]_2$ was added. The closed

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[1] The article was translated by the authors.

Crystallographic characteristics and details of XRD experiment for the complex **I**

Parameter	Value
CCDC	1416810
Chemical formula	$C_{20}H_{12}Na_4O_{43}Rh_2Ta_6$
M	2323.78
Crystal system	Monoclinic
Space group	$P2_1/m$
a, b, c, Å	13.5029(3), 15.1512(3), 14.8046(3)
β (deg)	110.653(3)
V, Å^3	2834.15(12)
Z	2
ρ(calc), g/cm^3	2.723
μ, mm^{-1}	12.23
F(000)	2096
Crystal dimensions, mm	0.07 × 0.06 × 0.03
θ Ranges, deg	3.32–31.04
h, k, l ranges	$-18 \leqslant h \leqslant 19$ $-20 \leqslant k \leqslant 21$ $-21 \leqslant l \leqslant 21$
Measured reflections	16877
Independent reflections (R_{int})	8164 (0.022)
Observed reflections $I > 2\sigma(I)$	6593
No. of parameters	367
GOOF	1.05
R_1 ($I > 2\sigma(I)$)	0.027
wR_2 (all reflections)	0.061
$\Delta\rho_{\min}/\Delta\rho_{\max}$, e/Å^3	−1.15/1.69

vial was kept under stirring 80°C for 24 h, and the final pH dropped to 9. After cooling the opened vial with reaction solution was placed in a jar filled with acetone. Acetone vapor diffusion at 2°C yielded single crystals of complex **I** as yellow plates. The chemical composition and structure of **I** were determined by X-ray analysis. Yield 70%.

^{1}H NMR (δ, ppm, room temperature): 1.754 s., 1.731 s.; ^{13}C NMR (δ, ppm, room temperature): 8.553 s., 8.501 s., 94.2 d. ($J^2_{\mathrm{C-Rh}}$ 10 Hz), 94 d. ($J^2_{\mathrm{C-Rh}}$ 10 Hz).

IR (KBr; ν, cm^{-1}): 3430 s, 2967 w, 2938 w, 1636 m, 1473 w, 1380 w, 1082 w, 1024 w, 863 s, 845 s, 786 s, 680 s.

Reaction of [Cp*$_2$Rh$_2$(OH)$_3$](NO$_3$) with in situ generated [Mn(Ta$_6$O$_{19}$)$_2$]$^{12-}$: 0.10 g (50 μmol) of $Na_8[Ta_6O_{19}] \cdot 24.5H_2O$ were dissolved (80°C) in 5 mL of water in a vial (V = 25 mL) with a tight screw-cap. To the freshly prepared hot solution of tantalate, a solution of 6 mg (25 μmol) of $Mn(O_2CCH_3)_2 \cdot 4H_2O$ in 1 mL of water was added. A white precipitate appears which gradually dissolves with the formation of a brown solution of $[Mn(Ta_6O_{19})_2]^{12-}$. To this solution, 1.6 mL of stock solution of $[Cp_2^*Rh_2(OH)_3](NO_3)$ (c = 0.016 M, pH = 3) was added. The reaction mixture was kept for 24 h at 80°C. After cooling the brown solution was placed in acetone vapors at 2°C, producing a dark-red precipitate and orange solution. Gradually yellow single crystals of **I** appear on the surface of the precipitate.

X-ray structure determination. The crystal structure of **I** was determined by X-ray analysis in an essentially routine way on an Xcalibur (Agilent Technologies) single crystals diffractometer, at 130 K, using graphite-monochromated MoK_α (λ = 0.71073 Å) radiation. The reflections intensities were measured φ-scanning of narrow (0.5°) frames. Empirical absorption correction was applied with SCALE3 ABSPACK program [12]. The structure was solved by direct method and refined with full-matrix least-squares treatment, anisotropically for non-hydrogen atoms using SHELXLe program [13]. No disorder was found for Na$^+$ cations and H_2O molecules. The hydrogen atoms were hot localized. Crystallographic data, refinement details and CCDC deposition code for **I** are listed in table.

RESULTS AND DISCUSSION

The structure of Lindqvist anions $[M_6O_{19}]^{8-}$ (M = Mo, W, Nb, Ta) can be described as a superoctahedron, built of six equivalent {MO$_6$} octahedra, each of which shares five of its oxo-ligands with other octahedra. This way of joining six MO$_6$ octahedra together gives on μ$_6$-O, twelve μ$_2$-O, and six terminal M=O groups. Each triangular face {M$_3$O$_3$} can be regarded as a metallomacrocycle capable of coordination to various metal cations [1–3] or cationic organometallic fragments [5–7].

Previously we reported on the reactions between $[M_6O_{19}]^{8-}$ (M = Nb, Ta) and $[Cp^*RhCl_2]_2$ (Cp* = η^5-C$_5$(CH$_3$)$_5$) in $[M_6O_{19}]^{8-}/\{Cp^*Rh\}^{2+}$ = 2 : 1 molar ratio [7]. In all cases they produced [*trans*-{Cp*Rh}$_2$M$_6$O$_{19}$]$^{4-}$ hybrid organometallic-POM complexes, which were isolated and characterized as $K_4[\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 17H_2O$ and $Cs_4[\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 18H_2O$. By using ^{1}H DOSY NMR technique for the first time in the chemistry of niobates and tantalates, we were able to estimate the diffusion coefficients, hydrodynamic radii and molecular mass of $[\{Cp^*Rh\}_2M_6O_{19}]^{4-}$ in water solution, and rule out any association or condensation processes. By following temperature dependence of ^{1}H NMR spectra we have also ruled out equilibration of [*trans*-

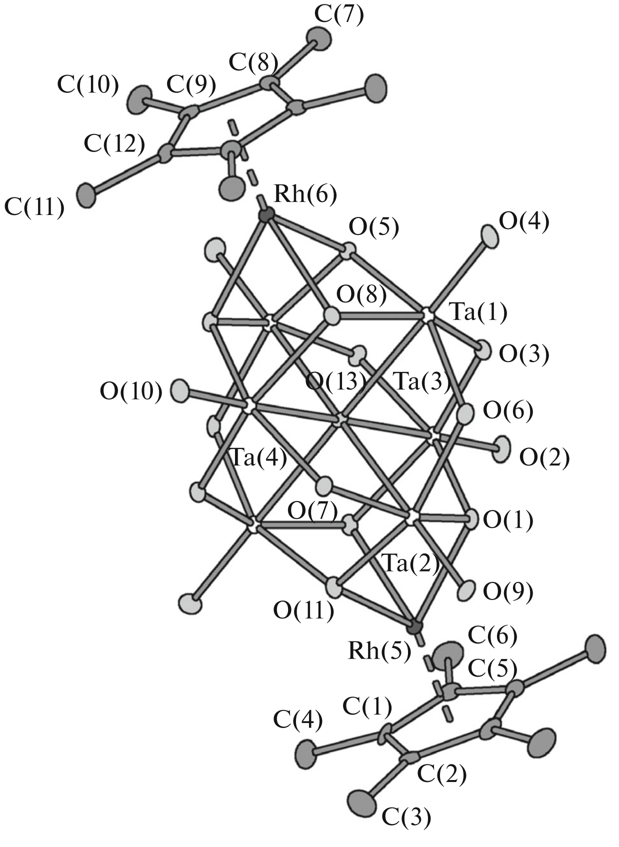

Fig. 1. View of $[trans\text{-}\{Cp^*Rh\}_2Ta_6O_{19}]^{4-}$. Hydrogen atoms form the CH_3 groups in Cp* are omitted for clarity (with 50% probability ellipsoids).

$\{Cp^*Rh\}_2M_6O_{19}]^{4-}$ with their hypothetical *cis*-isomers. In the crystal structure both $K_4[\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 17H_2O$ and $Cs_4[\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 18H_2O$ have, despite difference in the cationic composition and different symmetry of the elementary cells, the same layered structure. The $[trans\text{-}\{Cp^*Rh\}_2M_6O_{19}]^{4-}$ anions are connected by their respective K^+ or Cs^+ counter-ions into layers (the coordination around K^+ and Cs^+ is completed by water molecules). The layers are mutually arranged in way as to permit π–π stacking interactions between the Cp* ligands.

In this work we ran reaction of sodium hexatantalate with $[Cp^*RhCl_2]_2$ in molar ratio $[Ta_6O_{19}]^{8-}/\{Cp^*Rh\}^{2+} = 1 : 2$, which also yielded *trans*-complex $[\{Cp^*Rh\}_2Ta_6O_{19}]^{4-}$, isolated and structurally characterized as $Na_4[\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 24H_2O$ (**I**) (Fig. 1).

In the structure of **I**, half-sandwich organometallic fragments $\{Cp^*Rh\}^{2+}$ are coordinated at two mutually opposing $\{Ta_3O_3\}$ faces of the Ta_6 octahedron (which can be described as *anti-trans* coordination mode [14]). Average Rh–O bond length (2.150(3) Å) is close to the values found in $K_4[\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 17H_2O$ (2.149(5) Å) and $Cs_4[\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 18H_2O$ (2.138(8) Å). In the crystal structure of **I** there are three sorts of Na^+ ions, which differ in their coordination environment. Na(1) has coordination number six, with five water molecules and a μ_2-O atom of the anion (Na(1)–O(6) 2.497(4) Å). The coordination sphere around Na(2) is built exclusively of six H_2O molecules. The coordination polyhedra of both types of Na^+ ions are severely distorted and resemble little regular octahedra. These distortions are most probably due to the packing effects. Na(3) coordinates only four water molecules, while bonding two μ_2-O atoms from neighboring anions (Na(3)–O(7) 2.800(3) Å), which are mutually *trans* in the coordination sphere. The

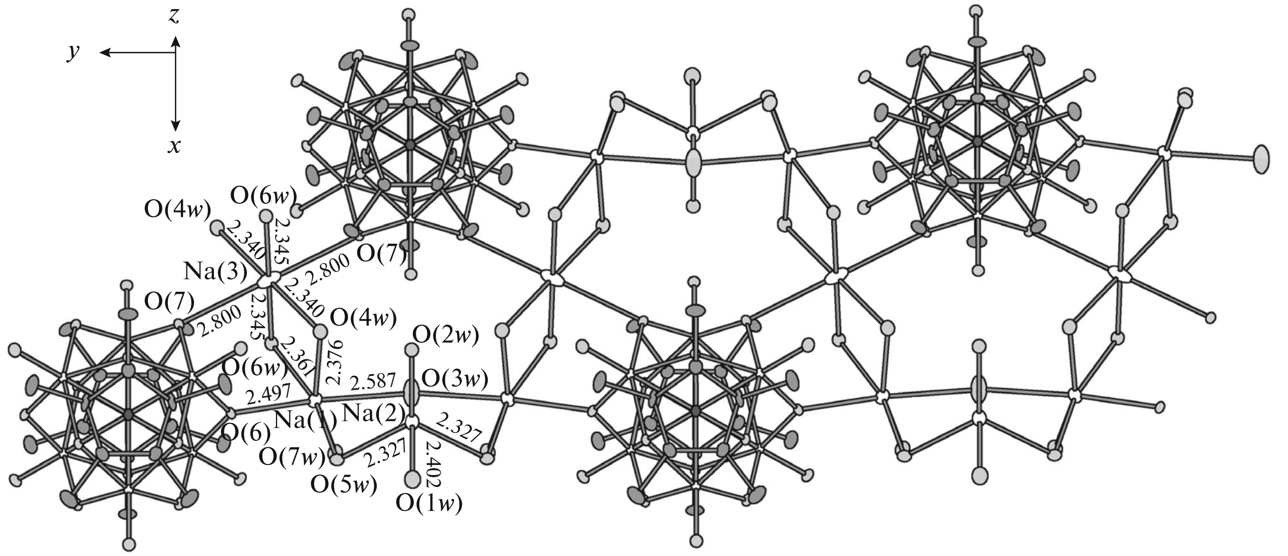

Fig. 2. Cation-anionic zig-zag chains formed in the structure of **I**. The hydrogen atoms are omitted for clarity.

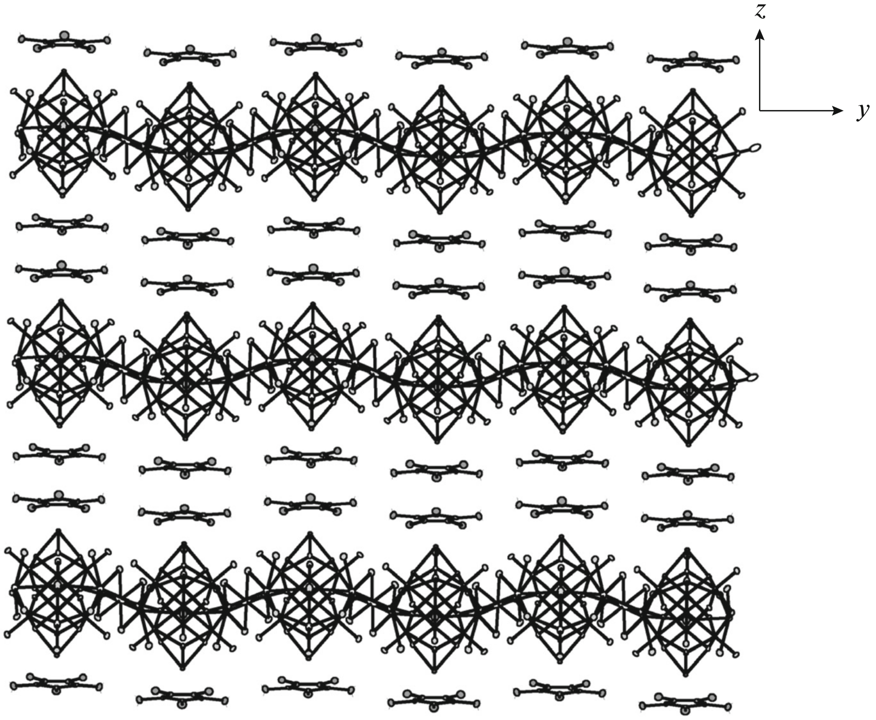

Fig. 3. Crystal packing of **I**. Rh–C bonds, hydrogen atoms, and interlayer water of crystallization are omitted for clarity.

coordination polyhedron around Na3 has point symmetry D_{4h} and is more close to idealized octahedral geometry than in the case of Na(1) and Na(2) (Fig. 2).

In the crystal structure of **I** the cations, water molecules, and anions, form layers spreading along the [110] crystallographic direction, which form contacts with each other through π–π stacking interactions between the Cp* ligands (Fig. 3). Similar packing mode was reported for $K_4[\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 17H_2O$, $Cs_4[\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 18H_2O$ [7] and $K_4[\{(p\text{-}Cym)Ru\}_2Nb_6O_{19}] \cdot 4H_2O$ (*p*-Cym = *p*-Cymene) [5]. Thus, despite dramatic variation in the ionic radii between Na^+ and Cs^+, the tendency to form layered structures persists, probably supported by the presence of η^5 or η^6 aromatic ligands grafted to POM.

In aqueous solution **I** does not show tendency to lose the $\{Cp^*Rh\}^{2+}$ units, which was confirmed by temperature-independent ^1H NMR spectra. At room temperature the methyl groups of the Cp* ligand appear as two singlets of equal intensity, because free rotation around $C_{(ring)}$–$C_{(CH3)}$ bond is hindered in order to avoid $H_{(CH3)}\cdots O_{(POM)}$ repulsions. That these signals come from differently oriented protons of the same *trans*-isomer, and not from *cis-trans* isomerization, is evident from the absence of temperature or time dependence of their intensities. The same effect was observed for solutions of $K_4[\{Cp^*Rh\}_2Nb_6O_{19}] \cdot 17H_2O$ and $Cs_4[\{Cp^*Rh\}_2Ta_6O_{19}] \cdot 18H_2O$. However, in solutions of $K_4[\{(p\text{-}Cym)Ru\}_2Nb_6O_{19}]$ *cis-trans* isomerization was detected, which demonstrates lability of the Ru^{II}–O bonding with respect to Rh^{III}–O bonding. Accordingly, ^{13}C NMR spectra show four signals, each conformer giving two signals. The doublets at 94.0 and 94.2 ppm with $^2J_{C-Rh} = 10$ Hz come from the cyclopentadienyl rings, and the singlets at 8.553 and 8.501 ppm from the carbon atoms of the CH_3 groups.

As mentioned above, grafting organometallic fragments can provide convenient markers for study of polyoxometalates. For example, no exact information exists about the complex which is formed by rapid oxidation of Mn^{2+} with air in hot sodium tantalate solutions. In the case of niobate the formation of a Mn(IV) sandwich-type complex $[Mn(Nb_6O_{19})_2]^{12-}$ was convincingly proven already in late 1960s [1, 2]. For hexatantalate no crystalline product could be isolated, even though $[Mn(Ta_6O_{19})_2]^{12-}$ is the most probable formulation of the resulting complex. In this work we attempted to coordinate $\{Cp^*Rh\}^{2+}$ to the putative $[Mn(Ta_6O_{19})_2]^{12-}$, generated in situ, in order to facilitate its crystallization. For this purpose we reacted it with solution of $[Cp^*_2Rh_2(\mu\text{-}OH)_3]^+$, which had been obtained from $[Cp^*RhCl_2]_2$ and $AgNO_3$ in water. Mixing the solutions of $[Cp^*_2Rh_2(\mu\text{-}OH)_3]^+$ and $[Mn(Ta_6O_{19})_2]^{12-}$ produces a clear solution without any opalescence or precipitation. Acetone vapor diffusion into this solution produces a dark-red precipitate, which gradually becomes overgrown with yellow plates. X-ray analysis has shown that the plates are identical with complex **I**. We have to assume that under given experimental conditions, $[Mn(Ta_6O_{19})_2]^{12-}$ is gradually transformed into $[trans\text{-}\{Cp^*Rh\}_2Ta_6O_{19}]^{4-}$ and Mn is lost (i.e., $[Ta_6O_{19}]^{8-}$ is transferred from Mn^{4+} to $\{Cp^*Rh\}^{2+}$).

We are continuing experiments in polyoxotantalate chemistry.

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