

## Supplementary materials

### Rh(III) hydroxocomplexes speciation using HPLC-ESI-MS

Victoria V. Volchek<sup>a,\*</sup>, Semen N. Berdyugin<sup>a</sup>, Olga V. Shuvaeva<sup>a</sup>, Dmitriy G. Sheven<sup>a</sup>, Danila B. Vasilchenko<sup>a</sup>, Sergey V. Korenev<sup>a</sup>

a. Nikolaev Institute of Inorganic Chemistry, 3 Acad. Lavrentiev Ave., Novosibirsk, Russia, 630090

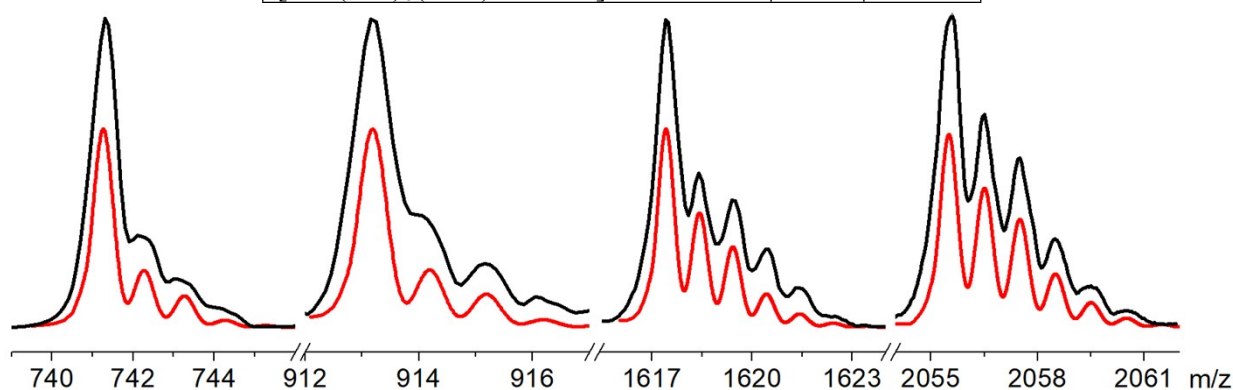
\*Corresponding author

E-mail: [volchek@niic.nsc.ru](mailto:volchek@niic.nsc.ru)

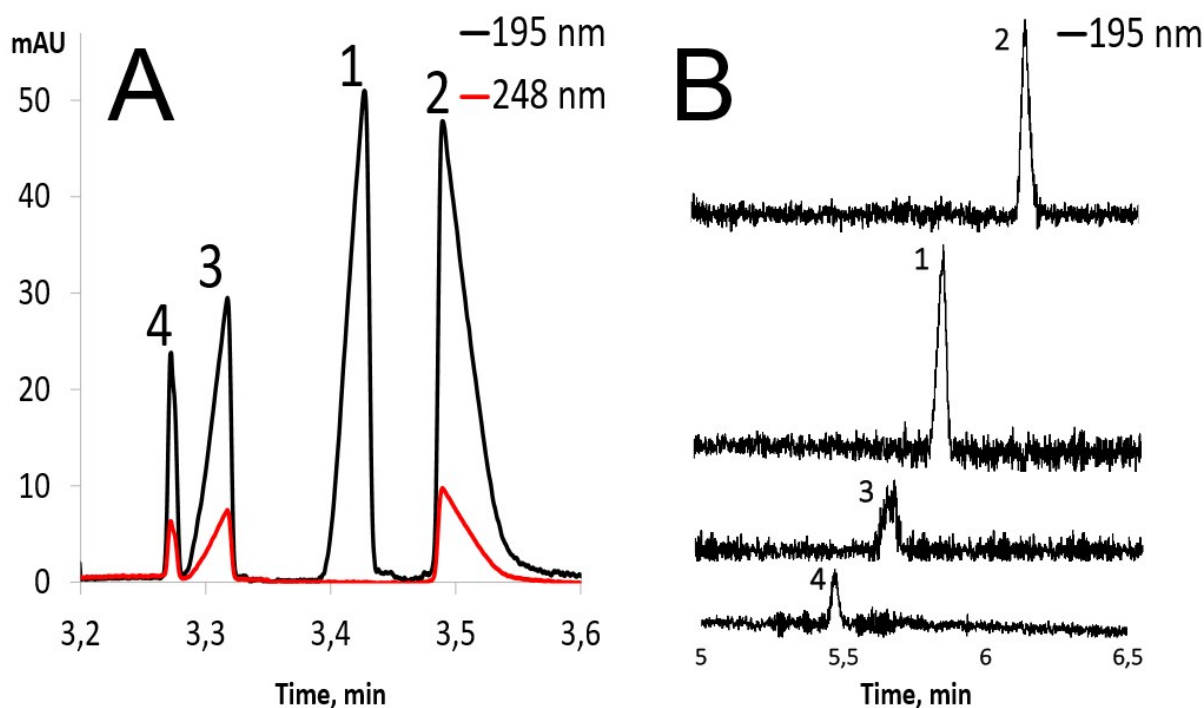
**Table S1.** Peak assignment for ESI-MS

assignment	exp	calc
$[\text{Na}^+ + 3\text{ACN}]^+$	146	146.0
$[\text{DS}^- + \text{H}^+ + \text{Na}^+ + \text{ACN}]^+$	330	330.2
$[\text{DS}^- + 2\text{Na}^+ + 2\text{ACN}]^+$	339	339.2
$[\text{SDS} + \text{Na}^+ + \text{ACN}]^+$ [31]	352	352.1
$[2\text{DS}^- + 2\text{H}^+ + \text{Na}^+]^+$	555	555.3
$[2\text{SDS} + \text{H}^+]^+$	577	577.3
$[2\text{SDS} + \text{Na}^+]^+$ [37]	599	599.3
$[\text{SDS} + \text{Na}^+ + \text{ACN} + \text{DS}^- + \text{H}^+]^+$	618	618.3
$[2\text{SDS} + \text{Na}^+ + \text{ACN}]^+$	640	640.3
$[2\text{SDS} + \text{H}^+ + \text{Na}^+ + \text{ClO}_4^-]^+$	699	699.2
$[2\text{SDS}^- + \text{Na}^+ + 3\text{ACN}]^+$	722	722.3
$[\text{Rh}(\text{H}_2\text{O})_6 + 2\text{DS}^-]^+$	741	741.3
$[3\text{DS}^- + 3\text{H}^+ + \text{Na}^+]^+$	821	821.5
$[2\text{DS}^- + 2\text{H}^+ + \text{Na}^+ + \text{SDS}]^+$	843	843.4
$[3\text{SDS} + \text{H}^+]^+$	865	865.4
$[3\text{SDS} + \text{Na}^+]^+$ [31]	887	887.4
$[\text{Rh}_2(\text{OH})_3(\text{H}_2\text{O})_7 + 2\text{DS}^-]^+$	913	913.2
$[3\text{SDS} + \text{H}^+ + \text{Na}^+ + \text{ClO}_4^-]^+$	987	987.3
$[\text{Rh}(\text{H}_2\text{O})_6 + 3\text{DS}^- + \text{H}^+]^+$	1007	1007.4
$[3\text{SDS}^- + \text{Na}^+ + 3\text{ACN}]^+$	1010	1010.5
$[\text{Rh}(\text{H}_2\text{O})_6 + 2\text{DS}^- + \text{SDS}]^+$	1029	1029.4
$[3\text{DS}^- + 3\text{H}^+ + \text{Na}^+ + \text{SDS}]^+$	1109	1109.6
$[2\text{DS}^- + 2\text{H}^+ + \text{Na}^+ + 2\text{SDS}]^+$	1132	1131.6
$[4\text{SDS} + \text{H}^+]^+$	1154	1153.6
$[4\text{SDS} + \text{Na}^+]^+$	1175	1175.5
$[\text{Rh}_2(\text{OH})_3(\text{H}_2\text{O})_7 + 3\text{DS}^- + \text{H}^+]^+$	1179	1179.3
$[4\text{SDS} + \text{H}^+ + \text{Na}^+ + \text{ClO}_4^-]^+$	1275	1275.5
$[\text{Rh}(\text{H}_2\text{O})_6 + 3\text{DS}^- + \text{H}^+ + \text{SDS}]^+$	1295	1295.6
$[4\text{SDS}^- + \text{Na}^+ + 3\text{ACN}]^+$	1298	1298.6
$[\text{Rh}(\text{H}_2\text{O})_6 + 2\text{DS}^- + 2\text{SDS}]^+$	1317	1317.5
$[3\text{DS}^- + 3\text{H}^+ + \text{Na}^+ + 2\text{SDS}]^+$	1398	1397.7
$[2\text{DS}^- + 2\text{H}^+ + \text{Na}^+ + 3\text{SDS}]^+$	1420	1419.7
$[5\text{SDS} + \text{H}^+]^+$	1442	1441.7
$[5\text{SDS} + \text{Na}^+]^+$	1464	1463.7
$[\text{Rh}_2(\text{OH})_3(\text{H}_2\text{O})_7 + 3\text{DS}^- + \text{H}^+ + \text{SDS}]^+$	1467	1467.5

$[5\text{SDS}+\text{H}^++\text{Na}^++\text{ClO}_4^-]^+$	1563	1563.6
$[5\text{SDS}^-+\text{Na}^++3\text{ACN}]^+$	1587	1586.8
$[\text{Rh}_3(\text{OH})_4(\text{H}_2\text{O})_{10}+4\text{DS}^-]^+$	1617	1617.4
$[3\text{DS}^-+3\text{H}^++\text{Na}^++3\text{SDS}]^+$	1685	1685.9
$[2\text{DS}^-+2\text{H}^++\text{Na}^++4\text{SDS}]^+$	1707	1707.9
$[6\text{SDS}+\text{H}^+]$	1730	1729.8
$[3\text{DS}^-+3\text{H}^++\text{Na}^++4\text{SDS}]^+$	1974	1974.0
$[2\text{DS}^-+2\text{H}^++\text{Na}^++5\text{SDS}]^+$	1996	1996.0
$[7\text{SDS}+\text{H}^+]$	2018	2018.0
$[\text{Rh}_4(\text{OH})_6(\text{H}_2\text{O})_{12}+5\text{DS}^-]^+$	2055	2055.5



**Fig. S1.** The ESI mass spectra of the Rh(III) polynuclear complexes during HPLC-analysis. Experimental data is shown with black line; red line corresponds to the distribution patterns calculated for  $[\text{Rh}(\text{H}_2\text{O})_6 \times 2(\text{C}_{12}\text{H}_{25}\text{SO}_4)]$ ,  $[\text{Rh}_2(\text{OH})_3(\text{H}_2\text{O})_7 \times 2(\text{C}_{12}\text{H}_{25}\text{SO}_4)]$ ,  $[\text{Rh}_3(\text{OH})_4(\text{H}_2\text{O})_{10} \times 4(\text{C}_{12}\text{H}_{25}\text{SO}_4)]$  and  $[\text{Rh}_4(\text{OH})_6(\text{H}_2\text{O})_{12} \times 5(\text{C}_{12}\text{H}_{25}\text{SO}_4)]$ , respectively.



**Fig. S2.** CZE electropherograms of  $[\text{Rh}_y(\text{OH})_m(\text{H}_2\text{O})_{z-m}]^{3y-m}$ . A – CZE analysis of the mixture of polynuclear complexes (in accordance with [17]); B – CZE analysis of the collected fractions (1-4) after HPLC separation.