Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Tuning interactions of decavanadate with thaumatin, lysozyme, proteinase K and human serum proteins by its coordination to a pentaaquacobalt(II) complex cation

Lukáš Krivosudský, [a†] Alexander Roller, [b] and Annette Rompel *[a]

[a.] *Universität Wien, Fakultät für Chemie, Institut für Biophysikalische Chemie, Althanstraße 14, Wien 1090, Austria.*
[b.] *Universität Wien, Fakultät für Chemie, Zentrum für Röntgenstrukturanalyse, Währinger Straße 42, 1090 Wien, Austria.*
† Comenius University in Bratislava, Faculty of Natural Sciences, Department of Inorganic Chemistry, Ilkovičova 6, 842 9 15 Bratislava, Slovakia.

SUPPORTING INFORMATION

1. Stability of $\mathbf{V_{10}}$, $\mathbf{V_{10}Cu}$ and $\mathbf{V_{10}Co}$ at pH = 8.0.

The stability of $\mathbf{V_{10}}$, $\mathbf{V_{10}Cu}$ and $\mathbf{V_{10}Co}$ was investigated under following conditions: 0.1 M MES buffer, 0.5 M NaCl at pH = 8.0. While $\mathbf{V_{10}}$ decomposed significantly into lower vanadates (mostly V_4, V_5), $\mathbf{V_{10}Co}$ was comparably stable as at pH = 5.8. $\mathbf{V_{10}Cu}$ is decomposed into $\mathbf{V_{10}}$ and lower vanadates. The chemical shifts of the decavanadate species are almost identical to $\mathbf{V_{10}}$ and the peak broadening in this case is a consequence of much higher proportion of V^V consumed in the decavanadate in the spectrum of $\mathbf{V_{10}Cu}$ as in $\mathbf{V_{10}}$. The broad peak at −570.0 ppm (1291.88 Hz) corresponds to an unknown species that cannot be assigned to a vanadate oligomer. Due to the very broad linewidth it is most likely a complex of Cu(II) with a lower oligovanadate.

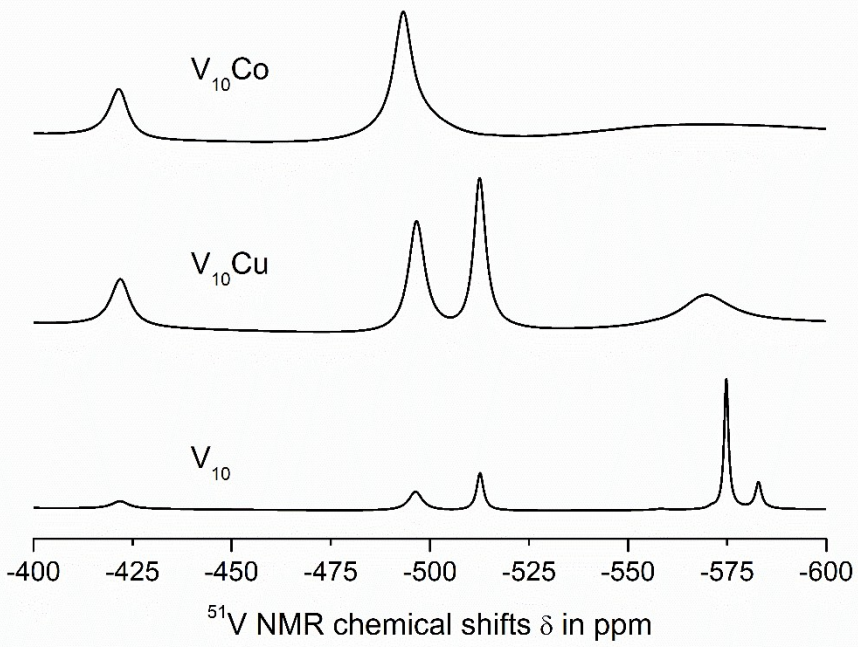

Fig S1. ^{51}V NMR spectra of 1 mM aqueous solutions of $\mathbf{V_{10}}$, $\mathbf{V_{10}Cu}$ and $\mathbf{V_{10}Co}$ in 0.1 M MES buffer, 0.5 M NaCl at pH = 8.0. Proportion of vanadium(V) in decavanadate species: $\mathbf{V_{10}}$ 37 %, $\mathbf{V_{10}Cu}$ 81 % and $\mathbf{V_{10}Co}$ 100 %.

Table S1. The ^{51}V NMR parameters of peaks in spectra of solutions of $\mathbf{V_{10}}$, $\mathbf{V_{10}Cu}$ and $\mathbf{V_{10}Co}$ in 0.1 M MES, 0.5 M NaCl at pH = 8.0. The chemical shifts are given in ppm (upper) and the linewidths at half-height in Hz (lower). The linewidths are not given for species with concentrations < 5 %.

	$\mathbf{H_xV_{10}O_{28}^{(6-x)-}}$			$\mathbf{H_2VO_4^-}$	$\mathbf{H_2V_2O_7^{2-}}$	$\mathbf{V_4O_{12}^{4-}}$	$\mathbf{V_5O_{15}^{5-}}$
	V_A	V_B	V_C				
$\mathbf{V_{10}}$	−421.5 636.22	−496.4 483.86	−512.5 309.16	−558.4	−570.9	−574.8 167.61	−582.9 228.0
$\mathbf{V_{10}Cu}$	−421.9 682.68	−496.6 558.63	−512.5 428.16	X	X	X	X
$\mathbf{V_{10}Co}$	−421.5 586.97	−493.2 1618.45[a]		X	X	X	X

[a] The linewidth was calculated from the half-heights at the low-field and high-field components of the merged broad signal.

2. Stability of **V_{10}Co** at c(V) = 10 µM.

Upon dissolution of **V_{10}Co** at c(V) = 10 µM in 0.1 M MES buffer, 0.5 M NaCl, pH = 5.8 the species is decomposed into $H_xV_{10}O_{28}^{(6-x)-}$, $H_2VO_4^-$, $H_2V_2O_7^{2-}$ and some minor oligovanadates. The Co(II) was obviously hydrolyzed out based on the peak appearance in the region -400 – -550 ppm. The existence of decavanadate is promoted by acidic pH and high ionic strength. It seems that the factor of concentration is more important for the **V_{10}Co** to stay intact than the factors of ionic strength and pH.

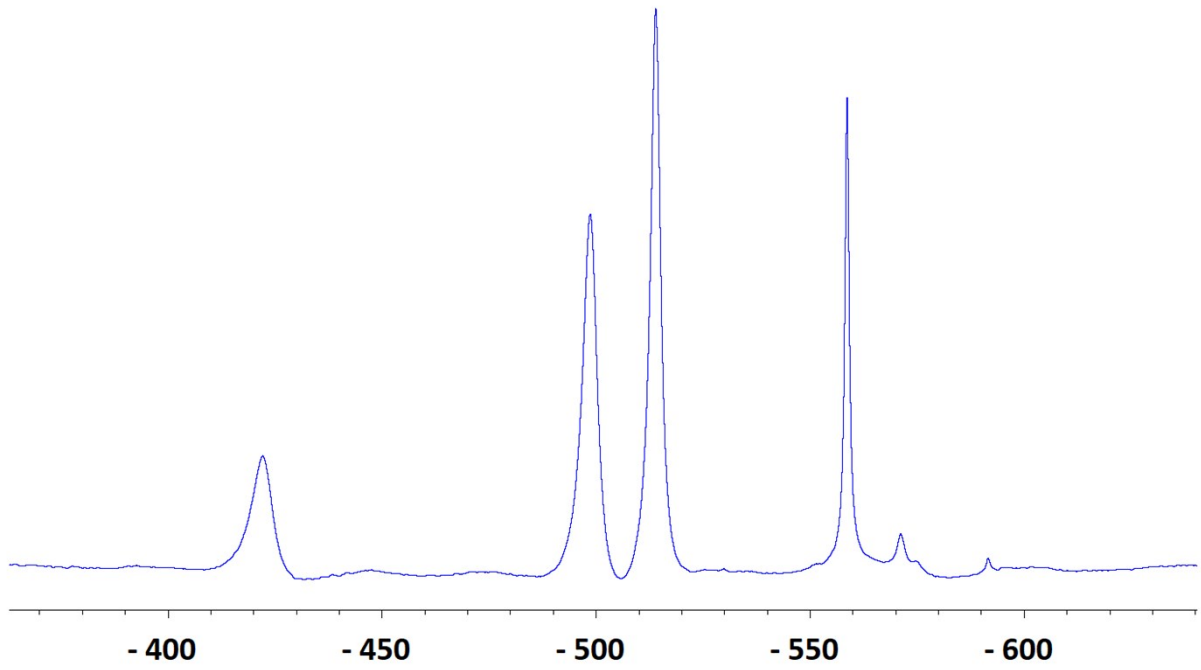

Fig S2. ^{51}V NMR spectrum of 1 µM aqueous solutions of **V_{10}Co** in 0.1 M MES buffer, 0.5 M NaCl at pH = 5.8. The spectrum was processed and magnified to eliminate background effects. Chemical shits assignment: -422.1 ppm, -498.6 ppm and -514.0 ppm $H_xV_{10}O_{28}^{(6-x)-}$, -558.6 ppm $H_2VO_4^-$, -571.2 ppm $H_2V_2O_7^{2-}$.

3. Commentary on stability of the complexes

If the transition metal decavanadato complexes do not decompose in solutions because of thermodynamic or kinetic reasons is not clear to us so far. The thermodynamic stability may be determined by theoretical calculation of potential energies of the systems. For the POM-protein complexes this is not possible to be done until a crystal structure of the complex is known.

In the experiment described in section 3.3.3, Fig. S2, we collected the ^{51}V NMR spectrum of $V_{10}Co$ at 1 mM concentration (10 mM total vanadium). We observed that the cobalt(II) center is no longer coordinated to decavanadate and we also observed substantial decomposition of decavanadate into lower vanadates. Therefore, one can suggest that the coordination of Co(II) to V_{10} is not causing kinetic inertness of the complex, but rather thermodynamic stabilization. Kinetically inert complex should be stable regardless of its concentration.

On the other hand, in the presence of the protein, the situation is more complicated. Without knowing the structure of the POM-protein complex it is not reasonable to propose any reasoning regarding the stability of the complex.

4. Infrared spectra

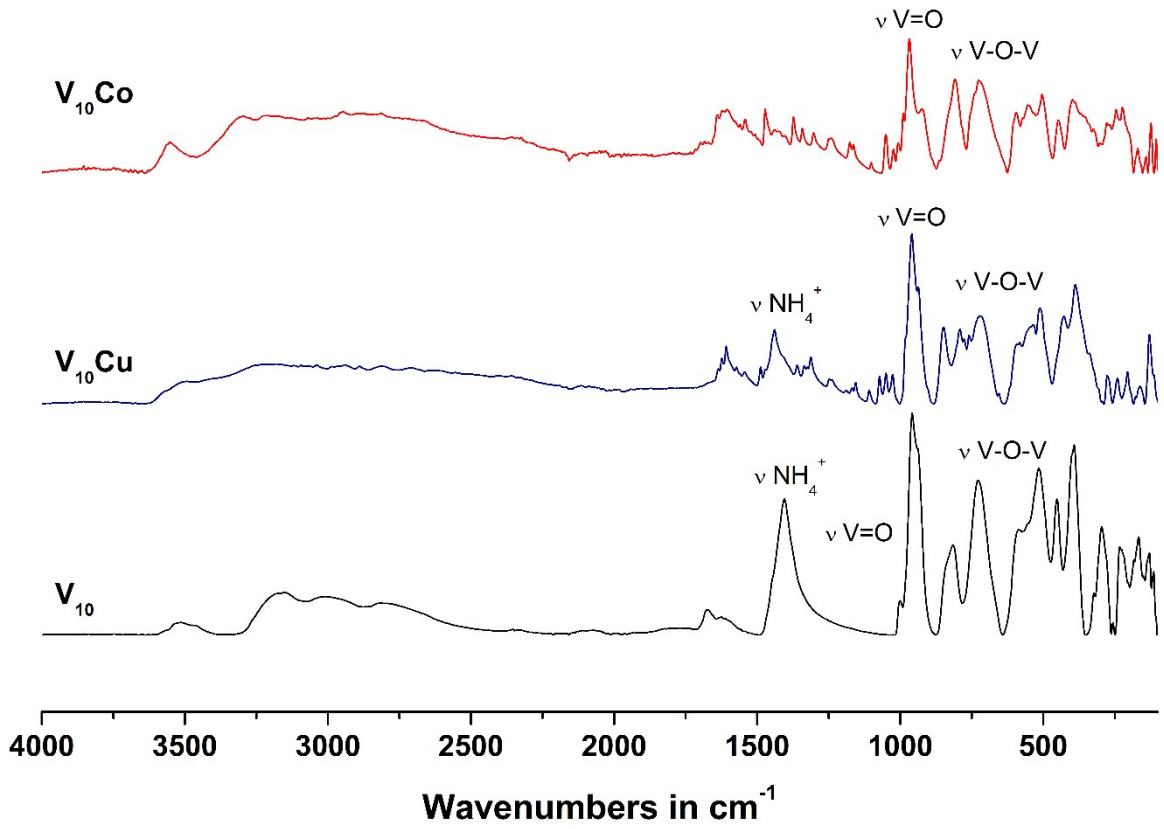

Fig. S3 FT-IR spectra of compounds **V_{10}**, **V_{10}Cu** and **V_{10}Co** collected by ATR technique in the region 100 – 4000 cm-1 with designation of the most important bands. For full band assignment see section 2.4.