ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

Speciation in human blood of Metvan, a vanadium based potential anti-tumor drug

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Figure S1. Concentration distribution curves of the species formed in the system $V^{IV}O^{2+}/Me_2phen$ with a molar ratio of 1/5 and $V$ concentration of $1.0 \times 10^{-3}$ M.
Figure S2. High field region of the X-band anisotropic EPR spectra recorded at 120 K as a function of pH in the system V$^{IV}$O$^{2+}$/Me$_2$phen with a molar ratio of 1/5 and V concentration of 1.0 $\times$ 10$^{-3}$ M.

The $M_I = 7/2$ resonance of [VO(Me$_2$phen)(H$_2$O)$_3$]$^{2+}$ (equatorial-equatorial coordination) is indicated with I, of [VO(Me$_2$phen)(H$_2$O)$_3$]$^{2+}$ (equatorial-axial coordination) with II, of cis-[VO(Me$_2$phen)$_2$(H$_2$O)]$^{2+}$ with III, and of cis-[VO(Me$_2$phen)$_2$(OH)]$^+$ with IV.
Figure S3. ESI mass spectrum recorded in the positive mode at pH 4.80 in ultrapure LC-MS water in the system V^{IV}O^{2+}/Me\textsubscript{2}phen with a molar ratio of 1/2 and V concentration of 1.0 × 10^{-5} M.
Figure S4. Experimental (a) and calculated (b) isotopic pattern for the peak of $[\text{V}^{IV}\text{O(Me}_{2}\text{phen})_{2}]^{2+}$ revealed at m/z = 241.57 in the positive ESI-MS spectrum recorded on the system $\text{V}^{IV}\text{O}^{2+}/\text{Me}_{2}\text{phen}$ (ultrapure LC-MS water, pH 4.80, molar ratio 1/2, V concentration $1.0 \times 10^{-5}$ M).
Figure S5. Experimental (a) and calculated (b) isotopic pattern for the peak of $[\text{V}^{\text{IV}}\text{O(Me}_2\text{phen})(\text{OH})]^+$, revealed at m/z = 292.04 in the positive ESI-MS spectrum recorded on the system $\text{V}^{\text{IV}}\text{O}^{2+}/\text{Me}_2\text{phen}$ (ultrapure LC-MS water, pH 4.80, molar ratio 1/2, V concentration $1.0 \times 10^{-5}$ M).
Figure S6. Experimental (a) and calculated (b) isotopic pattern for the peak of $[\text{V}^{\text{IV}}\text{O}_2(\text{Me}_2\text{phen})_2]^+$ revealed at m/z = 499.13 in the positive ESI-MS spectrum recorded on the system $\text{V}^{\text{IV}}\text{O}_2^+/\text{Me}_2\text{phen}$ (ultrapure LC-MS water, pH 4.80, molar ratio 1/2, V concentration $1.0 \times 10^{-5}$ M).
Figure S7. ESI-MS/MS spectrum of the fragment \([\text{V}^\text{IV} \text{O}_2(\text{Me}_2\text{phen})_2]^+\) recorded on the system \(\text{V}^\text{IV} \text{O}_2^+/\text{Me}_2\text{phen}\) (positive ion mode, m/z = 499.5 ± 1.0, ultrapure LC-MS water, pH 4.80, molar ratio 1/2, V concentration 1.0 × 10^{-5} \text{ M}).
Figure S8. High field region of the X-band anisotropic EPR spectra recorded at 120 K as a function of pH in the system V$^{IV}$O$^{2+}$/Me$_2$phen/H$_3$cit with a molar ratio of 1/2/2 and V concentration of 1.0 × 10$^{-3}$ M. The $M_I = 7/2$ resonance of [VO(citrH)(H$_2$O)$_2$]$^{2+}$ is indicated with I, of [VO(Me$_2$phen)(citrH)]$^{-}$ with II, of [VO(Me$_2$phen)(citr)]$^{2-}$ with III and of [VO(Me$_2$phen)(citrH$^{-1}$)]$^{2-}$ with IV.
Figure S9. ESI mass spectrum recorded in the negative mode at pH 4.90 in ultrapure LC-MS water in the system $V^{IVO}^{2+}/Me_2phen/H_3citr$ with a molar ratio of 1/2/2 and $V$ concentration of $2.5 \times 10^{-6}$ M.
Figure S10. Experimental (a) and calculated (b) isotopic pattern for the peak of \([V^{IV}O(\text{Me}_2\text{phen})(\text{citr})]^-\) revealed at m/z = 464.03 in the negative ESI-MS spectrum recorded on the system V^{IV}O^{2+}/Me_2phen/H_3citr (ultrapure LC-MS water, pH 4.90, molar ratio 1/2/2, V concentration 2.5 × 10^{-6} M).
Figure S11. ESI-MS/MS spectrum of the fragment \([\text{IV}^\text{O(Me}_2\text{phen)}(\text{citr})]^-\) recorded on the system \(\text{IV}^\text{O}^{2+}/\text{Me}_2\text{phen}/\text{H}_3\text{citr}\) (negative ion mode, m/z = 464.0 ± 1.0, ultrapure LC-MS water, pH 4.90, molar ratio 1/2/2, V concentration \(2.5 \times 10^{-6}\) M).
Figure S12. Experimental (a) and calculated (b) isotopic pattern for the peak of \([\text{V}^{IV}\text{O}(\text{Me}_2\text{phen})(\text{citr})+2\text{H}]^+\) revealed at m/z = 466.06 in the positive ESI-MS spectrum recorded on the system \(\text{V}^{IV}\text{O}^{2+}/\text{Me}_2\text{phen}/\text{H}_3\text{citr}\) (ultrapure LC-MS water, pH 4.90, molar ratio 1/2/2, V concentration \(2.5 \times 10^{-6} \text{ M}\)).
Figure S13. High field region of the X-band anisotropic EPR spectra recorded at 120 K as a function of pH in the system $\text{V}^{IV}\text{O}^{2+}/\text{Me}_2\text{phen}/\text{Hlact}$ with a molar ratio of 1/2/4 and V concentration of $1.0 \times 10^{-3}$ M. The $M_I = 7/2$ resonance of $[\text{VO(Me}_2\text{phen})(\text{H}_2\text{O})_3]^{2+}$ (equatorial-equatorial coordination) is indicated with I, of $[\text{VO(Me}_2\text{phen})(\text{H}_2\text{O})_3]^{2+}$ (equatorial-axial coordination) with II, of $[\text{VO(Me}_2\text{phen})(\text{lact})(\text{H}_2\text{O})]^+$ with III, of cis-$[\text{VO(Me}_2\text{phen})_2(\text{H}_2\text{O})]^{2+}$ with IV and of cis-$[\text{VO(Me}_2\text{phen})_2(\text{OH})]^+$ with V.
Figure S14. Experimental (a) and calculated (b) isotopic pattern for the peak of $[\text{V}^\text{IV}\text{O}_2\text{(Me}_2\text{phen)}\text{(lact)}+\text{H}]^+$ revealed at $m/z = 381.06$ in the positive ESI-MS spectrum of the system $\text{V}^{\text{IV}}\text{O}^{2+}/\text{Me}_2\text{phen}/\text{Hlact}$ in ultrapure LC-MS water (pH 3.80, molar ratio of 1/2/4, V concentration of $5.0 \times 10^{-6}$ M).
Figure S15. Concentration distribution curves of the species formed in the system V$^{IV}$O$^{2+}$/Me$_2$phen/Melm with a molar ratio of 1/5/4 and V concentration of $1.0 \times 10^{-3}$ M.
Figure S16. High field region of the X-band anisotropic EPR spectra recorded at 120 K at pH 7.4 in the system containing: a) $\text{V}^{IV}\text{O}^{2+}$/Me$_2$phen/MeIm 1/2/4 ($\text{V}^{IV}\text{O}^{2+}$ 1.0 $\times$ 10$^{-3}$ M); b) $\text{V}^{IV}\text{O}^{2+}$/Me$_2$phen/Hb 2/4/1 ($\text{V}^{IV}\text{O}^{2+}$ 6.2 $\times$ 10$^{-4}$ M); c) $\text{V}^{IV}\text{O}^{2+}$/Me$_2$phen/Hb 2/10/1 ($\text{V}^{IV}\text{O}^{2+}$ 6.2 $\times$ 10$^{-4}$ M) and d) $\text{V}^{IV}\text{O}^{2+}$/Hb 2/1 ($\text{V}^{IV}\text{O}^{2+}$ 6.2 $\times$ 10$^{-4}$ M). The $M_I = 7/2$ resonance of the species $\text{[VO(Me}_2\text{phen)(MeIm)(OH)]}^+$ and $\text{cis-[VO(Me}_2\text{phen})_2(\text{MeIm})]^{2+}$ is indicated with I, of VO–Me$_2$phen–Hb with II and of the sites $\beta$ and $\gamma$ of Hb ($\text{(VO)Hb}$ and $\text{(VO)Hb}^\gamma$) with III and IV. The $M_I = 7/2$ resonance of VO–Me$_2$phen–Hb is also denoted by the dotted line.