Supporting information:

Synthesis, Structure and Redox Properties of a *trans*-Diaqua Ru Complex That Reaches Seven Coordination at High Oxidation States

Roc Matheu,[a,b] Jordi Benet-Buchholz,[a] Xavier Sala*,[c] and Antoni Llobet*[a,c]

[a] Institute of Chemical Research of Catalonia (ICIQ), Avinguda Països Catalans 16, 43007 Tarragona, Spain.

[b] Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, Marcel·lí Domingo s/n, 43007 Tarragona, Spain.

[c] Departament de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193 Barcelona, Spain.

Corresponding authors: xavier.sala@uab.cat; allobet@iciq.cat

Outline

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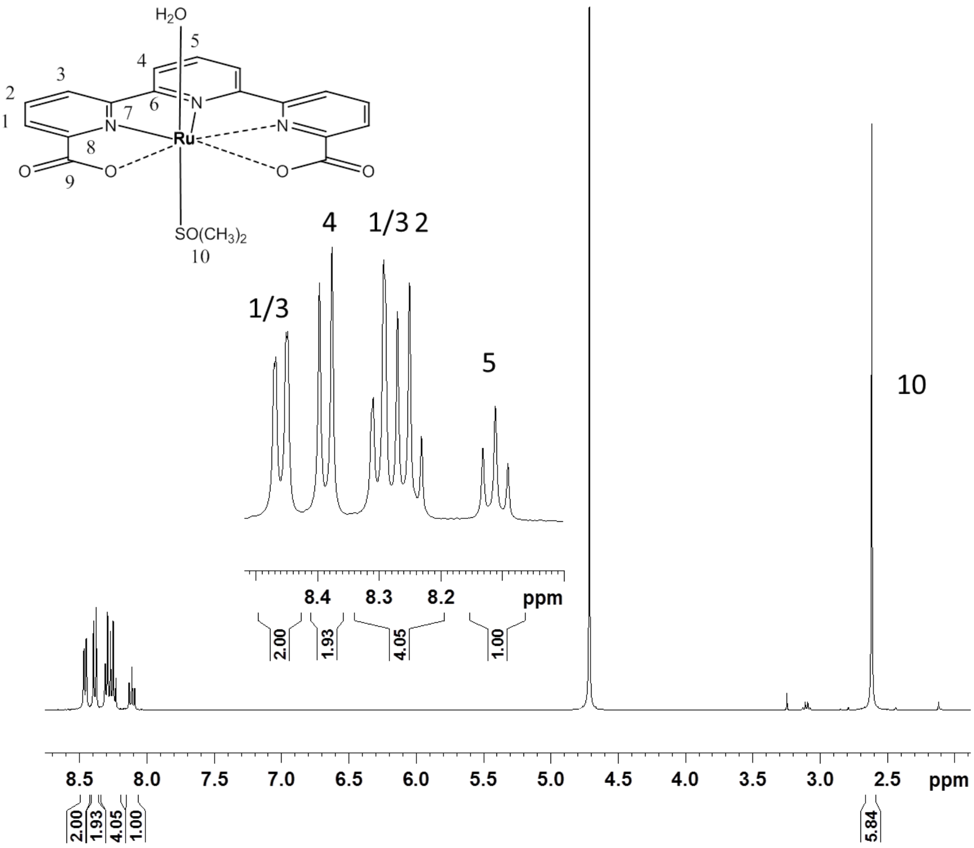

Figure S1: ^{1}H NMR spectra of $\mathbf{4^{II}}$ in D_2O (0.1 M CF_3SO_3D).

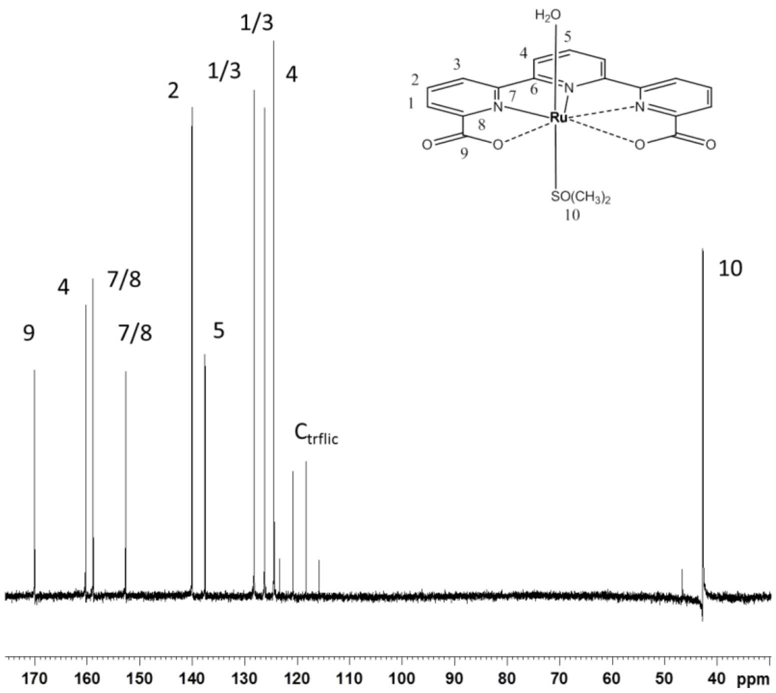

Figure S2: ^{13}C NMR spectrum of **4^{II}** in D₂O (0.1 M CF_3SO_3D).

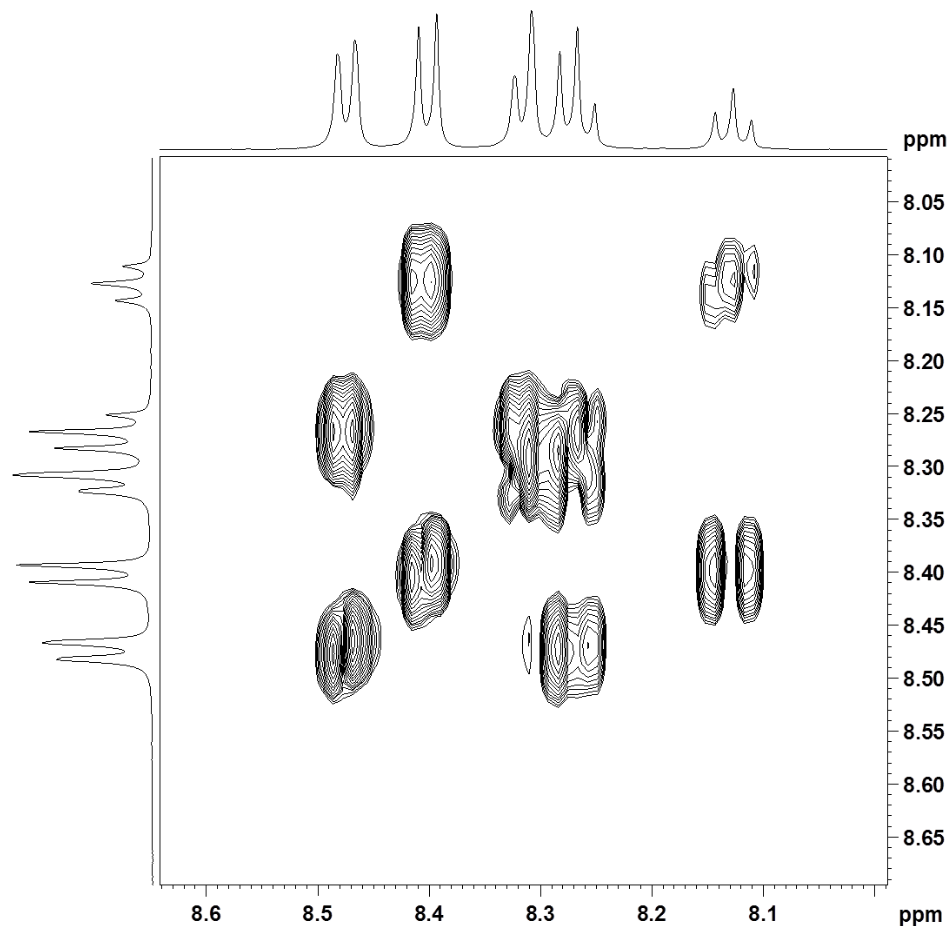

Figure S3: ^{1}H- ^{1}H COSY spectrum of **4^{II}** in D₂O (0.1 M CF_3SO_3D).

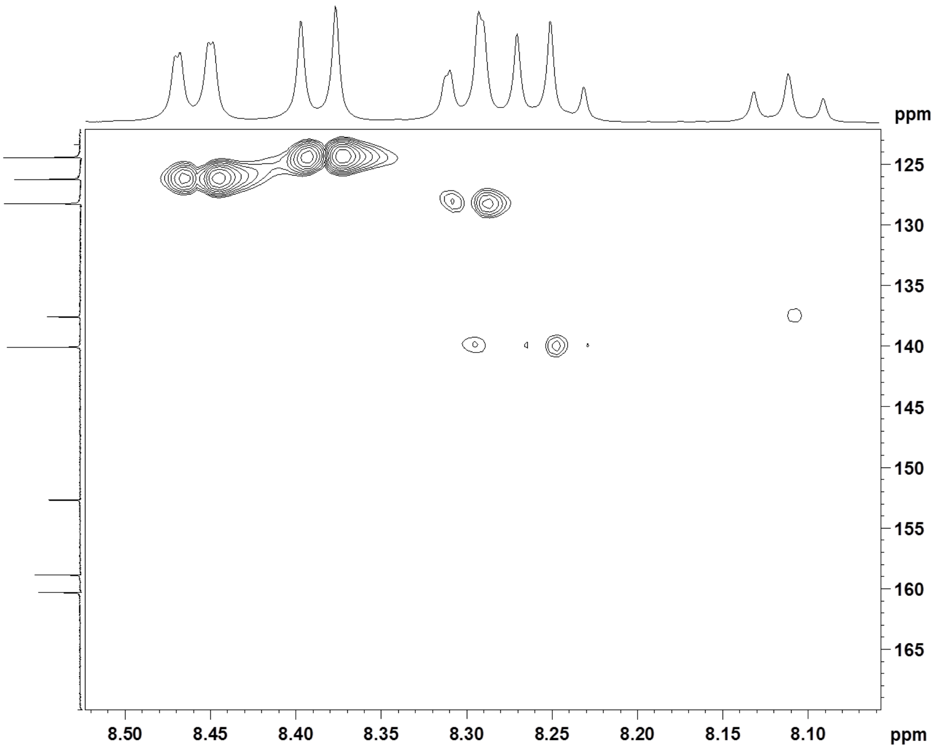

Figure S4: ^{13}C-^{1}H HSQC spectrum of **4**^{II} in D_2O (0.1 M CF_3SO_3D).

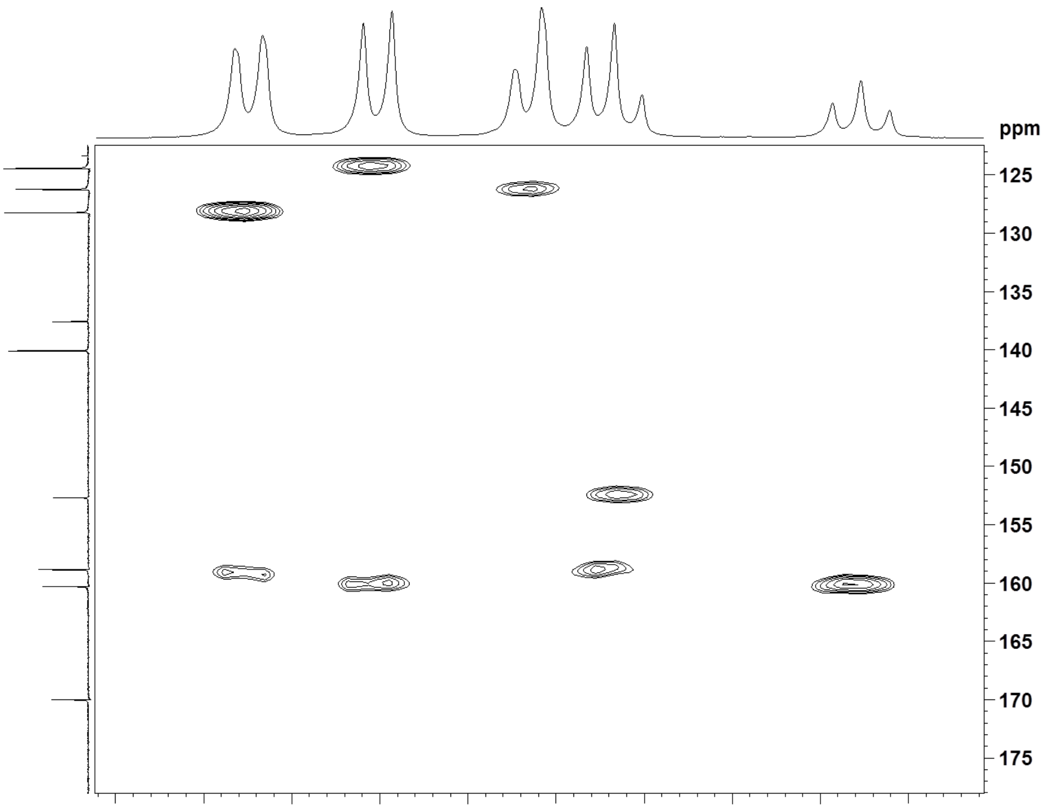

Figure S5: ^{13}C-^{1}H HMBC spectrum of **4**^{II} in D_2O (0.1 M CF_3SO_3D).

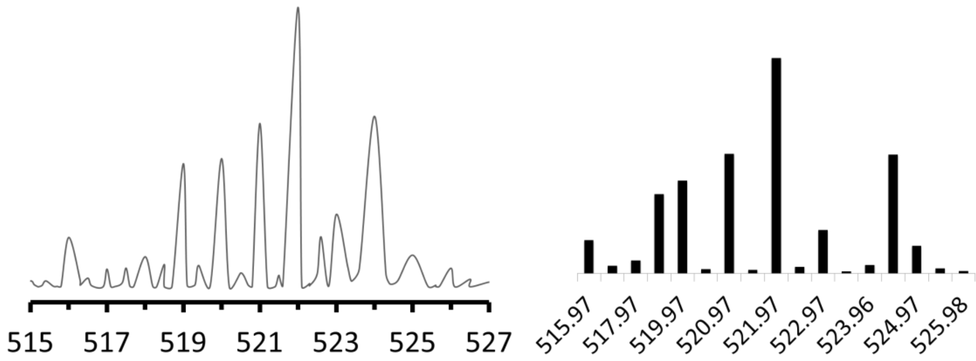

Figure S6: Measured HR-MS of [$\mathbf{4^{II}}$-H_2O+Na^+] (left) and simulated spectra for [$\mathbf{4^{II}}$-H_2O+Na^+] (right)

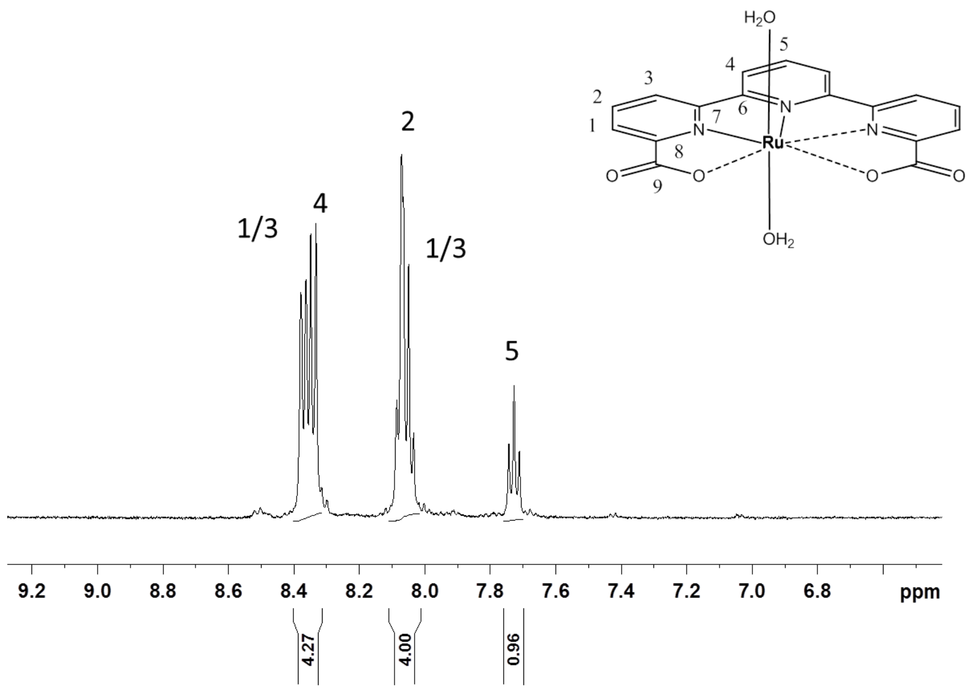

Figure S7: ^{1}H NMR spectrum of $\mathbf{3^{II}(OH_2)_2}$ in D_2O with ascorbic acid as reducing agent.

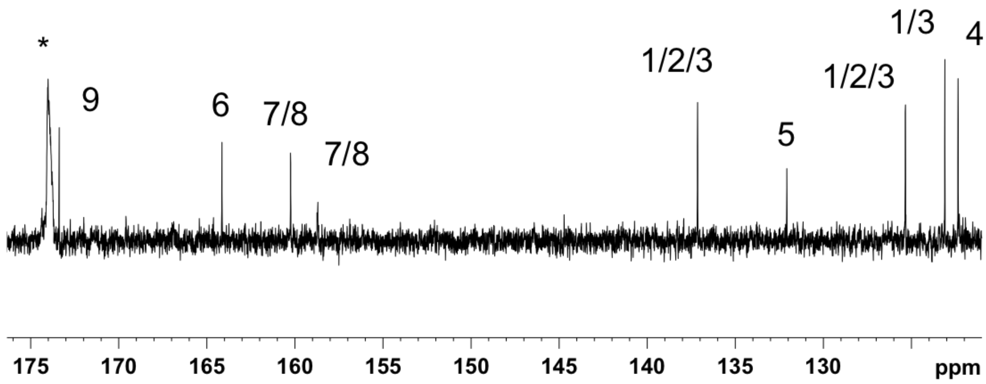

Figure S8: ^{13}C NMR spectrum of $\mathbf{3^{II}(OH_2)_2}$ in D_2O with ascorbic acid as reducing agent. Asterisk indicates a ^{13}C resonance of ascorbic acid

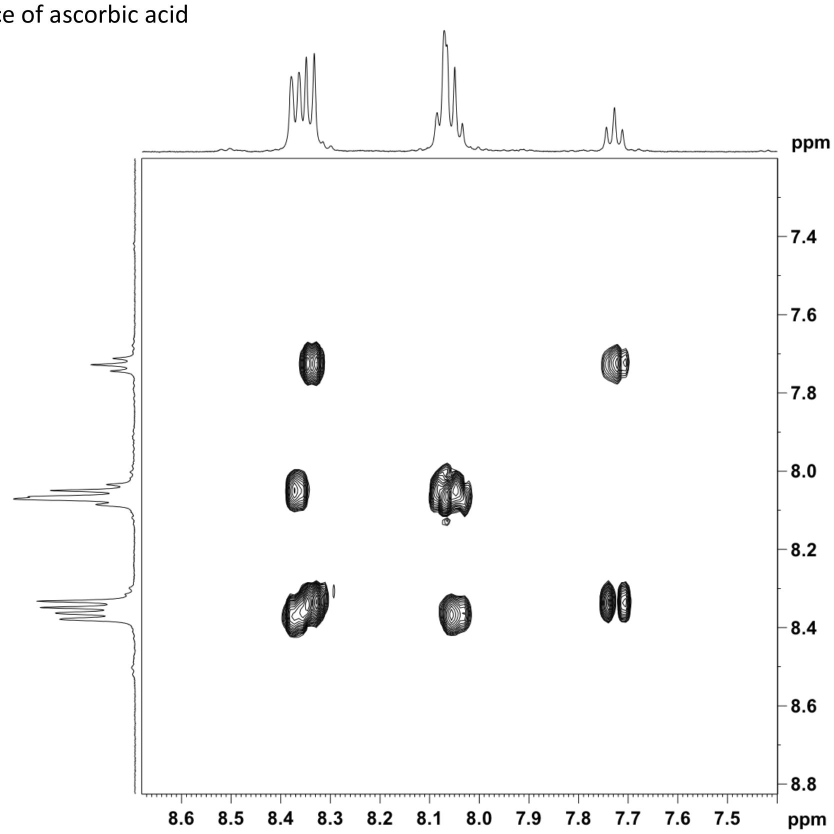

Figure S9: ^{1}H-^{1}H COSY spectrum of $\mathbf{3^{II}(OH_2)_2}$ in D_2O with ascorbic acid as reducing agent.

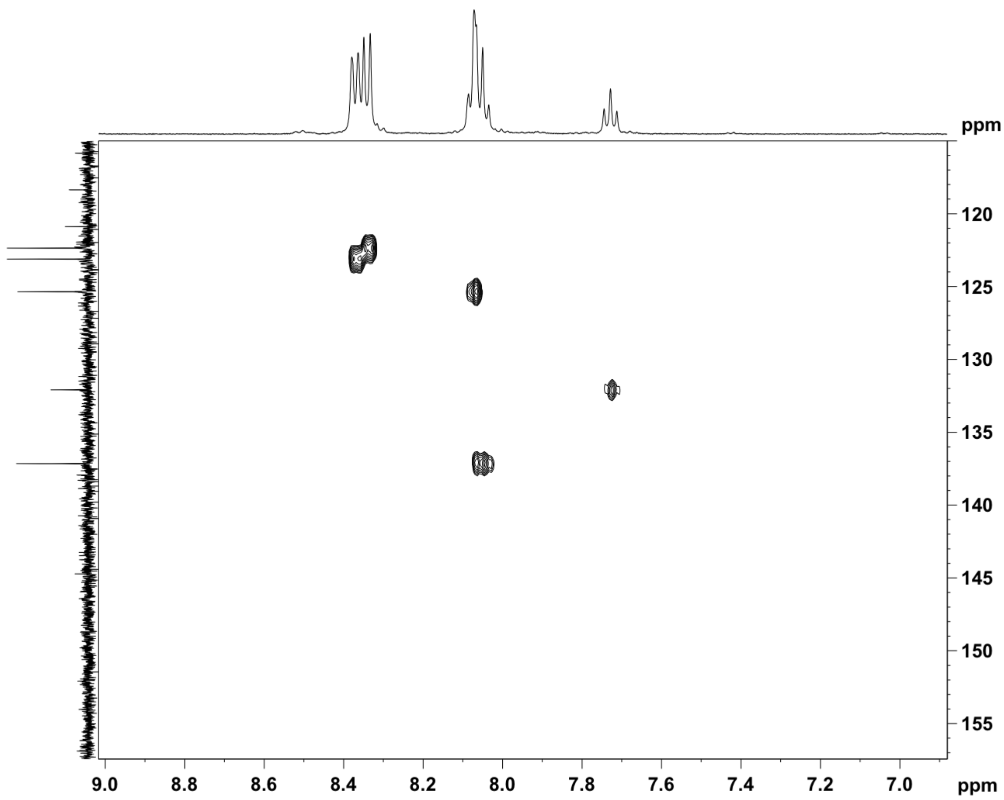

Figure S10: ^{13}C-^{1}H HSQC spectrum of **$3^{II}(OH_2)_2$** in D_2O with ascorbic acid as reducing agent.

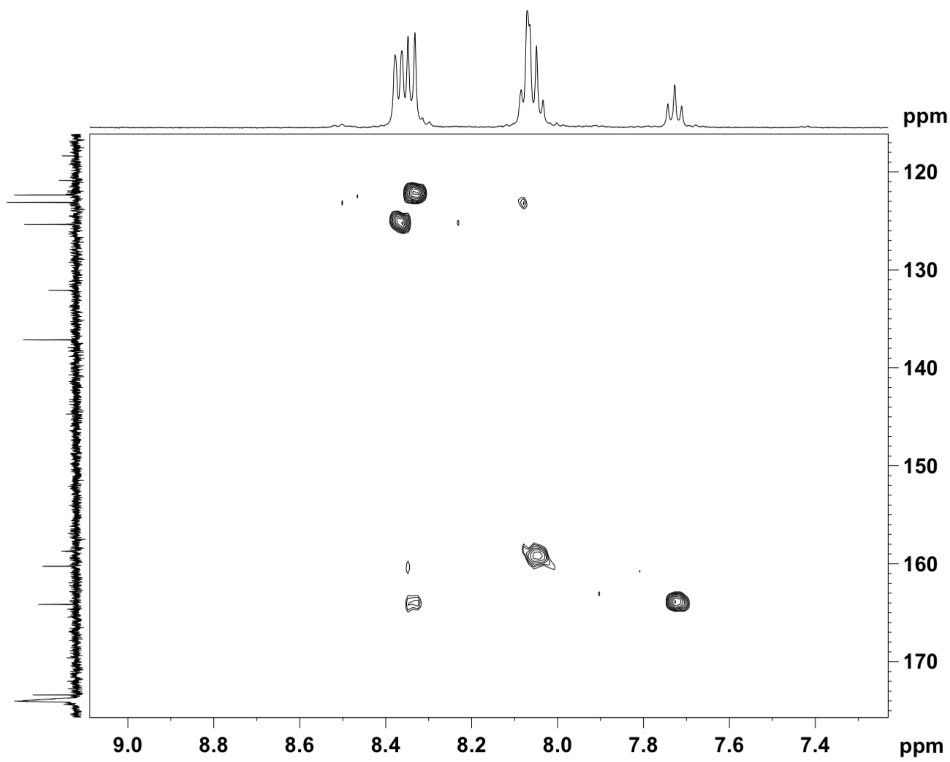

Figure S11: ^{13}C-^{1}H HMBC spectrum of **$3^{II}(OH_2)_2$** in D_2O with ascorbic acid as reducing agent.

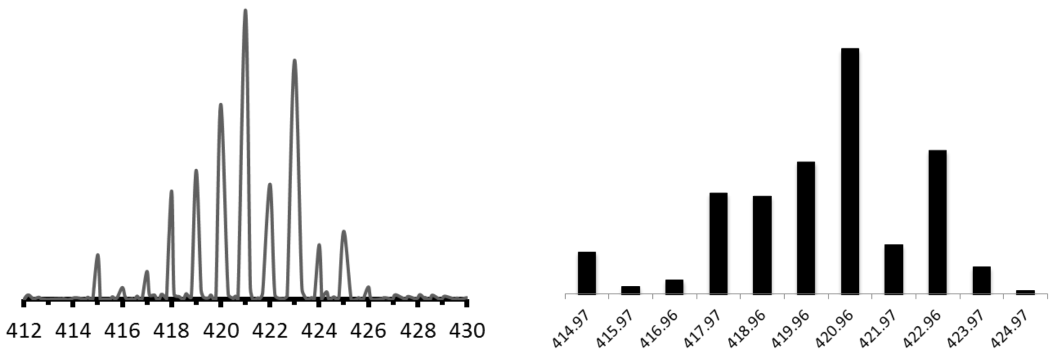

Figure S12: Measured HR-MS of [$\mathbf{3^{III}(OH_2)_2}$-2·H_2O]$^+$ (left) and simulated HR-MS of [$\mathbf{3^{III}(OH_2)_2}$-2·H_2O]$^+$ (right)

Table S1: Metric parameters of $\mathbf{3^{III}(OH_2)_2^+}$, $\mathbf{4^{II}}$, $\mathbf{5^{II}}$, $\mathbf{6^{II}}$ and $\mathbf{7^{II,+}}$ in Å.

		$\mathbf{3^{III}(OH_2)_2^+}$	$\mathbf{4^{II}}$	$\mathbf{5^{II}}$	$\mathbf{6^{II}}$	$\mathbf{7^{II,+}}$
Equatorial coordination	Ru-OH_2	---		---	---	2.2
	Ru-N1	2.0	2.0	2.2	2.0	2.1
	Ru-N2	2.0	1.9	2.0	1.9	1.9
	Ru-N3	2.1	2.2	2.0	2.1	2.1
	Ru-O1	2.2	2.3	2.2	2.2	3.5
	Ru-O2	2.4	3.1	3.3	---	3.7
Axial coordination	Ru-N4	---	---	2.1	2.1	---
	Ru-N5	---	---	---	2.1	---
	Ru-$O3H_2$	2.1	2.1	---	---	2.1
	Ru-$O4H_2$	2.1	---	---	---	---
	Ru-S1	---	2.2	2.2	---	2.2
Ox. State		III	II	II	II	II
Reference		This work	This work	1	2	This work

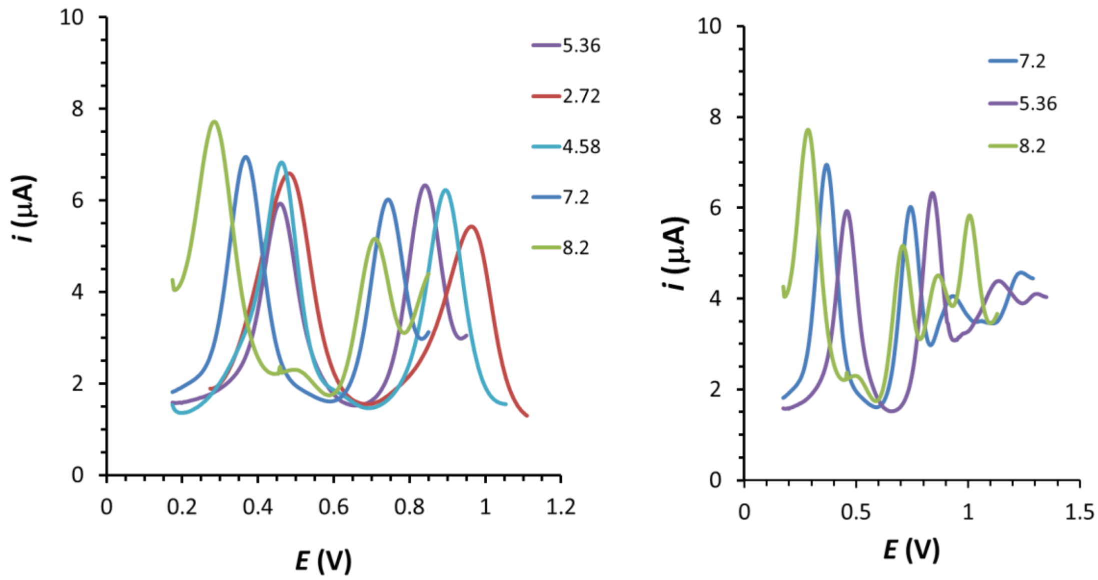

Figure S13: DPVs of $\mathbf{3^{III}(OH_2)_2^+}$ at pH from 2.72 to 8.20.

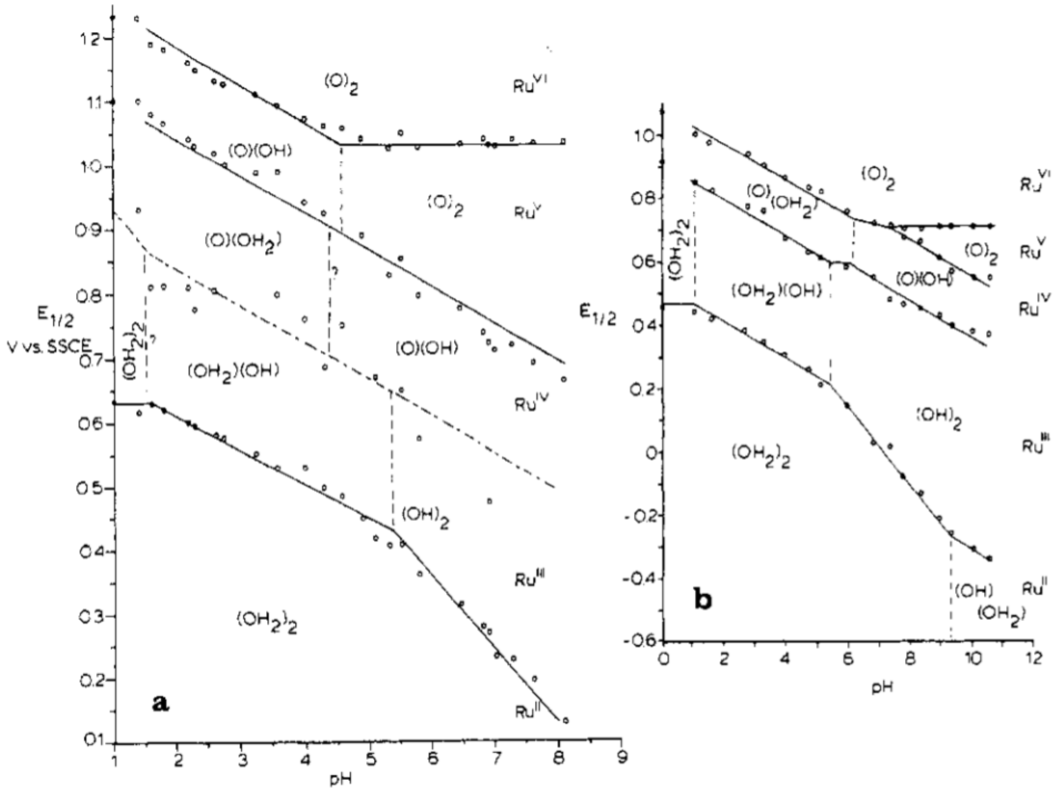

Figure S14. Pourbaix diagram for complexes for complex $\mathbf{12^{II}(OH_2)_2^{2+}}$ (**a**) and $\mathbf{11^{II}(OH_2)_2^{2+}}$ (**b**). Reprinted from reference 3. Potential vs SSCE.

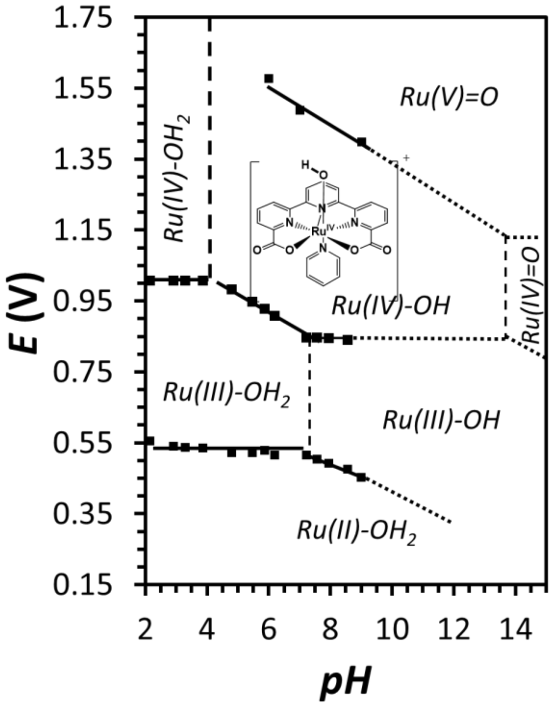

Figure S15. Pourbaix diagram for complexes for complex $\mathbf{2^{III}(OH)^{+}}$. Reprinted from reference 1.

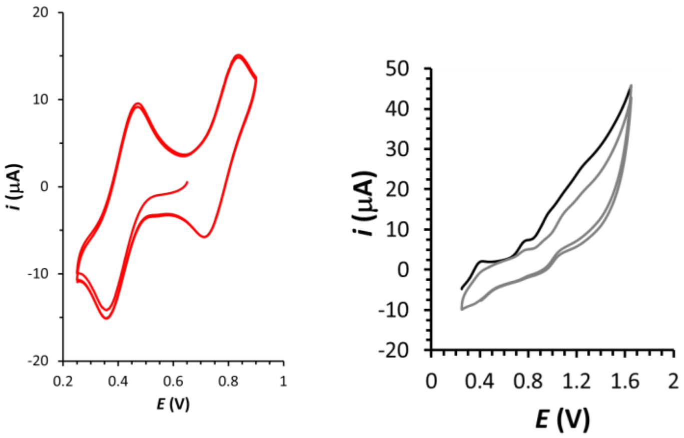

Figure S16: Left, two consecutive CVs of $\mathbf{3^{III}(OH_2)_2^+}$ at pH = 7.0 cycled from 0.25 V to 0.9 V (red line). Right, two consecutive CVs of $\mathbf{3^{III}(OH_2)_2^+}$ cycled between 0.25 and 1.65 V (black line first segment and grey the rest).

References

[1] Matheu, R.; Ertem, M. Z.; Gimbert-Suriñach, C.; Benet-Buchholz, J.; Sala, X.; Llobet, A. Hydrogen Bonding Rescues Overpotential in Seven-Coordinated Ru Water Oxidation Catalysts. *ACS Catal.* **2017**, 7, 6525-6532.

[2] Matheu, R.; Ertem, M. Z.; Benet-Buchholz, J.; Coronado, E.; Batista, V. S.; Sala, X.; Llobet, A. Intramolecular Proton Transfer Boosts Water Oxidation Catalyzed by a Ru Complex. *J. Am. Chem. Soc.* **2015**, *137,* 10786-10795.

[3] Dobson, J. C.; Meyer, T. J. Redox properties and ligand loss chemistry in aqua/hydroxo/oxo complexes derived from cis- and trans-$[(bpy)_2Ru^{II}(OH_2)_2]^{2+}$. *Inorg. Chem.* **1988**, *27*, 3283-3291.