Supporting Information

Oxidation of Ascorbic Acid by a (Salen)ruthenium(VI) Nitrido Complex in Aqueous Solution

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Materials. $[Ru^{VI}(N)(L)(MeOH)](PF_6)$ and the 50% ^{15}N-labeled complex were prepared by a literature method.[1] *L*-Ascorbic acid (Aldrich) was purified by recrystallization from $MeOH/Et_2O$. Trifluoroacetic acid (Aldrich, ≥99.0%), sodium acetate (Aldrich, ≥99.0%), acetic acid (Aldrich, 99.8%), sodium phosphate monobasic dihydrate (Sigma, ≥99.0%), sodium phosphate dibasic dihydrate (Sigma, ≥99.0%), and deuterium oxide (Cambridge Isotope, 99.8 atom % D) were used as received. Water for kinetic experiments was distilled twice from alkaline permanganate. Ionic strength was maintained with sodium trifluoroacetate (Aldrich, 98%). The pH values of solutions used for kinetic experiments were determined either by direct titration with standard NaOH solutions or by using a pH meter (Mettler Toledo, FE 20). For D_2O solutions, the pD values were obtained from a pH meter using the relationship $pD = pH_{meas} + 0.4$.

Instrumentation. Kinetic experiments were carried out using either an Agilent 8453 diode-array spectrophotometer for slow reactions, or an Applied Photophysics SX20 stopped-flow spectrophotometer for fast reactions. The temperature of the solutions was maintained with a PolyScience digital temperature controller connected to a circulating water bath. Electrospray ionization mass spectra (ESI-MS) were obtained on a PE SCIEX API 2000 mass spectrometer. The analyte solution was continuously infused with a syringe pump at a constant flow rate of 5 μL min^{-1} into the pneumatically assisted electrospray probe with nitrogen as the nebulizing gas. The declustering potential was typically set at 10 V. Cyclic voltammetry (CV) was performed with a CH Instruments Electrochemical Workstation CHI660C. A glassy carbon working electrode, a calomel reference electrode, and a Pt wire counter electrode. ^1H NMR spectra were recorded on a Bruker (400 MHz) FT-NMR spectrometer.

Kinetics. The concentrations of H_2A were at least in 10-fold excess than that of $Ru^{VI}(N)$. The reaction progress was monitored by observing absorbance changes at 640 nm. Pseudo-first-order rate constants, k_{obs}, were obtained by nonlinear least-squares fits of A_t versus time t according to the equation $A_t = A_\infty + (A_0 - A_\infty) \exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbances, respectively.[2]

Product analysis by ESI-MS. In a typical reaction, H_2A (2.38×10^{-4} M) was allowed to react with $Ru^{VI}(N)$ (1.19×10^{-4} M) in H_2O (2 mL) at different pH at 25 ^oC. The resulting green solution was analysed by ESI-MS after 5 min (pH = 5.5) and 60 min (pH = 1.0).

Product analysis by ^1H NMR. In a typical reaction, a mixture containing H_2A (6.16×10^{-3} mmol) and $Ru^{VI}(N)$ (3.08×10^{-3} mmol) in 20 mL H_2O (pH = 5.5) was stirred for 15 min at 25 ^oC under argon atmosphere. At pH 1.0, H_2A (6.52×10^{-3} mmol) and $Ru^{VI}(N)$ (3.26×10^{-3} mmol) were used and the mixture was stirred for 60 min. The volatiles were then removed by reduced pressure at 25 ^oC. The residue was dissolved in 1 mL of D_2O containing methanol (1.63×10^{-3} mmol) as internal standard, and the mixture was analyzed by ^1H NMR.

References

1. W. L. Man, T. M. Tang, T. W. Wong, T. C. Lau, S. M. Peng, W. T. Wong. *J. Am. Chem. Soc*. **2004**, *126*, 478

2. J. H. Espenson. *Chemical Kinetics and Reaction Mechanisms*; McGraw Hill: New York, 1981.

Table S1. Representative second-order rate constants for the oxidation of H_2A by $Ru^{VI}(N)$ at 298.0 K and $I = 0.1$ M.

pH/pD	k_2 / M^{-1} s^{-1}
1.00	(3.87 ± 0.02)
1.00 [a]	(1.39 ± 0.01)
2.12	(5.14 ± 0.01) × 10^1
2.12 [a]	(2.08 ± 0.11) × 10^1
2.67	(1.20 ± 0.01) × 10^2
3.20	(3.82 ± 0.04) × 10^2
3.57	(7.99 ± 0.02) × 10^2
3.68 [a]	(3.52 ± 0.01) × 10^2
3.94	(1.35 ± 0.01) × 10^3
3.99	(1.60 ± 0.01) × 10^3
4.03 [a]	(6.74 ± 0.04) × 10^2
4.41	(2.56 ± 0.05) × 10^3
4.47 [a]	(1.41 ± 0.04) × 10^3
4.80 [a]	(2.32 ± 0.03) × 10^3
4.90	(3.52 ± 0.06) × 10^3
5.39	(4.36 ± 0.01) × 10^3
6.05 [a]	(4.63 ± 0.10) × 10^3
6.16	(4.93 ± 0.11) × 10^3

[a] Experiments were carried out in D_2O.

Table S2. Temperature dependence of the second-order rate constant for the oxidation of H_2A by $Ru^{VI}(N)$.

T / K	**pH**	k_2 / M^{-1} s^{-1}
292.0	1.00	(2.87 ± 0.04)
298.0	1.00	(3.87 ± 0.02)
305.5	1.00	(5.80 ± 0.04)
313.0	1.00	(8.82 ± 0.01)
291.0	5.39	(2.93 ± 0.01) × 10^3
298.0	5.39	(4.36 ± 0.18) × 10^3
305.9	5.39	(6.33 ± 0.12) × 10^3
313.0	5.39	(8.75 ± 0.06) × 10^3

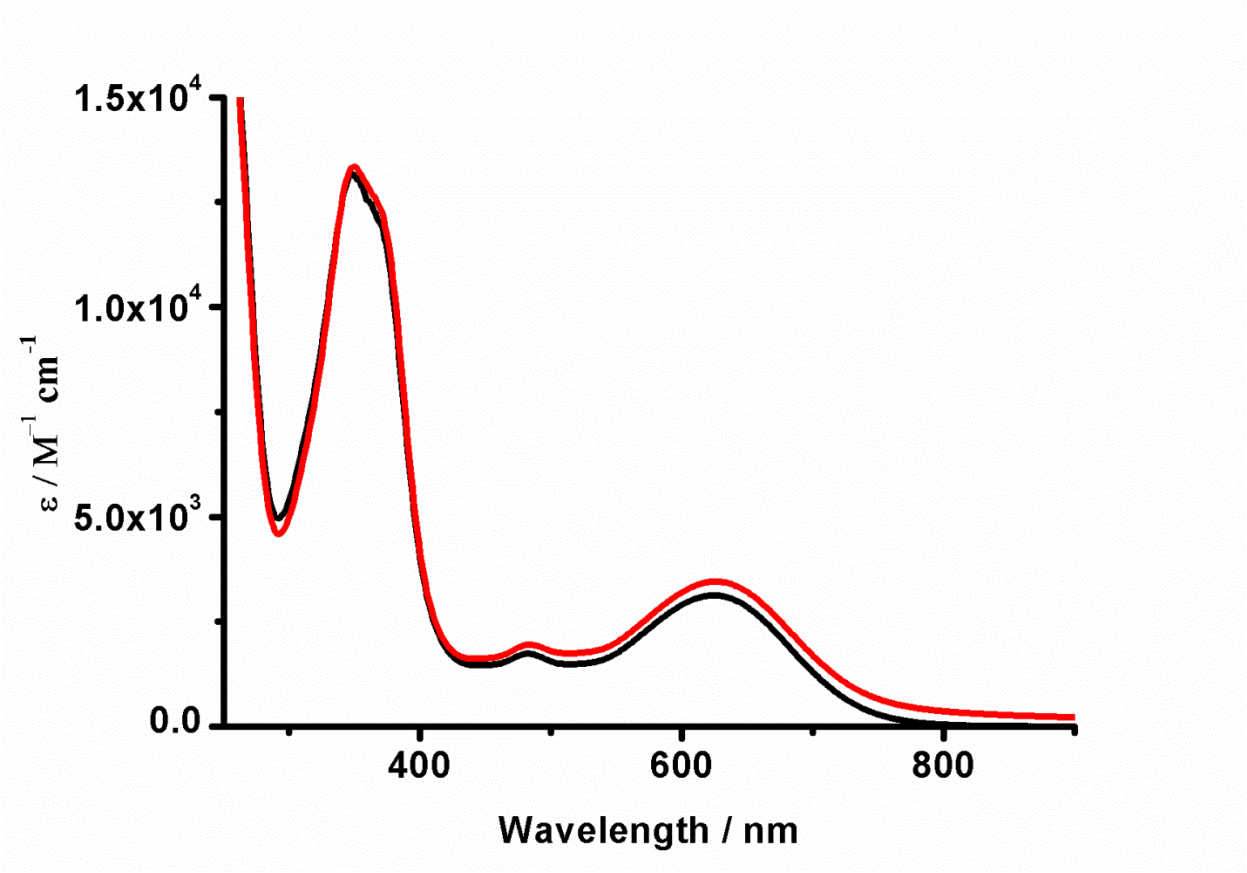

Fig. S1 UV-vis spectrum of pure $[Ru^{III}(L)(OH_2)_2]^+$ in 1 mM TFA (red) and the final UV-vis spectrum obtained for the decomposition (N···N coupling) of $Ru^{VI}(N)$ (1.30×10^{-4} M) in 1 mM TFA after 7 d (black).

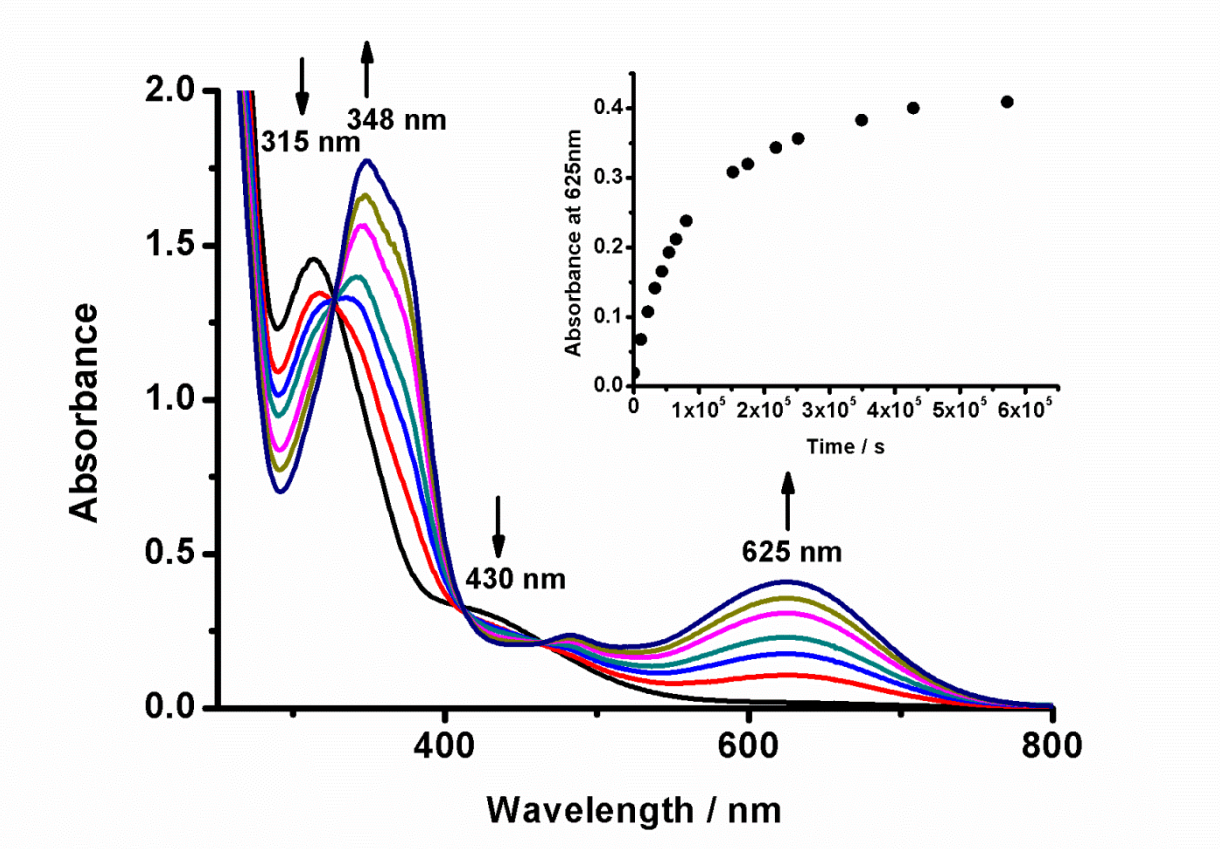

Fig. S2 UV-vis spectral changes for the decomposition (N···N coupling) of $Ru^{VI}(N)$ (1.30×10^{-4} M) in 1 mM TFA solution (data are collected at 0 h, 6 h, 13 h, 21 h, 42 h, 70 h, and 159 h, respectively). Inset shows the absorbance-time trace at 625 nm.

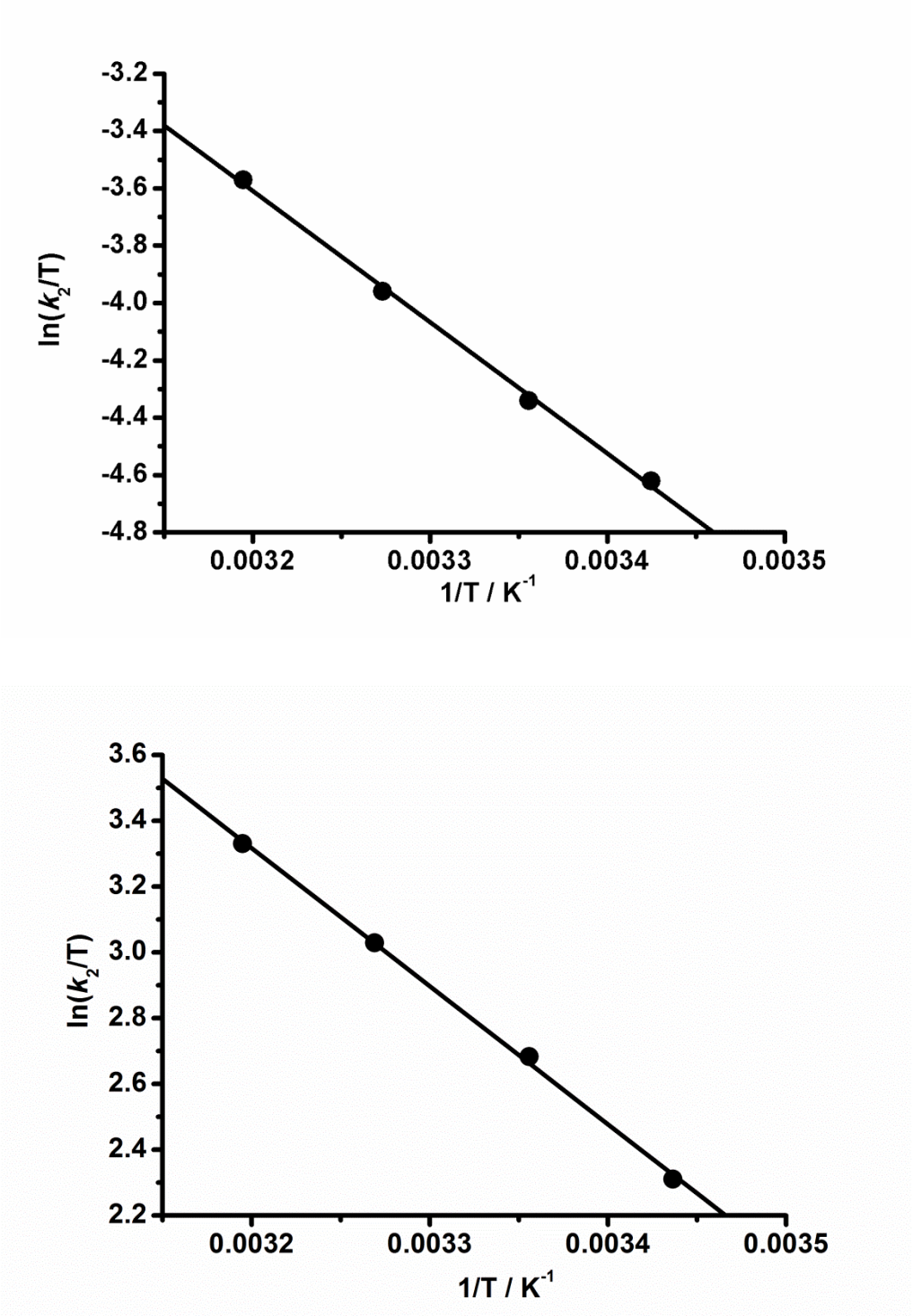

Fig. S3 Temperature dependence for the reactions of $Ru^{VI}(N)$ and H_2A in pH = 1.00 and I = 0.1 M (top) [slope = –(4.58 ± 0.14) × 10^3; y-intercept = (1.10 ± 0.05) × 10^1; r^2 = 0.9973] and pH = 5.39 and I = 0.1 M (bottom) [slope = –(4.20 ± 0.10) × 10^3; y-intercept = (1.68 ± 0.03); r^2 = 0.9983].

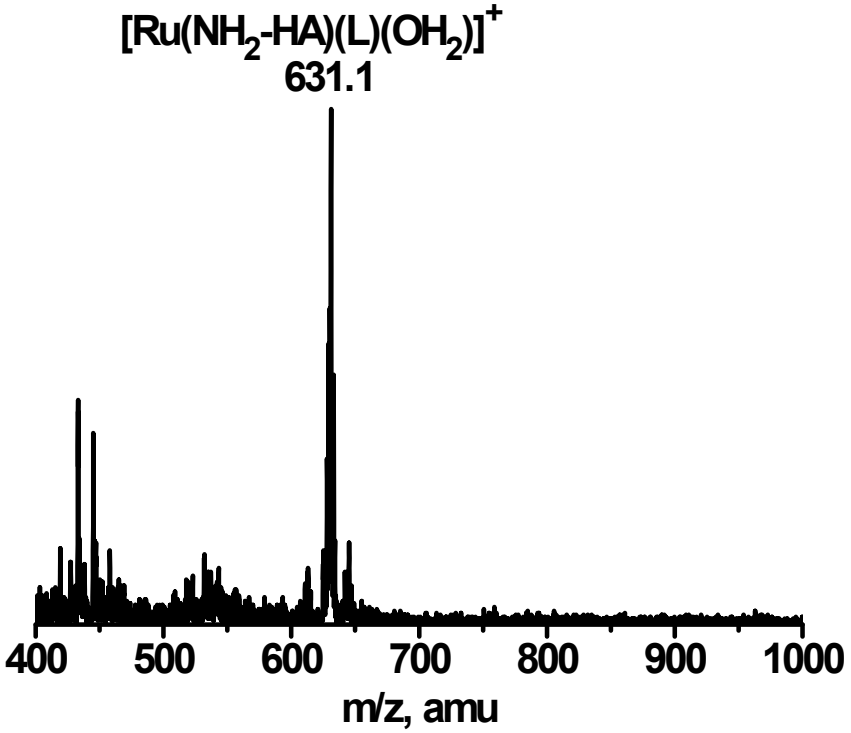

Fig. S4 ESI mass spectrum of the reaction mixture of $Ru^{VI}(N)$ and H_2A in H_2O (pH = 1.0) taken after 60 min.

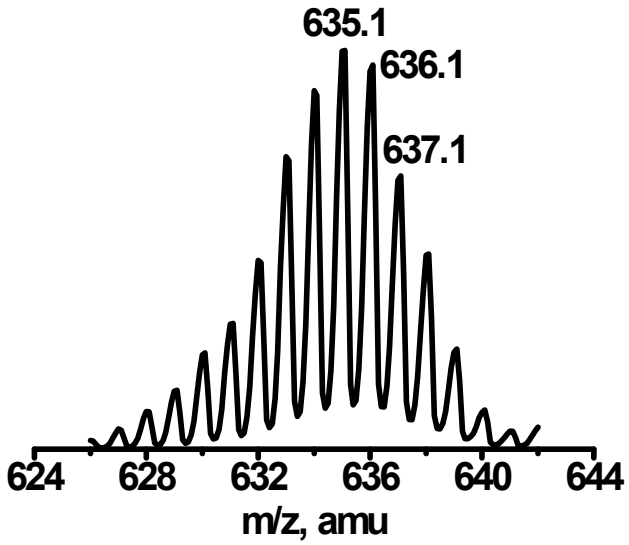

Fig. S5 The expanded peak at *m/z* 635 for the reaction mixture of $Ru^{VI}(N)$ and H_2A carried out in D_2O.

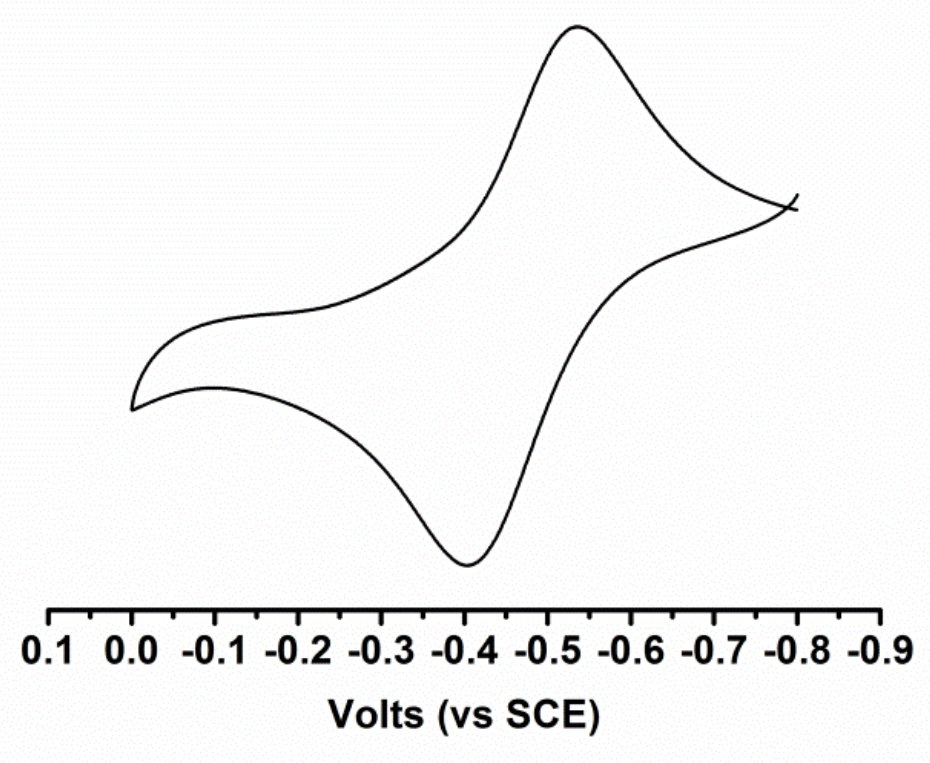

Fig. S6 CV of the product solution taken at pH 4.9.

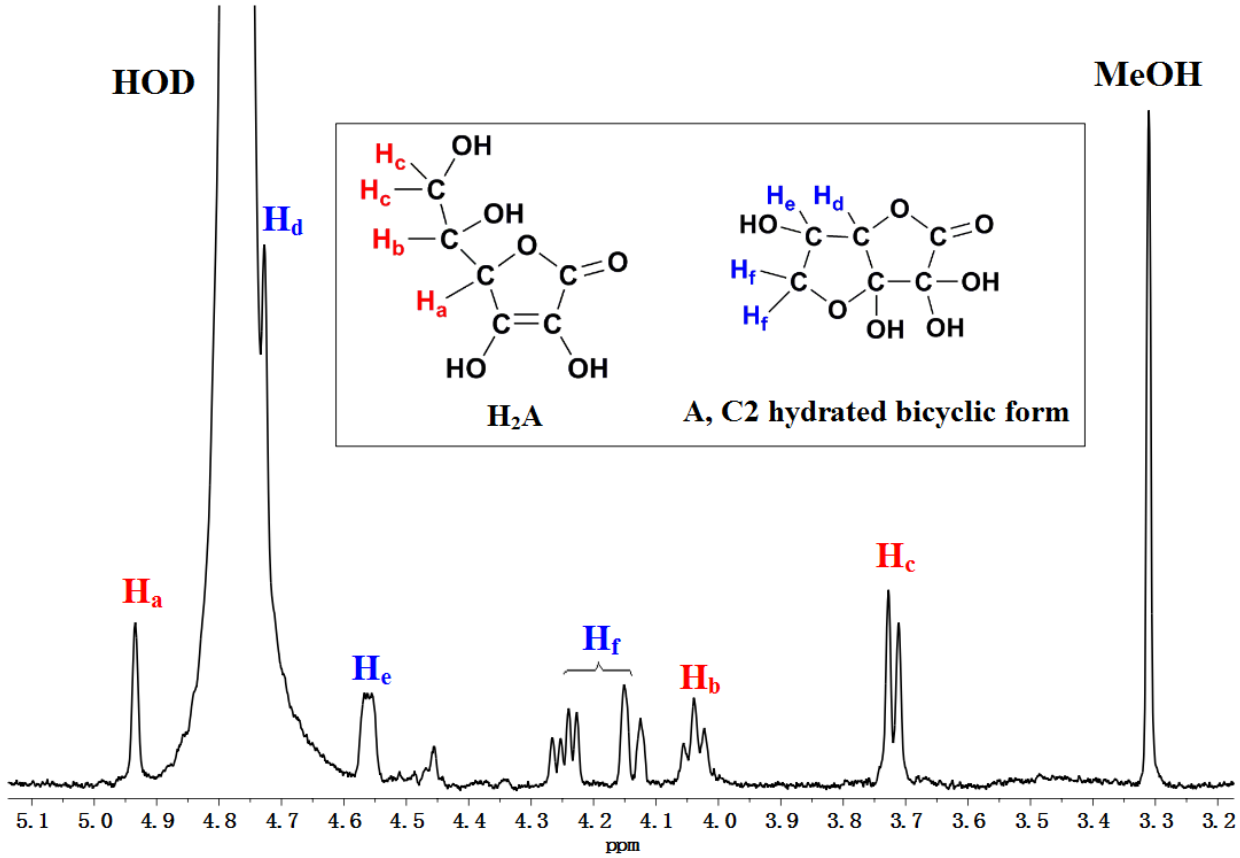

Fig. S7 ^{1}H NMR spectrum in D_2O of the residue obtained from the reaction of $Ru^{VI}(N)$ (3.26×10^{-3} mmol) and H_2A (6.52×10^{-3} mmol) in H_2O at pH 1.0. The amount of A produced and H_2A remained were determined to be $(1.74 \pm 0.04) \times 10^{-3}$ mmol and $(1.65 \pm 0.09) \times 10^{-3}$ mmol, respectively.