Electronic Supplementary Information

$Ru_2^{II,III}$ diphosphonato complex with metal-metal bond for water oxidation

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Experimental Section

***General considerations*.** $K_3[Ru_2(hedp)_2(H_2O)_2]$ (K_3·**1**) was prepared according to our porous work.[S1,S2] All of other chemicals were obtained from J&K Scientific. DI water was employed throughout the whole study for preparing a series of solutions. The UV-visible spectroscopic titration was performed with a spectrophotometer Cary 8454. Infrared spectra (KBr) were recorded on Nicolet 6700 spectrometer FT-IR spectrophotometer. Electrochemical measurements were accomplished with a CHENHUA CHI660E. Measurements of pH values were carried out on a INESA PHS-3C pH meter. Gas quantifications were conducted with a Shimadzu GC-2014 gas chromatograph. XRD crystallography studies were carried out at the Bruker Smart ApexII CCD diffractometer (Mo Kα radiation). ESI-MS was performed in a Bruker Daltonik GmbH, Bremen mass spectrometer equipped with an electrospray ionization (ESI) source.

***Oxygen evolution measurements*.** 100 equiv. of CAN (10 mM, 5 mL) was purged with Ar for 20 min, catalyst K_3·**1** (5 mM, 100 μL) was immediately injected to the above solution under vigorous stirring. The oxygen amount was measured by GC experiment, which performed on a Shimadzu GC-2014 gas chromatograph. Ar was used as the carrier gas. 200 μL volumes of headspace mixture were manually injected to the GC using a gastight syringe (SGE Analytical Science).

***Electrochemical measurements*.** The typical three-electrode cell was employed, including a Ag/AgCl electrode, a Pt wire, and a glassy carbon electrode (GCE), which were used as the reference electrode, the counter electrode, and the working electrode with a diameter of 3 mm, respectively. All potentials are reported versus Ag/AgCl electrode in saturated KCl. Cyclic voltammetry (CV) chronoamperometry and differential pulse voltammogram (DPV) were measured using 1 mM solutions of K_3·**1**. The scan rate in all CV experiments was 100 mVs^{-1}. The current of chronoamperometry (CA) was tested at the overpotential of 1.50 V (*vs.*

NHE). The 0.1 M pH 1.0 HNO_3 solution and 0.1 M pH 7.0 PBS were employed as electrolyte, respectively.

The diffusion coefficient (D_{Ru}) was determined from the dependence of the i_p on $v^{1/2}$ based on the Randles–Sevcik relation:

$$i_p = 0.446nFAC_{cat}\sqrt{nFvD_{Ru}/RT} \quad \text{(eqn. 1)}$$

where n is the number of transferred electrons (1e$^-$), F is the Faraday constant, A is the area of the working electrode (0.07065 cm^2), C_{cat} is the concentration of the catalyst (mol L^{-1}), D_{Ru} is the catalyst diffusion coefficient (cm^2 s^{-1}), R is the ideal gas constant and T is the temperature (K).[S3,S4]

The rate constant (k_{cat}) was determined by linear fitting of i_{cat}/i_p with $v^{-1/2}$ based on the following equation:

$$i_{cat}/i_p = 2.242n_{cat}\sqrt{k_{cat}RT/nFv} \quad \text{(eqn. 2)}$$

where n_{cat} is the number of electrons involved in water oxidation (4), k_{cat} is the rate constant for water oxidation (s^{-1}), R is the ideal gas constant, T is the temperature (K), n is the number of electrons transferred (1e$^-$), F is the Faraday constant and v is the scan rate (V s^{-1}).[S3,S4]

Redox titration. UV-visible spectra were taken after every addition of 5 μL $(NH_4)[Ce(NO_3)_6]$ (CAN, 12.5 mM in 0.1 M HNO_3) solution to 2.0 mL K_3·**1** (0.5 mM in 0.1 M HNO_3). The absorbances at λ = 320 nm were plotted against the ratio of mol of CAN to mol of K_3·**1**.

Gas Chromatography (GC) methods. Gas quantification was performed using a molecular sieve column attached to a thermal conductivity detector. Ar was used as the carrier gas. Standard curves were generated by direct injection of calibrating gas. 200 μL volumes of headspace mixture were manually injected to the GC using a gastight syringe (SGE Analytical Science).

***X-Ray Crystallography*.** The measurement of the crystals was performed using a Bruker Smart ApexII CCD diffractometer using graphite-mono-chromated Mo Kα radiation from an X-ray tube. The collected frames were processed with the software SAINT. The absorption correction was treated with SADABS. Structures were solved using direct methods with SHELXS or SHELXT and refined against F^2 on all data by full-matrix least squares with SHELXL.[S5] The atomic positions of non-hydrogen atoms were refined with anisotropic parameters. The hydrogen atoms were introduced at their geometric positions and refined as riding atoms.

***ESI-MS spectra*.** The given CAN solution (0.5 M in 0.1 HNO_3) was injected into K_3·**1** solution (0.5 mM in 0.1 M HNO_3, 2 mL), and the mixture was stirred for 5 min. ESI-MS spectra was measured. The experimental parameters were as follows: capillary temperature, 200 ^{o}C; capillary voltage, 3500 V; flow rate, 4 L/min; hexapole, 400 Vpp.

***DFT calculation*.** All the calculations were performed with Gaussian09 software via DFT methods.[S6] Geometry optimizations were carried out under B3LYP functional[S7] with SDD basis set[S8] for Ru and P and 6-31G** basis set for C, H and O. Additional polarization f exponent (ζ_f = 1.235) was added for Ru, and d exponent (ζ_d = 0.387) was added for P.[S9] Frequency calculations were carried out at the same level to get the free energy and to verify the geometries corresponding to minima. And single-point energy corrections were performed at the M06 functional[S10] with 6-311++G** basis set for C, H and O except for Ru and P. All calculated solvation free energies use a standard state of ideal gas (1 M, 298.15 K, 1atm) dissolving as an ideal dilute solution (1 M), but for water, the standard state for water solvent is 55.6 M. Thus the concentration correction of 1.9 kcal/mol was added for all the species except for water, for which 4.3 kcal/mol is added. The standard redox potential of hydrogen electrode is 4.281 V and the corresponding reference free energy of solvation of a proton is −1101 kJ/mol.[S11] The calculated energies and coordinates are shown in table S2.

In our calculation, we failed to coordinate water molecule to the Ru center of catalyst **1**$^{3-}$. This suggests that the interaction between H_2O and Ru center in **1**$^{3-}$ is very weak which explains why the Ru-OH_2 bond in the crystal structure of K_3·**1** (2.31 Å) is much larger than those in other Ru-based catalysts (2.136Å for $[(bpy)^{2-}(OH_2)Ru^{III}ORu^{III}(OH_2)(bpy)_2]^{4+}$, bpy = 2,2'-bipyridine;[S12] 2.100Å for $[Ru^{II}-(CO)_3(H_2O)_3]^{2+}$;[S13] 2.198(5)Å for $[Ru^{II}(dppe)(CO)(O_3SCF_3)_2(OH_2)]$,[S14] dppe = 1,2-bis(diphenylphosphino)ethylene). Therefore, only two explicit water molecules, one on each side of catalyst **1**$^{3-}$, were included in our calculation. Other solvent effect of water was estimated by single-point calculations using SMD continuum solvation model[S15] based on gas-phase optimized structures.

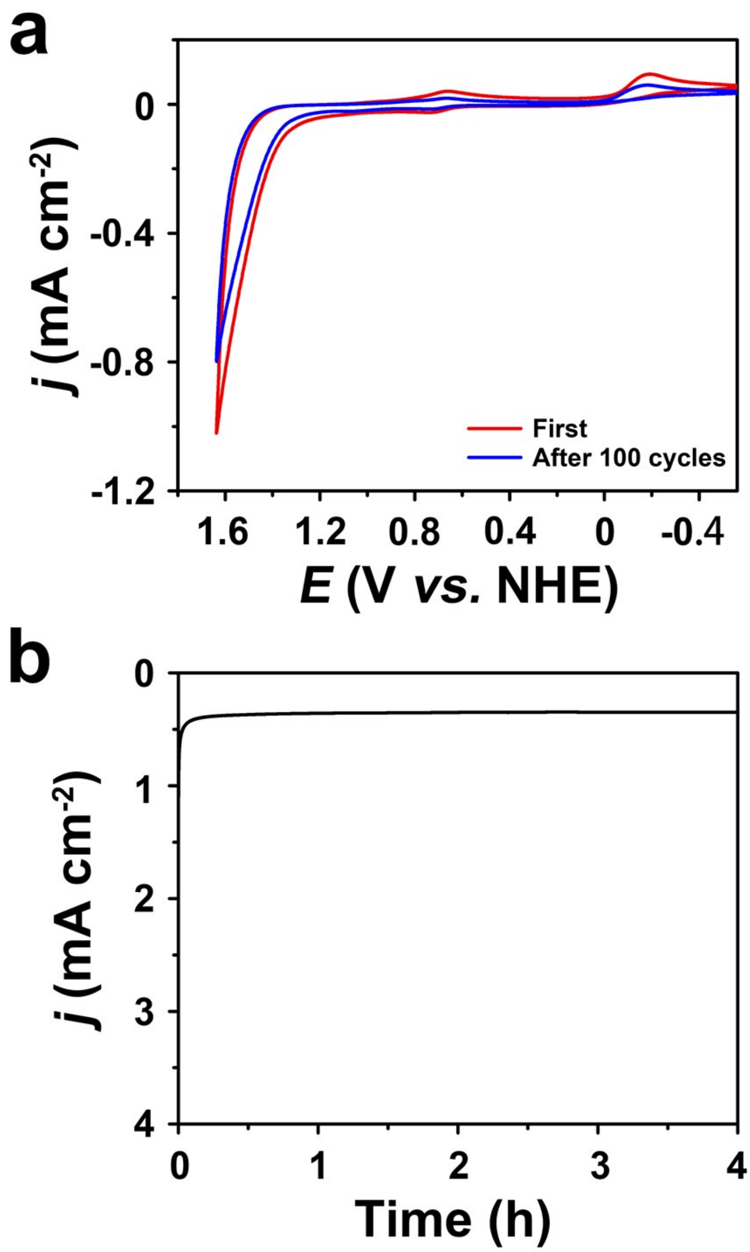

Fig. S1 (a) CVs of K_3·**1** (1.0 mM) in 0.1 M pH 7 PBS at a scan rate of 100 mV s^{-1}. (b) Chronoamperometric response of K_3·**1** (1.0 mM) at a constant potential of 1.50 V (*vs.* NHE) in 0.1 M pH 7.0 PBS.

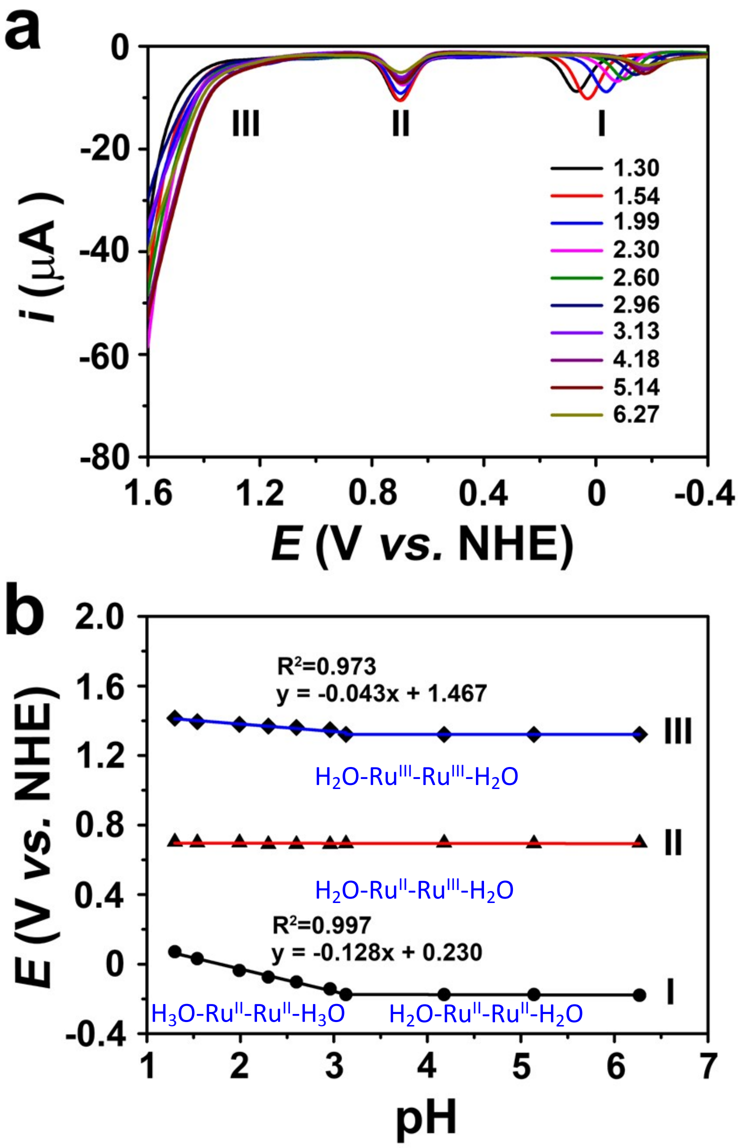

Fig. S2 (a) DPVs of K_3·**1** (1.0 mM) in 0.1 M HNO_3 with pH varied from 1.30 to 6.27. (b) Pourbaix diagram for I (Ru_2^{5+}/Ru_2^{4+}), II (Ru_2^{6+}/Ru_2^{5+}) and III (onset potential).

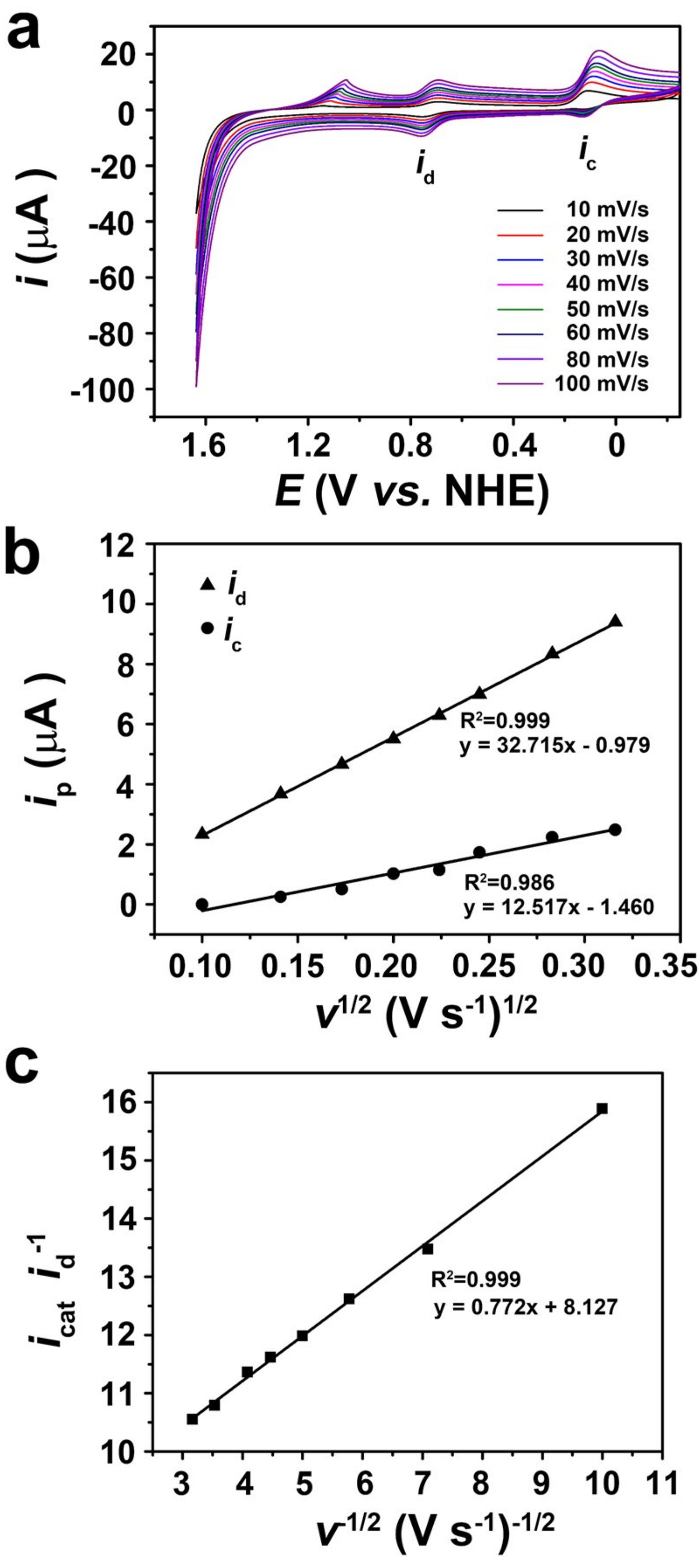

Fig. S3 (a) CVs of K_3·**1** (1.0 mM) in 0.1 M HNO_3 with scan rate varying from 10 to 100 mV s^{-1}. (b) Plot of the anodic current maximum of the i_c (Ru_2^{5+}/Ru_2^{4+}) and i_d (Ru_2^{6+}/Ru_2^{5+}) couples as a function of the square root of scan rate. (c) Plot of i_{cat}/i_p *vs.* $v^{-1/2}$ at 1.64 V (*vs.* NHE).

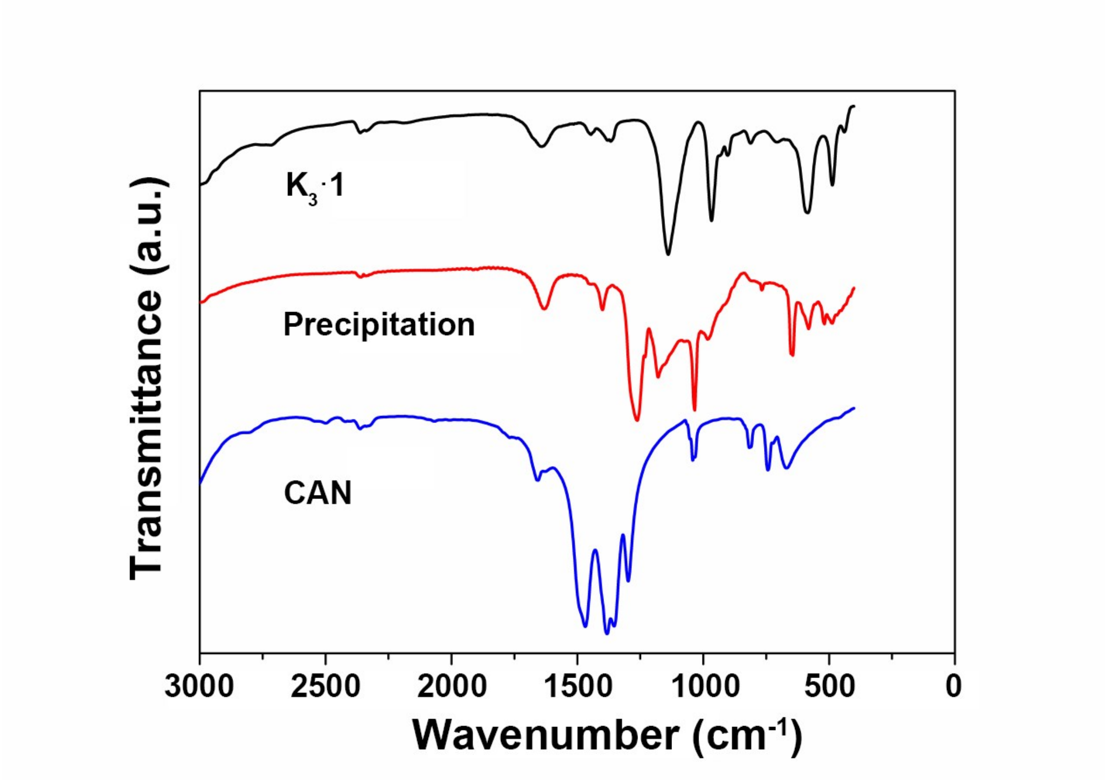

Fig. S4 IR spectra of K_3.**1**, brown precipitate and CAN.

Table S1. The element analysis of brown precipitate by the inductively coupled plasma spectrum

	Ce	Ru	P
Content (wt%)	17.7 %	3.7 %	4.8 %

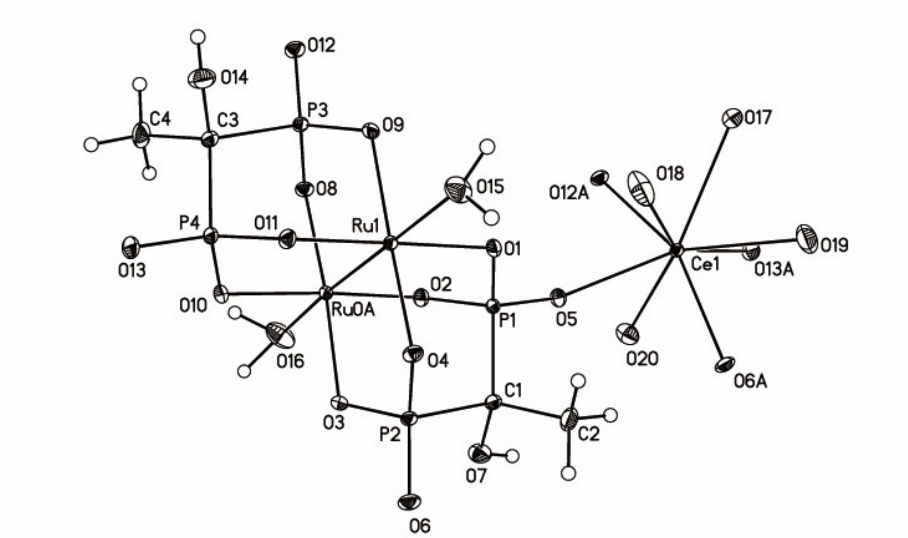

Fig. S5 The X-ray structure of $[Ce^{III}(H_2O)_4]$[**1**]$\cdot 4H_2O$ and crystallographic data.

Table S2. Crystallographic data of $[Ce^{III}(H_2O)_4]$[**1**]$\cdot 4H_2O$

compound	$[Ce^{III}(H_2O)_4]$[**1**]$\cdot 4H_2O$
Empirical formula	$C_4H_{20}CeKO_{24}P_4Ru_2$
Fw	918.34
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.8558(19)
b/Å	12.808(2)
c/Å	17.015(2)
α/° /o	90
β/°	118.539(8)
γ/°	90
V/ Å^3	2461.2(6)
Z	4
2Θ range for data collection/°	3.606 to 55.376
*Refle*ctions collected/unique	41788/ 5704
F(000)	1768.0
ρ_{calcd} (g cm^{-3})	2.478
μ (Mo Kα)/ mm^{-1}	10.692
R_1/wR_2 ($I > 2\sigma(I)$)^a	0.0191 /0.0445
R_1, wR_2 (all data)	0.0230/0.0461

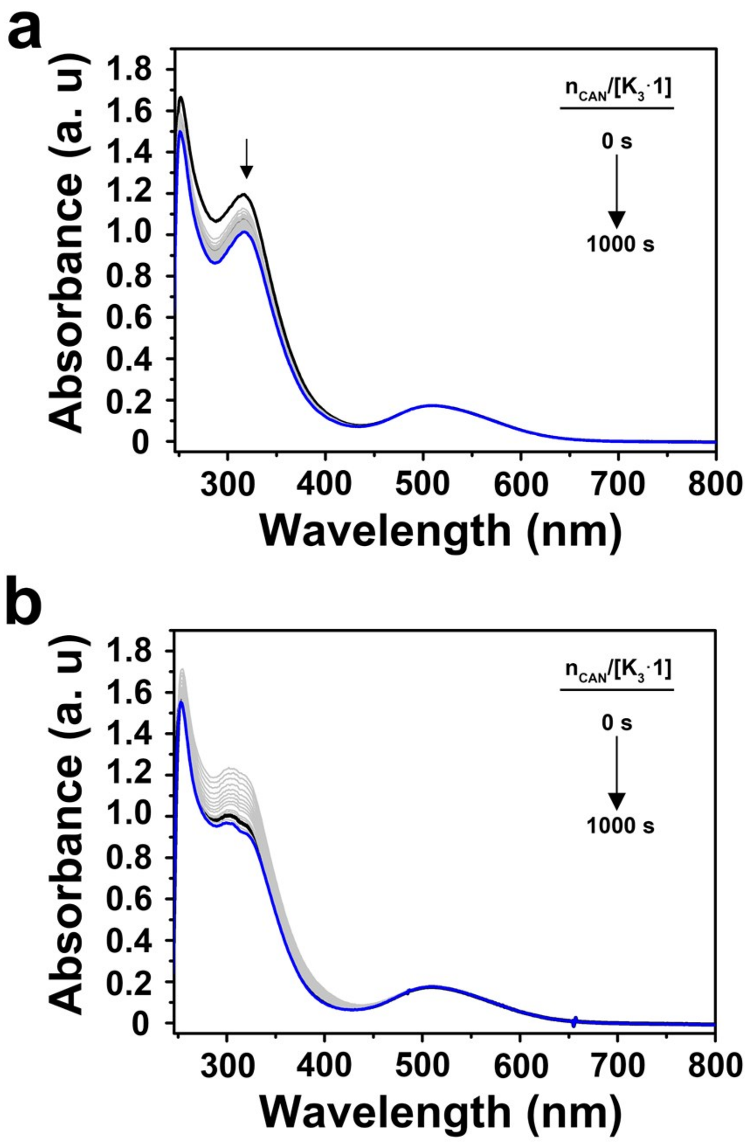

Fig. S6 (a) UV-visible spectral change of K_3·**1** after addition of 3 equiv. of CAN within 3 min, time interval of spectral change = 40 s. (b) UV-visible spectral change of K_3·**1** after direct addition of 4 equiv. of CAN, time interval of spectral change = 40 s. t=0 (black line), t=1000 s (blue line).

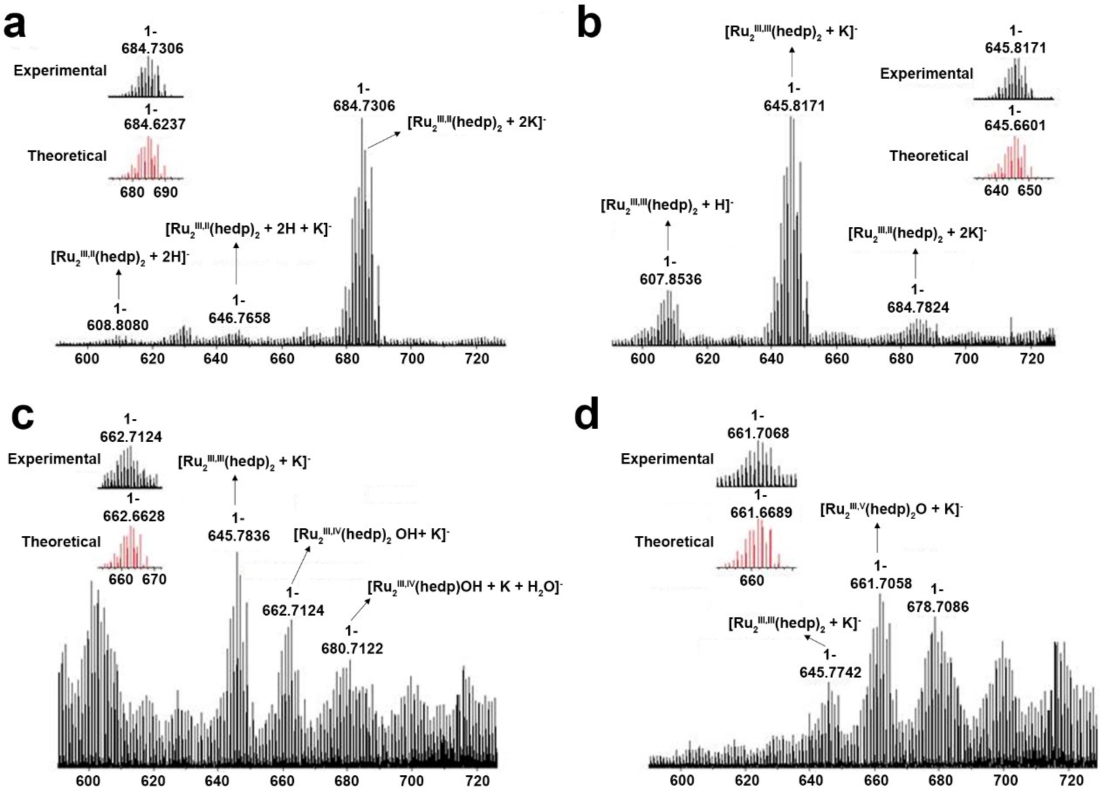

Fig. S7 ESI-MS spectra of $K_3\cdot$**1** upon addition of 0-3 equiv. of CAN. (a) $K_3\cdot$**1**; (b) $K_3\cdot$**1** and 1 equiv. of CAN; (c) $K_3\cdot$**1** and 2 equiv. of CAN; (d) $K_3\cdot$**1** and 3 equiv. of CAN.

Table S3. The calculated energies at b3lyp level, solvent energies and the single-point energies at M06 level.

Species	Multiplicity	E (a.u.)	G (a.u.)	Esol (a.u.)	Em06 (a.u.)
H2ORu3-Ru2H_2O	2	-2918.865647	-2918.695498	-2919.443817	-2918.484371
	4	-2918.887736	-2918.71868	-2919.460781	-2918.505455
H2ORu3-Ru3H_2O	1	-2918.946711	-2918.775642	-2919.258419	-2918.547243
	3	-2918.973977	-2918.805759	-2919.282172	-2918.568799
	5	-2918.99516	-2918.99516	-2919.305421	-2918.590973
H2ORu3-Ru4OH	2	-2918.319267	-2918.162617	-2918.630218	-2917.904594
	4	-2918.336396	-2918.179922	-2918.655727	-2917.921733
	6	-2918.338698	-2918.183099	-2918.667413	-2917.925268
HORu4-Ru4OH	1	-2917.693905	-2917.543308	-2918.002777	-2917.270666
	3	-2917.699761	-2917.552363	-2918.009138	-2917.275048
	5	-2917.70916	-2917.561267	-2918.013169	-2917.285064
H2ORu3-Ru5O	1	-2917.663572	-2917.515913	-2917.96647	-2917.256241
	3	-2917.692728	-2917.547613	-2918.017035	-2917.273531
	5	-2917.685694	-2917.541583	-2918.014637	-2917.263514
H2ORu3-Ru3OOH	1	-2993.368238	-2993.206673	-2993.917918	-2992.973371
	3	-2993.398656	-2993.239024	-2993.96169	-2992.996458
	5	-2993.408456	-2993.248762	-2993.970756	-2993.007235
H2ORu3-Ru4OO	2	-2992.773307	-2992.625532	-2993.33867	-2992.348854
	4	-2992.784251	-2992.63704	-2993.346249	-2992.350159
	6	-2992.779236	-2992.632967	-2993.343215	-2992.376563
H2O	1	-76.41815901	-76.414431	-76.43051144	-76.41785716
O2	3	-150.316605	-150.332809	-150.3170769	-150.2908496

Coordinates

H2ORu3-Ru2H2OM2

44	-0.112588	0.169227	1.072599
15	2.411273	1.556666	0.019317
15	2.395318	-1.525794	0.559574
6	4.498819	-0.198264	-0.733664
1	4.041494	-0.409267	-1.703024
1	5.108638	0.708559	-0.826683
1	5.134610	-1.043802	-0.447918
6	3.449198	0.022090	0.368169
8	1.299589	1.637420	1.168641
8	1.623298	1.268837	-1.351052
8	3.410626	2.713112	0.043088
8	1.262333	-1.187389	1.656028
8	1.578244	-1.587909	-0.852431
8	3.252835	-2.742609	0.841128
8	4.151443	0.304551	1.601754
1	4.274171	1.269873	1.560013
8	-2.234357	0.559946	3.426440
1	-2.155051	1.205967	2.698397
1	-2.177779	-0.272122	2.914351
44	0.112625	-0.169201	-1.072575
15	-2.411233	-1.556654	-0.019322
15	-2.395286	1.525803	-0.559528
6	-4.498960	0.198200	0.733410
1	-4.041807	0.409156	1.702858
1	-5.108788	-0.708632	0.826283
1	-5.134712	1.043743	0.447592
6	-3.449162	-0.022102	-0.368263
8	-1.299529	-1.637407	-1.168626
8	-1.623288	-1.268789	1.351065
8	-3.410559	-2.713120	-0.043096
8	-1.262278	1.187441	-1.655972
8	-1.578235	1.587882	0.852504
8	-3.252801	2.742625	-0.841056
8	-4.151225	-0.304548	-1.601958
1	-4.273940	-1.269872	-1.560265
8	2.233759	-0.560119	-3.426301
1	2.154715	-1.206029	-2.698120
1	2.177538	0.272032	-2.914319

H2ORu3-Ru2H2OM4

44	5.286433	13.617698	-0.513698
15	2.328959	13.780796	-1.342428
15	3.122004	12.575075	1.435922
6	0.469923	13.063775	0.659026
1	0.516765	14.047341	1.131566
1	-0.275777	13.097443	-0.144874
1	0.168783	12.323794	1.409095
6	1.823924	12.636758	0.068091
8	3.798358	13.283551	-1.801325
8	2.501413	15.247386	-0.733559
8	1.270511	13.564426	-2.423120
8	4.508272	12.216605	0.679139

8	3.249608	14.120192	1.876173	H2ORu3-Ru3H2OM1				
8	2.715914	11.615200	2.536538	44	-0.059039	1.001815	0.343550
8	1.656332	11.334634	-0.538624	15	-2.407020	-0.565753	1.433373
1	1.357869	11.555999	-1.439305	15	-2.427421	0.492241	-1.505797
8	8.164789	12.732930	-1.723433	6	-4.288844	-1.339010	-0.507418
1	7.629166	13.465655	-2.087121	1	-3.661056	-2.153521	-0.879355
1	8.025171	12.895704	-0.770795	1	-4.872667	-1.708744	0.342398
44	4.200764	15.378567	0.508150	1	-4.962396	-1.021075	-1.308836
15	7.149865	15.223551	1.348695	6	-3.454137	-0.127072	-0.060322
15	6.367231	16.425805	-1.427461	8	-1.443209	0.699239	1.739323
6	9.023628	15.964549	-0.635997	8	-1.367149	-1.711152	0.957369
1	8.995001	14.977863	-1.103816	8	-3.373904	-0.900116	2.550724
1	9.763025	15.943677	0.173993	8	-1.454621	1.649664	-0.922023
1	9.317327	16.704676	-1.388623	8	-1.385274	-0.739096	-1.765623
6	7.660190	16.371825	-0.056045	8	-3.280315	0.864220	-2.689071
8	5.708326	15.691604	1.845482	8	-4.342707	0.915554	0.374669
8	6.959680	13.764577	0.668575	1	-4.538811	0.691820	1.300835
8	8.251011	15.358181	2.398541	8	0.626494	3.263074	1.165887
8	4.975970	16.800629	-0.745245	1	1.158189	2.716865	1.775588
8	6.258542	14.835262	-1.812423	1	1.152082	3.264834	0.345249
8	6.826192	17.299353	-2.578897	44	0.059077	-1.001654	-0.343544
8	7.805296	17.678530	0.550590	15	2.407058	0.565919	-1.433364
1	8.118764	17.468045	1.447417	15	2.427458	-0.492077	1.505803
8	1.468588	16.289847	1.707348	6	4.288879	1.339180	0.507430
1	1.956474	15.522191	2.070358	1	3.661089	2.153689	0.879368
1	1.548712	16.099307	0.752089	1	4.872702	1.708917	-0.342385
				1	4.962431	1.021244	1.308848

6	3.454175	0.127241	0.060331
8	1.443249	-0.699073	-1.739314
8	1.367184	1.711316	-0.957360
8	3.373941	0.900285	-2.550714
8	1.454661	-1.649500	0.922027
8	1.385308	0.739257	1.765631
8	3.280353	-0.864055	2.689078
8	4.342749	-0.915382	-0.374660
1	4.538854	-0.691645	-1.300826
8	-0.626438	-3.262905	-1.165875
1	-1.158147	-2.716709	-1.775576
1	-1.152029	-3.264687	-0.345238

H2ORu3-Ru3H2OM3

44	-0.056784	1.108689	0.386826
15	-2.392407	-0.596411	1.420147
15	-2.414001	0.471770	-1.504737
6	-4.302018	-1.331546	-0.512006
1	-3.682923	-2.151862	-0.885631
1	-4.891242	-1.696908	0.336012
1	-4.970807	-1.003586	-1.313447
6	-3.452198	-0.132718	-0.060410
8	-1.455843	0.691156	1.713318
8	-1.386461	-1.746674	0.896387
8	-3.340078	-0.941587	2.549954
8	-1.461710	1.631806	-0.900607
8	-1.406050	-0.795726	-1.723934
8	-3.239967	0.837056	-2.708606
8	-4.321860	0.921114	0.382966
1	-4.507803	0.706594	1.312899
8	0.693798	3.416805	1.208579
1	1.195980	2.827471	1.800114
1	1.181949	3.352915	0.368231
44	0.056810	-1.108526	-0.386822
15	2.392438	0.596575	-1.420140
15	2.414026	-0.471609	1.504739
6	4.302041	1.331717	0.512020
1	3.682939	2.152025	0.885650
1	4.891265	1.697087	-0.335996
1	4.970832	1.003756	1.313458
6	3.452233	0.132883	0.060416
8	1.455881	-0.690998	-1.713301
8	1.386490	1.746835	-0.896376
8	3.340099	0.941751	-2.549954
8	1.461740	-1.631644	0.900608
8	1.406075	0.795887	1.723934
8	3.239987	-0.836896	2.708611
8	4.321908	-0.920943	-0.382954
1	4.507849	-0.706452	-1.312893
8	-0.693675	-3.416586	-1.208555
1	-1.195912	-2.827309	-1.800101
1	-1.181854	-3.352766	-0.368220

H2ORu3-Ru3H2OM5

44	-0.051638	1.105663	0.384316

15	-2.392595	-0.595121	1.420645
15	-2.412472	0.471622	-1.505474
6	-4.301566	-1.331839	-0.510829
1	-3.682839	-2.151420	-0.886514
1	-4.888065	-1.697760	0.338825
1	-4.972724	-1.003802	-1.310227
6	-3.451283	-0.132519	-0.060877
8	-1.452756	0.688693	1.713805
8	-1.389387	-1.749524	0.896983
8	-3.340547	-0.939151	2.550521
8	-1.462449	1.632795	-0.901763
8	-1.408641	-0.800201	-1.725236
8	-3.238135	0.835578	-2.710025
8	-4.321041	0.921825	0.381235
1	-4.508996	0.707855	1.310863
8	0.692572	3.417041	1.212240
1	1.196198	2.827108	1.802181
1	1.181801	3.358328	0.372245
44	0.051667	-1.105497	-0.384307
15	2.392623	0.595284	-1.420636
15	2.412501	-0.471457	1.505483
6	4.301591	1.332006	0.510839
1	3.682862	2.151586	0.886521
1	4.888091	1.697927	-0.338815
1	4.972748	1.003971	1.310238
6	3.451311	0.132684	0.060886
8	1.452784	-0.688529	-1.713797
8	1.389414	1.749688	-0.896974
8	3.340575	0.939314	-2.550512
8	1.462478	-1.632631	0.901772
8	1.408668	0.800364	1.725245
8	3.238165	-0.835414	2.710033
8	4.321073	-0.921660	-0.381225
1	4.509035	-0.707690	-1.310852
8	-0.692451	-3.416839	-1.212218
1	-1.196112	-2.826954	-1.802177
1	-1.181712	-3.358177	-0.372239

H2ORu3-Ru4OHM2

44	-0.044706	1.108507	-0.511448
15	-2.491086	0.772142	1.329256
15	-2.490197	-0.495597	-1.507733
6	-4.475779	-0.974417	0.378214
1	-3.909784	-1.858884	0.681838
1	-5.058656	-0.615574	1.233187
1	-5.149776	-1.245926	-0.439999
6	-3.541844	0.148855	-0.099675
8	-1.447724	1.824840	0.691180
8	-1.616715	-0.501449	1.799472
8	-3.443350	1.377245	2.338591
8	-1.397743	0.673043	-1.821234
8	-1.593775	-1.625427	-0.752757
8	-3.281163	-0.985098	-2.686682
8	-4.317164	1.269485	-0.549108

1	-4.505165	1.773186	0.261273
8	2.060526	3.344769	-1.643257
1	1.988120	3.156899	-0.693683
1	1.992037	2.450986	-2.020947
44	-0.176434	-1.156896	0.543872
15	2.287546	-0.771235	-1.320601
15	2.294708	0.546746	1.489298
6	4.347628	0.900992	-0.385807
1	3.853981	1.798310	-0.766256
1	4.949343	0.469619	-1.192890
1	4.998121	1.179002	0.448877
6	3.346058	-0.156409	0.104851
8	1.226489	-1.811368	-0.658676
8	1.407215	0.493040	-1.794854
8	3.214631	-1.419043	-2.323699
8	1.220703	-0.607108	1.836126
8	1.388537	1.667668	0.700961
8	3.095156	1.089110	2.638868
8	4.061571	-1.295528	0.605003
1	4.237724	-1.842256	-0.178706
8	-0.394656	-2.850773	1.486019
1	-1.110655	-2.682709	2.121917

H2ORu3-Ru4OHM4

44	0.036699	1.223544	0.249620
15	-2.447669	-0.199725	1.506976
15	-2.439611	0.559413	-1.500835
6	-4.472719	-0.906240	-0.302040
1	-3.940677	-1.808081	-0.615464
1	-5.061590	-1.133947	0.593152
1	-5.139596	-0.587129	-1.108693
6	-3.494333	0.237704	0.011732
8	-1.333884	0.987717	1.618276
8	-1.642042	-1.528678	1.116524
8	-3.383577	-0.242675	2.695959
8	-1.338881	1.672440	-1.039781
8	-1.567396	-0.806130	-1.589580
8	-3.230073	0.905006	-2.730280
8	-4.222803	1.422019	0.363428
1	-4.397332	1.320861	1.315388
8	2.221024	3.621775	0.684781
1	2.141524	2.885959	1.313526
1	2.147551	3.158829	-0.166099
44	-0.168500	-1.283690	-0.273166
15	2.322685	0.078887	-1.536548
15	2.317012	-0.520453	1.511041
6	4.405504	0.828384	0.214970
1	3.937603	1.789771	0.438909
1	5.011202	0.942830	-0.690079
1	5.047090	0.541603	1.053641
6	3.373880	-0.285408	-0.019479
8	1.280912	-1.137650	-1.646888
8	1.449027	1.401667	-1.143629
8	3.260193	0.218744	-2.714383

8	1.199100	-1.613208	1.115974
8	1.466244	0.888936	1.550610
8	3.109919	-0.791892	2.757887
8	4.061566	-1.517974	-0.285929
1	4.241801	-1.506686	-1.239988
8	-0.363046	-3.172490	-0.625254
1	-1.078837	-3.436917	-0.020571

H2ORu3-Ru4OHM6

44	0.191411	1.318192	-0.356545
15	-2.292318	0.546204	1.441946
15	-2.318805	-0.103965	-1.589913
6	-4.417550	-0.782573	0.151614
1	-3.974364	-1.768173	0.309859
1	-5.011950	-0.524236	1.034932
1	-5.065871	-0.825820	-0.728307
6	-3.360553	0.307416	-0.079807
8	-1.170690	1.631076	1.039141
8	-1.488188	-0.853753	1.655865
8	-3.191616	0.987519	2.573798
8	-1.264373	1.094831	-1.728251
8	-1.467227	-1.407666	-1.022871
8	-3.146102	-0.434555	-2.801634
8	-4.018496	1.564673	-0.298842
1	-4.203669	1.909661	0.590460
8	0.411394	3.187868	-0.734542
1	1.172293	3.432375	-0.178081
44	-0.058501	-1.286273	0.344331
15	2.421088	-0.553890	-1.438462
15	2.446196	0.230709	1.560839
6	4.500328	0.862157	-0.214741
1	3.999855	1.814066	-0.408128
1	5.095617	0.591998	-1.093758
1	5.156181	0.971536	0.654250
6	3.482867	-0.253913	0.073749
8	1.302988	-1.653513	-0.969018
8	1.590743	0.787874	-1.705255
8	3.323763	-1.075529	-2.532948
8	1.320112	-0.948164	1.685109
8	1.670009	1.533960	0.995989
8	3.259480	0.453132	2.805781
8	4.170387	-1.485904	0.333802
1	4.366761	-1.846106	-0.547833
8	-2.303061	-3.599694	0.755769
1	-2.197665	-3.141061	-0.094790
1	-2.251189	-2.860334	1.382627

HORu4-Ru4OHM1

44	-0.134204	1.563462	0.160582
15	-2.298474	-0.561425	1.388350
15	-2.332692	0.617049	-1.417231
6	-4.107263	-1.391371	-0.621880
1	-3.401393	-2.123860	-1.021987
1	-4.677561	-1.859375	0.188417

1	-4.788123	-1.092175	-1.423331
6	-3.395008	-0.145382	-0.077716
8	-1.223419	0.665740	1.496962
8	-1.487684	-1.877440	1.032887
8	-3.230063	-0.580756	2.588266
8	-1.815617	2.050422	-1.004874
8	-0.817848	-0.156917	-1.118608
8	-2.851590	0.341481	-2.799550
8	-4.362022	0.798475	0.390720
1	-4.390438	0.636140	1.354058
44	0.166037	-1.509410	-0.206058
15	2.400586	0.290895	-1.482003
15	2.301991	-0.019971	1.608832
6	4.486868	1.083903	0.276111
1	4.037972	2.067450	0.442216
1	5.101694	1.121748	-0.627575
1	5.104711	0.826871	1.142273
6	3.403375	0.025680	0.091440
8	1.700703	-1.151426	-1.555855
8	1.247860	1.422138	-1.198907
8	3.257342	0.691377	-2.656757
8	1.202427	-1.264009	1.347373
8	1.417773	1.297150	1.521817
8	3.059214	-0.252356	2.889939
8	4.051456	-1.245116	-0.068858
1	3.406751	-1.793612	-0.549039
8	0.019136	-3.279697	-0.728975
1	-0.731024	-3.620785	-0.203163
8	0.014454	3.272574	0.867686
1	0.724512	3.201536	1.536298

HORu4-Ru4OHM3

44	-0.037624	1.399106	0.089799
15	-2.434469	-0.169733	1.515033
15	-2.398160	0.869358	-1.367245
6	-4.293702	-0.957823	-0.480922
1	-3.638934	-1.752513	-0.848984
1	-4.889761	-1.351781	0.349462
1	-4.956797	-0.646611	-1.292738
6	-3.498414	0.258420	0.015898
8	-1.334215	1.021000	1.541038
8	-1.707159	-1.561750	1.232028
8	-3.391307	-0.109446	2.693297
8	-1.599977	2.195186	-0.964768
8	-1.042011	-0.126879	-1.098289
8	-3.008426	0.743754	-2.731688
8	-4.396081	1.285786	0.440232
1	-4.442088	1.160599	1.408681
44	-0.107192	-1.516449	-0.101823
15	2.228942	-0.096249	-1.579654
15	2.300277	-0.483340	1.500267
6	4.250929	0.905301	0.106761
1	3.688648	1.821442	0.303262
1	4.818139	1.035859	-0.820809

1	4.937972	0.717285	0.937669
6	3.315711	-0.303417	-0.058911
8	1.295691	-1.397826	-1.559664
8	1.347378	1.257198	-1.327203
8	3.156354	-0.026844	-2.776040
8	1.186925	-1.690818	1.292925
8	1.418264	0.854466	1.442089
8	3.124489	-0.679326	2.742842
8	4.093095	-1.487445	-0.286923
1	4.241459	-1.501556	-1.247605
8	-0.610395	-3.270383	-0.550721
1	-1.338313	-3.459701	0.071666
8	0.507766	3.072749	0.802525
1	1.173245	2.831149	1.473413

HORu4-Ru4OHM5

44	0.065600	-0.775061	-1.163289
15	2.395568	-1.189859	0.939617
15	2.372393	0.803178	-1.394521
6	4.160618	1.019351	0.720230
1	3.447357	1.704398	1.186936
1	4.737886	0.524062	1.508838
1	4.834916	1.595457	0.080637
6	3.455682	-0.050778	-0.127020
8	1.361240	-1.848802	-0.109304
8	1.565976	-0.274427	1.969795
8	3.366505	-2.186639	1.545173
8	1.627283	-0.253539	-2.351590
8	1.013486	1.039905	-0.432383
8	2.992781	2.030958	-1.992297
8	4.423509	-0.890799	-0.759553
1	4.501519	-1.651070	-0.151313
44	-0.043321	0.753352	1.249681
15	-2.277710	1.335931	-0.801645
15	-2.398021	-1.077649	1.140631
6	-4.217679	-0.699434	-0.919477
1	-3.577845	-1.318869	-1.552663
1	-4.772551	-0.004267	-1.558564
1	-4.919715	-1.339967	-0.376982
6	-3.391665	0.112480	0.092215
8	-1.375090	1.966397	0.373238
8	-1.344950	0.464110	-1.813193
8	-3.189637	2.341265	-1.474517
8	-1.455234	-0.175105	2.159727
8	-1.382819	-1.661164	0.042712
8	-3.229162	-2.097047	1.869661
8	-4.264098	0.903335	0.908850
1	-4.394609	1.722554	0.400130
8	0.347934	2.041447	2.604785
1	1.041344	1.600503	3.128064
8	-0.476609	-2.269291	-2.203195
1	-1.124874	-2.719792	-1.628892

H2ORu3-Ru5OM1

44	-0.057552	1.096127	-0.340557
15	-2.549143	0.747587	1.357730
15	-2.414573	-0.515660	-1.490395
6	-4.441333	-1.034785	0.341202
1	-3.863521	-1.893599	0.692025
1	-5.081523	-0.682746	1.157246
1	-5.062771	-1.340058	-0.506019
6	-3.523795	0.115507	-0.112728
8	-1.486671	1.819137	0.671480
8	-1.671470	-0.441997	1.898017
8	-3.524603	1.448218	2.279737
8	-1.340887	0.685337	-1.741037
8	-1.505672	-1.656114	-0.775850
8	-3.181121	-0.988505	-2.692776
8	-4.314127	1.209096	-0.596455
1	-4.516758	1.729160	0.200418
8	2.069513	3.368646	-1.577440
1	2.001122	3.145163	-0.635131
1	1.920793	2.497907	-1.983828
44	-0.177090	-1.259936	0.632237
15	2.237444	-0.739925	-1.317982
15	2.370881	0.492230	1.515922
6	4.362706	0.881111	-0.432171
1	3.863259	1.786637	-0.785690
1	4.938000	0.457876	-1.262815
1	5.039063	1.143449	0.386886
6	3.365132	-0.170818	0.072611
8	1.166672	-1.784130	-0.688935
8	1.336131	0.534656	-1.712716
8	3.121236	-1.371908	-2.369684
8	1.322673	-0.619212	1.917919
8	1.457919	1.629437	0.694621
8	3.208480	1.105163	2.604733
8	4.075992	-1.341348	0.506322
1	4.246568	-1.840692	-0.310162
8	-0.350234	-2.547708	1.697452

H2ORu3-Ru5OM3

44	0.037208	-1.325166	0.123253
15	-2.435387	-0.269009	-1.503804
15	-2.441559	-0.050232	1.586607
6	-4.475671	0.951599	-0.025468
1	-3.947889	1.908457	-0.030604
1	-5.070431	0.869517	-0.941615
1	-5.136171	0.909991	0.845928
6	-3.490068	-0.225944	0.045062
8	-1.328213	-1.443595	-1.243028
8	-1.615432	1.104160	-1.537672
8	-3.353287	-0.588776	-2.662260
8	-1.334787	-1.250210	1.487929
8	-1.621418	1.306672	1.266206
8	-3.234942	-0.035880	2.862279
8	-4.205232	-1.468631	0.078948
1	-4.391437	-1.665563	-0.855257

8	2.327471	-3.672470	0.295625
1	2.205371	-3.127230	-0.498706
1	2.231324	-3.012339	1.001166
44	-0.189816	1.421356	-0.128907
15	2.295604	0.336717	1.500319
15	2.301255	0.108936	-1.591693
6	4.407612	-0.810087	0.022756
1	3.962644	-1.806947	0.056032
1	5.007323	-0.670023	0.928396
1	5.050278	-0.739148	-0.859672
6	3.353946	0.304792	-0.050511
8	1.228070	1.518841	1.271331
8	1.454428	-1.058236	1.492057
8	3.212123	0.559938	2.681047
8	1.225991	1.304237	-1.533772
8	1.453941	-1.259068	-1.236437
8	3.106470	-0.001974	-2.855789
8	4.015706	1.577689	-0.110098
1	4.204424	1.807953	0.814362
8	-0.327676	3.166631	-0.260583

H2ORu3-Ru5OM5

44	0.045536	1.377841	-0.083570
15	-2.428877	0.232998	1.508600
15	-2.431343	0.099778	-1.583969
6	-4.467632	-0.946353	-0.004087
1	-3.939760	-1.902818	-0.025874
1	-5.062442	-0.890173	0.913944
1	-5.128085	-0.880116	-0.873998
6	-3.482537	0.233370	-0.040994
8	-1.325804	1.418766	1.283955
8	-1.617537	-1.146942	1.505533
8	-3.346416	0.518905	2.676195
8	-1.323334	1.296352	-1.447228
8	-1.620147	-1.272083	-1.307069
8	-3.219895	0.129806	-2.862186
8	-4.197482	1.476284	-0.042240
1	-4.385205	1.647432	0.896685
8	2.373151	3.679111	-0.183387
1	2.246636	3.118556	0.599135
1	2.270159	3.035691	-0.903469
44	-0.201141	-1.458225	0.088730
15	2.286111	-0.293706	-1.507484
15	2.291730	-0.170979	1.585368
6	4.409260	0.786725	0.006300
1	3.973602	1.788069	0.009492
1	5.006060	0.673929	-0.905023
1	5.052873	0.678816	0.884239
6	3.346755	-0.321193	0.041647
8	1.215465	-1.480481	-1.316712
8	1.462688	1.111382	-1.453662
8	3.198527	-0.484404	-2.697043
8	1.217613	-1.364875	1.486928
8	1.452303	1.212966	1.274017

8	3.092012	-0.101861	2.855438
8	3.998615	-1.600026	0.060080
1	4.178346	-1.806596	-0.871667
8	-0.355378	-3.200718	0.166699

H2ORu3-Ru3OOHM1

44	0.102434	1.120612	0.226636
15	-2.403967	-0.220958	1.563108
15	-2.325816	0.283088	-1.550032
6	-4.642712	-0.571657	-0.172151
1	-4.377332	-1.615476	-0.365707
1	-5.244887	-0.522796	0.741453
1	-5.212983	-0.187650	-1.025423
6	-3.385607	0.266287	0.017692
8	-1.422456	1.022794	1.681963
8	-1.563878	-1.546213	1.097932
8	-3.316402	-0.497609	2.742943
8	-1.202052	1.397512	-1.263361
8	-1.497553	-1.127521	-1.531738
8	-3.160220	0.487099	-2.797696
8	-3.795268	1.632989	0.249307
1	-3.004707	2.049128	0.637117
8	0.393604	2.915585	0.777555
44	-0.050296	-1.368909	-0.179047
15	2.405879	-0.026462	-1.509919
15	2.381823	-0.715533	1.544299
6	4.367860	0.784455	0.324496
1	3.802451	1.670686	0.622800
1	4.959023	1.016157	-0.570035
1	5.039994	0.500243	1.142010
6	3.436281	-0.405263	0.020968
8	1.302782	-1.215314	-1.612507
8	1.644902	1.341179	-1.237652
8	3.409477	-0.073537	-2.663038
8	1.328064	-1.888056	1.039103
8	1.523534	0.606679	1.674064
8	3.207510	-1.128380	2.744120
8	4.239991	-1.551046	-0.325266
1	4.352237	-1.442234	-1.288806
8	-2.745594	-3.534036	-0.584792
1	-2.435665	-2.863277	-1.222228
1	-2.484297	-3.076830	0.238006
8	1.604401	3.532853	0.270833
1	1.867590	2.863486	-0.411649

H2ORu3-Ru3OOHM3

44	0.168710	1.165580	0.202971
15	-2.365025	-0.003859	1.544599
15	-2.342564	0.440951	-1.534874
6	-4.506918	-0.716827	-0.161296
1	-4.097507	-1.711150	-0.352484
1	-5.111265	-0.758088	0.752981
1	-5.137245	-0.424806	-1.008520
6	-3.409249	0.343213	0.016177

8	-1.282931	1.173281	1.608675
8	-1.577237	-1.390307	1.243958
8	-3.329496	-0.018841	2.724322
8	-1.212483	1.535525	-1.215359
8	-1.612298	-1.013324	-1.512333
8	-3.177656	0.693551	-2.773272
8	-4.050238	1.615933	0.258335
1	-4.162291	1.639694	1.223204
8	0.458344	3.112771	0.532498
44	-0.124254	-1.302445	-0.152862
15	2.410896	-0.138175	-1.512770
15	2.378333	-0.669944	1.548828
6	4.421680	0.714913	0.246450
1	3.879724	1.636601	0.471905
1	5.033311	0.865802	-0.652082
1	5.070272	0.468016	1.094180
6	3.452622	-0.457942	0.015180
8	1.269849	-1.280349	-1.555498
8	1.659999	1.255514	-1.254979
8	3.375660	-0.214547	-2.692519
8	1.296864	-1.802944	1.175743
8	1.611025	0.750053	1.553137
8	3.214347	-0.949008	2.781094
8	4.216463	-1.647860	-0.275544
1	4.348047	-1.588630	-1.239311
8	-2.534355	-3.537240	-0.584609
1	-2.325448	-2.792715	-1.184969
1	-2.367342	-3.101843	0.269632
8	1.665507	3.633926	-0.063607
1	1.925751	2.880190	-0.644923

H2ORu3-Ru3OOHM5

44	0.174389	1.157109	0.164256
15	-2.365804	0.032750	1.538031
15	-2.352884	0.418957	-1.545943
6	-4.513057	-0.714182	-0.144760
1	-4.102261	-1.711520	-0.316170
1	-5.115873	-0.737629	0.771220
1	-5.145878	-0.440387	-0.996221
6	-3.416636	0.351120	0.008359
8	-1.269894	1.202961	1.568876
8	-1.591418	-1.363305	1.264622
8	-3.322564	0.061709	2.723668
8	-1.224110	1.518433	-1.243170
8	-1.620088	-1.033584	-1.495960
8	-3.187730	0.648198	-2.788783
8	-4.058118	1.627037	0.228641
1	-4.165733	1.668080	1.193625
8	0.473475	3.126189	0.416944
44	-0.130448	-1.290744	-0.136843
15	2.408080	-0.190165	-1.522105
15	2.373162	-0.637588	1.552530
6	4.406569	0.731213	0.218177
1	3.856491	1.654064	0.418463

1	5.017620	0.862812	-0.683744
1	5.056988	0.512941	1.072380
6	3.448920	-0.456624	0.017245
8	1.273947	-1.335037	-1.540187
8	1.651286	1.209248	-1.294200
8	3.378033	-0.282649	-2.696213
8	1.288122	-1.772243	1.201512
8	1.599980	0.783775	1.529115
8	3.204733	-0.886601	2.793533
8	4.223039	-1.648281	-0.236149
1	4.359264	-1.615082	-1.200422
8	-2.533481	-3.543424	-0.498158
1	-2.330682	-2.820878	-1.125675
1	-2.362874	-3.076686	0.339271
8	1.757720	3.583783	-0.079359
1	1.994423	2.840995	-0.681123

H2ORu3-Ru4OOM2

44	-0.200681	1.153377	0.068449
15	2.342485	0.287490	-1.514072
15	2.349515	0.157349	1.590928
6	4.492797	-0.754266	0.005899
1	4.075391	-1.763413	0.014327
1	5.086347	-0.630993	-0.908028
1	5.136033	-0.629422	0.883920
6	3.406453	0.330605	0.040396
8	1.242962	1.432369	-1.329739
8	1.573597	-1.139846	-1.477087
8	3.295276	0.518290	-2.681024
8	1.242599	1.304924	1.493755
8	1.572535	-1.257244	1.290052
8	3.194675	0.121748	2.846609
8	4.060681	1.619380	0.032950
1	4.157827	1.821795	-0.912809
8	-0.393999	3.202618	0.153107
44	0.103910	-1.280606	-0.076745
15	-2.396697	-0.438644	1.502209
15	-2.403193	-0.307437	-1.607739
6	-4.371438	0.834609	-0.010236
1	-3.783202	1.755925	-0.024014
1	-4.973282	0.804661	0.906615
1	-5.035078	0.810289	-0.882409
6	-3.453782	-0.400715	-0.051160
8	-1.284835	-1.602146	1.287410
8	-1.616799	0.951942	1.527911
8	-3.360810	-0.761880	2.640024
8	-1.287099	-1.480332	-1.465739
8	-1.620115	1.079482	-1.358536
8	-3.233716	-0.377446	-2.870476
8	-4.253358	-1.600963	-0.016260
1	-4.370011	-1.748372	0.940350
8	2.499301	-3.586670	-0.149862
1	2.302044	-3.005493	0.609211
1	2.327870	-2.960256	-0.876863

8	-1.597528	3.700050	0.173741

H2ORu3-Ru4OOM4

44	0.194417	1.134405	-0.069945
15	-2.345649	0.278695	1.512521
15	-2.351961	0.143599	-1.592076
6	-4.496235	-0.759465	-0.006948
1	-4.079183	-1.768855	-0.012852
1	-5.091138	-0.633775	0.905815
1	-5.138535	-0.635557	-0.885854
6	-3.408454	0.324278	-0.042384
8	-1.241028	1.423972	1.323453
8	-1.579402	-1.145114	1.481854
8	-3.296893	0.526903	2.677291
8	-1.239747	1.292245	-1.491951
8	-1.579412	-1.267619	-1.293664
8	-3.194831	0.123428	-2.849594
8	-4.059848	1.614227	-0.035826
1	-4.157237	1.816164	0.910148
8	0.391168	3.223725	-0.162150
44	-0.101196	-1.275582	0.076514
15	2.397564	-0.450223	-1.501653
15	2.403665	-0.314251	1.606806
6	4.370796	0.833755	0.008230
1	3.780996	1.753950	0.021502
1	4.972177	0.804610	-0.908951
1	5.034699	0.812035	0.880258
6	3.456260	-0.403480	0.050850
8	1.293655	-1.615278	-1.288692
8	1.610929	0.941443	-1.521485
8	3.363521	-0.755746	-2.642753
8	1.295526	-1.488512	1.469864
8	1.614277	1.072656	1.349149
8	3.235100	-0.363430	2.870159
8	4.260890	-1.600865	0.018391
1	4.380573	-1.749005	-0.937529
8	-2.499103	-3.583889	0.153696
1	-2.298270	-3.002463	-0.604711
1	-2.323603	-2.958020	0.880494
8	1.591362	3.718713	-0.180220

H2ORu3-Ru4OOM6

44	0.192405	1.132670	-0.069762
15	-2.344101	0.276812	1.512146
15	-2.349480	0.142645	-1.592570
6	-4.490189	-0.771282	-0.007717
1	-4.069409	-1.779106	-0.013122
1	-5.086016	-0.647662	0.904683
1	-5.132545	-0.650058	-0.886922
6	-3.406896	0.316863	-0.042881
8	-1.241785	1.423512	1.322197
8	-1.571975	-1.145594	1.481873
8	-3.295659	0.519843	2.677209
8	-1.239922	1.293283	-1.489968

8	-1.570348	-1.267055	-1.295689
8	-3.191650	0.118734	-2.850130
8	-4.063461	1.603915	-0.037662
1	-4.160133	1.808677	0.907690
8	0.366140	3.251496	-0.153176
44	-0.098096	-1.274715	0.076406
15	2.397025	-0.447335	-1.502802
15	2.403618	-0.312105	1.606416
6	4.369560	0.833159	0.007535
1	3.779425	1.753243	0.020539
1	4.971290	0.803964	-0.909395
1	5.033255	0.811538	0.879697
6	3.455021	-0.404382	0.049994
8	1.289948	-1.612612	-1.290417
8	1.610604	0.942797	-1.521655
8	3.361388	-0.757094	-2.643745
8	1.292520	-1.486714	1.470811

8	1.614918	1.073170	1.348494
8	3.234714	-0.365972	2.869511
8	4.258318	-1.602379	0.017105
1	4.378675	-1.749896	-0.938825
8	-2.484671	-3.589895	0.158298
1	-2.288419	-3.013969	-0.605035
1	-2.310546	-2.957877	0.880176
8	1.576412	3.741153	-0.178214

H2O

8	0.000000	0.000000	0.118847
1	0.000000	0.760065	-0.475390
1	-0.000000	-0.760065	-0.475390

O2

8	-0.485856	0.006402	0.000000
8	-1.700072	0.006402	0.000000

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