Electronic Supplementary Material (ESI) for Dalton Transactions

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Dinuclear Complexes of Tetravalent Cerium in an Aqueous Perchloric Acid Solution

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<u>Contents</u>:

1. Experimental Procedure

1-1. Sample preparation

$Ce^{III}(ClO_4)_3{\cdot}nH_2O$ was prepared from $Ce^{III}Cl_3{\cdot}7H_2O$ (Rare Metallic Co. Ltd, 99.99%) according to the following procedure:

1. Dissolve a weighted amount of $Ce^{III}Cl_3{\cdot}7H_2O$ into deionized water.
2. Add NH_4OH into the above solution to obtain the hydrolysis precipitate of Ce(III).
3. Filtrate the obtained precipitate, and wash the precipitate by deionized water several times.
4. Dissolve the precipitate into 10 M $HClO_4$.
5. Evaporate the above solution by heating, and further dried in a vacuum desiccator for 1 week.

The obtained compound (*i.e.*, $Ce^{III}(ClO_4)_3{\cdot}nH_2O$) was then dissolved into 2 M $HClO_4$ to prepare 0.05 M Ce(III) in 2 M $HClO_4$. The cyclic voltammograms of this solution (Figure S1) using a Pt working electrode show cathodic peaks at around 1.3~1.4 V (*vs.* Ag/AgCl), which correspond to the oxidation from Ce(III) to Ce(IV). Based on this information, the bulk electrolysis of 0.05 M Ce(III) in 2 M $HClO_4$ was performed at 1.8 V by using Pt-plate working and counter electrodes, a Ag/AgCl reference electrode with the ALS Electrochemical Analyzer Model 600C. The obtained solution was a clear yellow solution, and stable in the air. The oxidation state of Ce in the obtained solution was confirmed as tetravalent from fluorescence spectroscopy (Figure S2) and Ce K-edge XANES spectroscopy (Figure S3). The prepared Ce(III) and -(IV) solution in 2 M $HClO_4$ were transferred into to a doubly sealed polystyrene/poly(methyl metacrylate) cuvette (optical path = 10.0 mm) for XAS experiments. Reference compounds of $Ce^{III}(NO_3)_3{\cdot}xH_2O$ ($x = 6\sim7$) and $Ce^{IV}O_2$ (both from Rare Metallic Co. Ltd, 99.99%) were ground, mixed with boron nitride powder, and then pressed into a pellet with a 10 mm diameter.

1-2. X-ray absorption experiment, data treatment, and simulation

X-ray absorption fine structure (XAFS) spectra, including both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) regions, were collected at Ce K-edge on the JAEA Quantum Dynamics Beamline BL11XU[S1] at SPring-8 under the ring operating conditions of 8 GeV and 99 mA with top-up mode. A liquid N_2-cooled Si(311) double crystal was employed to monochromatize white X-rays from the synchrotron. The beam position of incident X-rays was stabilized by a monochromator stabilization (MOSTAB) system[S2] with a position-sensitive ion chamber (PSIC).[S3] All the spectra were collected in transmission mode using ionization chambers filled with an Ar/N_2 mixture ($Ar/N_2 = 5/5$) at ambient temperature and pressure. Before each measurement, energy correction was carried out by measuring the first inflection point of Ce K-edge spectrum (defined as 40.447 keV) for the reference $Ce^{IV}O_2$ sample. For each sample, a single XAFS spectrum was acquired in 120 seconds with “quick scanning” mode, and the scan was repeated 30 times. The obtained 30 spectra were then averaged for data analysis.

EXAFS data analysis was performed according to a standard procedure[S4] using the program WinXAS (version 3.2).[S5] EXAFS structural parameters were obtained by the theoretical curve fitting both in the k space (*i.e.*, EXAFS oscillation spectra) and the R space (*i.e.*, Fourier-transformed spectra). The threshold energy, $E_{k=0}$, was defined as the first inflection point of each spectrum, regardless of Ce oxidation state.

Theoretical phase and amplitude required for the curve fitting were calculated by the program code FEFF 8.20[S6] based on the DFT-optimized complex structures given in Section 4. All the significant single-scattering (SS) and multiple-scattering (MS) paths, whose relative scattering amplitude was calculated to be more than 10%, were taken into account on the curve fitting. The amplitude reduction factor, S_0^2, was fixed at 0.9, and the shifts in the threshold energy, $\Delta E_{k=0}$, were constrained to be the same value for all shells, in order to reduce the free parameters on the curve fit procedure as much as possible. EXAFS-FT spectra of the DFT-optimized complexes were simulated on the same program and software. The input EXAFS structural parameters were as follows. Here we used the same value of Debye-Waller factors (σ^2) for similar scattering shells (*i.e.*, $O_{bridging}(OH) = O_{bridging}(oxo)$, $O(H_2O/OH) = O(H_2O)$, Ce-SS, and MSs) to compare the scattering magnitude of these shells directly. The σ^2 value of each scattering shell was set according to the values obtained for the actual sample of Ce(IV) in 2 M $HClO_4$ (Table S1).

Complex	**Shell**	**Path***	**Relative scattering amplitude**	***CN***	***R* / Å**	**Debye-Waller / Å^2**	**$\Delta E_{k=0}$**	**S_0^2**
Dimer1	$O_{bridging}(OH)$	SS	100.00	1	2.358	0.0065	-1.77	0.9
	$O(H_2O/OH)$	SS	50.10	7.5	2.453	0.0085		
	Ce	SS	18.98	1	4.524	0.0067		
Dimer2	$O_{bridging}(OH)$	SS	100.00	2	2.295	0.0065	-2.62	0.9
	$O(H_2O)$	SS	83.67	7	2.465	0.0085		
	Ce	SS	51.58	1	3.872	0.0067		
	Ce-O(OH)	MS-3	10.00	2	4.073	0.0043		
Diemr3	$O_{bridging}(oxo)$	SS	100.00	1	2.084	0.0065	0.47	0.9
	$O(H_2O)$	SS	56.91	7	2.433	0.0085		
	Ce	SS	25.67	1	4.158	0.0067		
	Ce-O(oxo)	MS-3	81.22	2	4.164	0.0043		
	Ce-O(oxo)-Ce	MS-4	64.72	1	4.164	0.0043		
Trimer	$O_{bridging}(\mu_2\text{-}O)$	SS	100.00	2	2.180	0.0065	7.14	0.9
	$O_{bridging}(\mu_3\text{-}O)$	SS	82.45	2	2.316	0.0065		
	$O(H_2O)$	SS	56.73	4	2.588	0.0085		
	Ce	SS	65.83	1.5	3.348	0.0067		

* SS: single scattering path, MS: multiple scattering path

1-3. Quantum chemical calculations

Density functional theory (DFT) calculations were performed to optimize the complex structures of possible Ce(IV) polynuclear complexes in aqueous phase without symmetry constraint on the program package Gaussian 09.[30] The structure optimization was carried out at the B3LYP level using the CPCM salvation model[S7] with UAHF radii.[S8] The energy-consistent small-core effective core potential (ECP) and the corresponding basis set (Stuttgart type) were employed on Ce. All electron 6-311G* basis set[S9] was used on O and H.

2. Figures

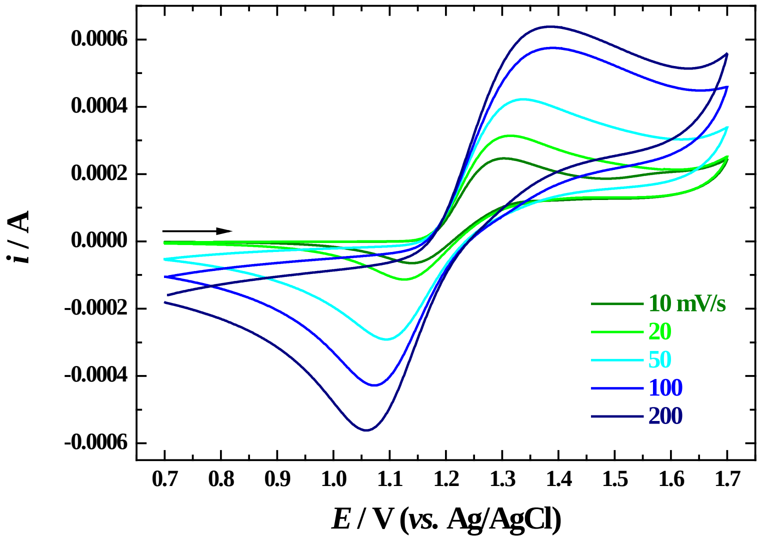


Figure S1. Cyclic voltammograms of 0.05 M Ce(IV) in 2 M $HClO_4$: working electrode; Pt (ø = 1.6 mm), counter electrode, Pt-wire, reference electrode; Ag/AgCl in 3 M NaCl, scan direction; cathodic from 0.7 V.

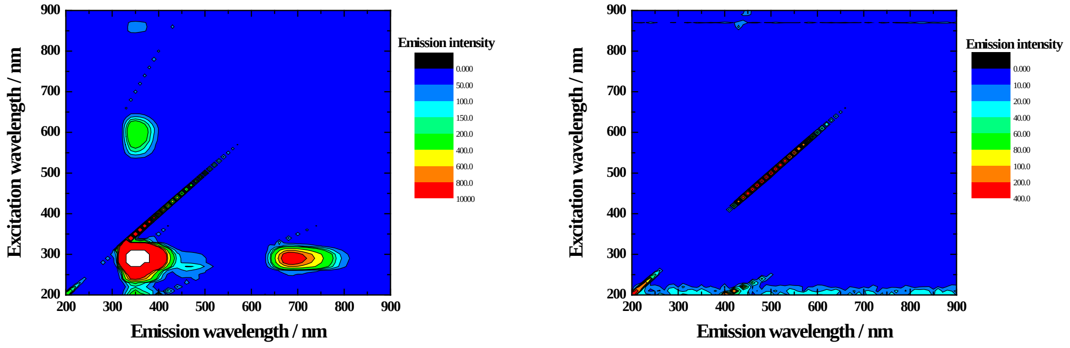


Figure S2. 2D fluorescence correlation spectra of 0.05 M Ce(III) (left) and -(IV) (right) in 2 M $HClO_4$. Data were collected on the fluorescence spectrophotometer Hitachi F-700. Fluorescence emission from Ce(III) (left) disappeared after the electrolysis (right), indicating that Ce(III) was completely oxidized to Ce(IV) by the electrolysis.

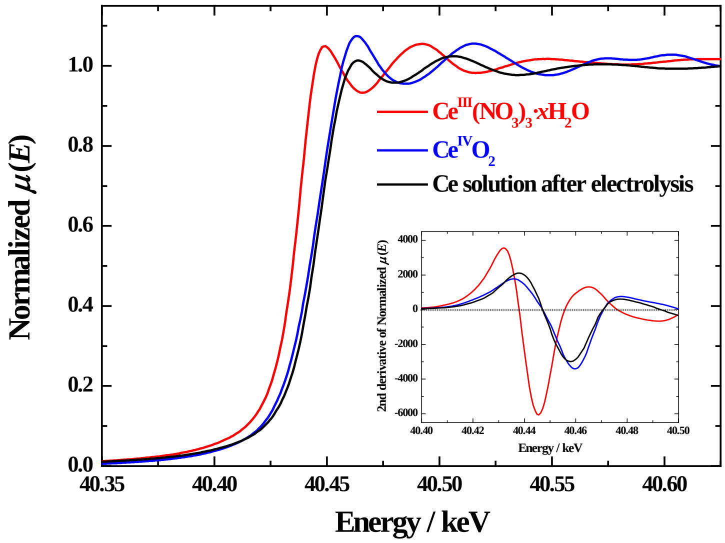


Figure S3. Ce K-edge XANES spectra for 0.05 M Ce (IV) in 2 M $HClO_4$, $Ce^{III}(NO_3)_3 \cdot xH_2O$, and $Ce^{IV}O_2$. The inset shows the second derivatives of the corresponding XANES spectra.

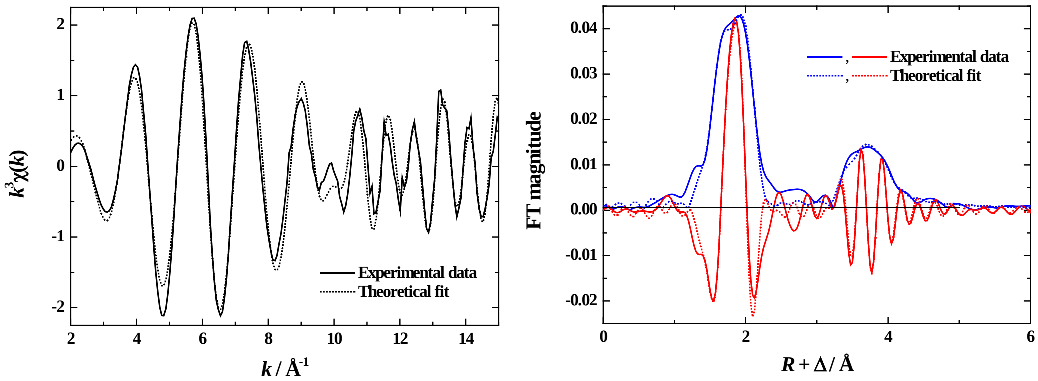


Figure S4. k^3-weighted Ce K-edge EXAFS spectrum (left) for Ce(IV) in 2 M $HClO_4$, its corresponding Fourier transform (right), and their theoretical curve fitting (dotted data).

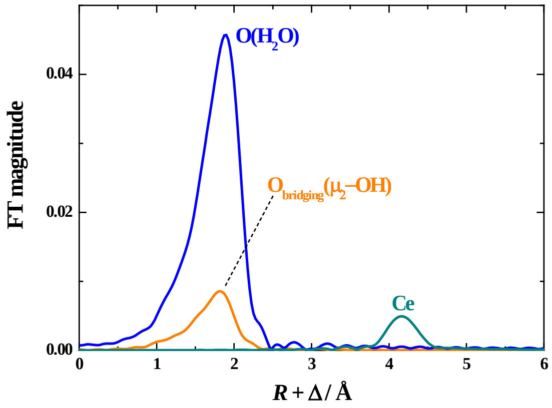


Figure S5. Simulated EXAFS-FT spectrum of the complex Dimer1 in Figure 3.

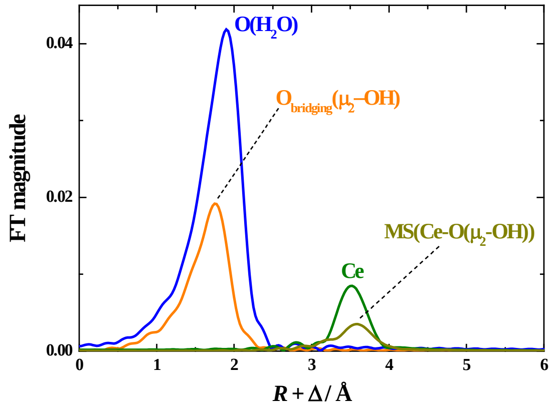


Figure S6. Simulated EXAFS-FT spectrum of the complex Dimer2 in Figure 3.

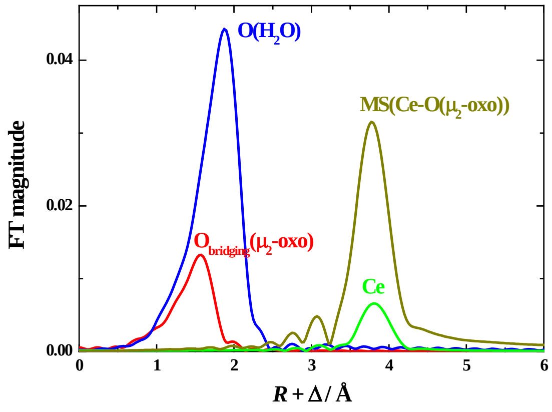


Figure S7. Simulated EXAFS-FT spectrum of the complex Dimer3 in Figure 3.

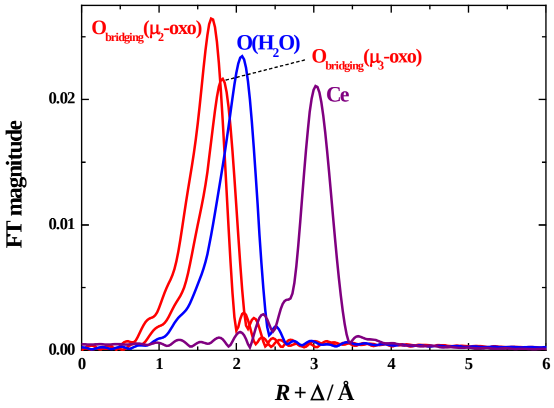


Figure S8. Simulated EXAFS-FT spectrum of the complex Trimer in Figure 3.

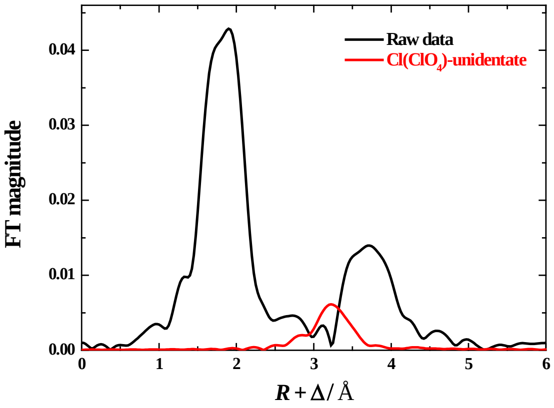


Figure S9. Simulated EXAFS-FT peak of Cl for unidentately coordination ClO_4^- ions (red data) along with the original EXAFS-FT spectrum of Ce(IV) in 2.0 M $HClO_4$ (black data).

The Cl peak was simulated based on the crystal structure of a U(IV) perchlorate complex [S12]. U(IV) is often referred to as an analogue of Ce(IV) because of their identical oxidation number and similar ionic radii. The peak was simulated by assuming R = 3.74 Å (the distance found in the corresponding U(IV) perchlorate complex), CN = 1.0, σ^2 = 0.004 Å^2 (the *lowest* value found in the literature [S13] for the Cl shell in solution), $\Delta E_{k=0}$ = 5.0 eV, and S_0^2 = 0.9. Given the fact that the complexation geometry of U(IV) is often found to be very similar to that of Ce(IV), the Cl shell for unidentately coordinating ClO_4^- is likely to be shorter than the observed 2nd peak at around $R + \Delta$ = 3.7 Å.

3. Tables

Table S1. Summary of EXAFS structural parameters for Ce(IV) in 2 M $HClO_4$.

	Shell	Path[a]	CN[b]	R / Å[c]	Debye-Waller / Å^{2}[d]	$\Delta E_{k=0}$ / eV[e]	S_0^2	Fitting results			FT-range
								χ^2	Residual	F-test	
Ce(IV) in 2 M $HClO_4$	$O_{bridging}$	SS	0.96	2.033	0.00645	2.18	0.9 (fixed)	57294.264	11.244	0.97028	k = 2.5-15.1
	$O(H_2O)$	SS	7.13	2.463	0.00854						
	Ce	SS	0.79	4.051	0.00668						
	Ce-$O_{bridging}$-Ce	MS3	1.57	4.117	0.00432						
	Ce-$O_{bridging}$-Ce	MS4	0.79	4.143	0.00432						

[a] SS; single scattering path, MS; multiple scattering path. [b] Coordination number; error; $CN \leq \pm 10\%$. [c] Interatomic distance, error; $R \leq \pm 0.015$ Å.
[d] Error; DW ≤ ± 0.0012 Å^{2}. [e] Shift in threshold energy, error; $\Delta E_{k=0} \leq \pm 0.05$ eV.

Table S2. Summary of interatomic distances for DFT-optimized complexes, and the reported crystal structures of Ce(IV) dinuclear complexes.

Complex	Average interatomic distance / Å			
	Ce-O(μ_2-OH)	Ce-O(μ_2-oxo)	Ce-O(H_2O)	Ce-Ce
Dimer1	2.358		2.453	4.524
Dimer2	2.295		2.465	3.872
Dimer3		2.084	2.433	4.158
	Ce-O(μ_2-oxo)	Ce-O(μ_3-oxo)	Ce-O(H_2O)	Ce-Ce
Trimer	2.180	2.316	2.588	3.348
Single crystal	Ce-O(μ_2-OH)	Ce-O(μ_2-oxo)	Ce-O(H_2O)	Ce-Ce
$Ce_2(\mu_2\text{-}O_{oxo})(NO_3)_6(H_2O)_6$ [S10]		2.045	2.471	4.090
$Ce_2(\mu_2\text{-}OH)_2(H_2O)_4(SO_4)_3$ [S11]	2.256		2.396	3.769

4. Cartesian Coordinates for DFT-optimized complexes

4-1. Cartesian Coordinate of $Ce_2(\mu_2\text{-}OH)(OH)(H_2O)_{14}$ (Dimer1)

O	-0.00211200	-0.02220100	0.67023900
O	2.74332200	-1.15091200	2.20547400
O	2.57493100	-0.12799200	-2.42427800
O	1.47130000	1.96833500	-0.83068100
O	2.30341300	1.53624700	1.84698600
H	0.50452900	2.20664100	-0.72587100
H	2.27315500	-0.94270300	3.06210600
H	3.30832100	-1.96679800	2.31063400
H	2.08897100	0.48748300	-3.04131600
H	3.15259600	-0.75789300	-2.93858000
H	0.09002900	0.13559600	1.68947700
O	1.40835100	-2.28310900	-0.38919200
O	4.02324900	-1.29221500	-0.31618600
H	0.44207200	-2.50667200	-0.28738500
H	1.93081700	-3.08461300	-0.67063800
H	2.74386500	1.44618700	2.73824700
H	5.13045500	1.25032700	-0.68910600
O	4.26641100	1.47496700	-0.24471700
H	4.28355400	2.40982100	0.10361100
H	1.93853400	2.45748200	1.72956700
H	1.97752300	2.67016400	-1.32597200
H	4.94607400	-1.70836900	-0.46085400
Ce	2.41085800	-0.10416500	0.01074300
Ce	-2.11203900	0.00052200	0.00400900
O	-3.60262400	-0.01725000	-1.93685000
H	-4.57945500	-0.22491100	-1.90248200
H	-3.30143300	0.13271900	-2.87691300
O	-2.21874400	1.09289300	2.18575400
H	-2.02044100	0.58664600	3.02530100
H	-2.37772500	2.05884600	2.39685100
O	-4.23971300	-0.97024200	0.69701700
H	-4.48798300	-1.93727000	0.64959500
H	-5.02698900	-0.41411000	0.95814600
O	-3.87866100	1.70659700	0.14178500
H	-4.14006100	2.25007000	0.93842700
H	-4.40972900	1.98163500	-0.65764800
O	-1.82780300	-1.66581000	1.75840500
H	-2.58009200	-2.14645200	2.20770000
H	-0.94697400	-1.98904400	2.10141500
O	-2.20539300	-2.22826400	-0.94418500
H	-1.87920300	-3.04776100	-0.47475100
H	-2.64444400	-2.46320200	-1.81065600
O	-1.15461900	2.37806500	-0.44108600
H	-1.20989000	2.98228200	0.36155200
H	-1.59967200	2.84444800	-1.21362600
O	-0.88675900	0.01780900	-2.09296600
H	-0.38553600	0.77896500	-2.50493200
H	-0.74876200	-0.81360700	-2.63165400

4-2. Cartesian Coordinate of $Ce_2(\mu_2\text{-}OH)_2(H_2O)_{14}$ (Dimer2)

O	0.03424600	-0.31875400	1.19898500
O	-3.18490700	1.21168800	1.74961000
O	-2.42468100	-0.45444100	-2.34400300
O	-1.39681000	-2.26244700	-0.45661700
O	-2.43823500	-1.34682500	1.98481000
H	-0.42287100	-2.51418800	-0.48771700
H	-3.02926400	1.17827900	2.73688100
H	-3.85538300	1.91732300	1.52679400
H	-2.09388900	-1.25729800	-2.83598300
H	-2.93184700	0.15564100	-2.94930500
H	-0.00224400	-0.60725100	2.18180000
O	-1.14069000	2.29075200	0.08632600
O	-3.55671100	1.59496900	-0.96008500
O	0.06937100	0.15778900	-1.22556600
H	-0.18251100	2.50006000	-0.11117900
H	-1.59372000	3.03199200	0.57623000
H	-3.32409100	2.53199000	-1.21570100
H	-3.07797400	-1.14161300	2.72395500
H	-4.56618600	-1.25474600	-1.10556400
O	-4.11099000	-1.08728100	-0.23282300
H	-4.61641800	-1.50665700	0.51877800
H	-2.07678800	-2.27245200	2.08073500
H	-2.01301500	-3.02357600	-0.64193900
H	-0.01199700	0.34325100	-2.23068500
H	-4.51251300	1.39647700	-1.17221000
Ce	-1.94750200	0.00867900	0.00382700
Ce	1.92444600	-0.01024000	0.00189300
O	2.58386400	0.60198900	-2.27966100
H	3.47762400	0.99226600	-2.50151200
H	2.02656700	0.52475000	-3.10651900
O	2.82620900	-1.40120000	1.78884500
H	2.88650600	-1.05457200	2.72446300
H	3.18361800	-2.33564000	1.74570900
O	4.06756900	1.16871000	0.14183000
H	4.22741000	2.13373600	0.34989200
H	4.93207800	0.70556700	-0.04715000
O	3.78984900	-1.38861900	-0.82685900
H	4.31451900	-2.06643600	-0.31287900
H	4.07976600	-1.37838500	-1.78272100
O	2.11152400	1.25972000	2.08185800
H	2.95053500	1.67495100	2.43277400
H	1.34661700	1.43691700	2.69968500
O	1.50312000	2.50646400	-0.36676400
H	1.89807400	3.14224700	0.30138600
H	1.67204800	2.84684800	-1.29494200
O	1.21648000	-2.52803200	-0.37671800
H	1.43928500	-3.15011100	0.37995400
H	1.61964300	-2.89466900	-1.22007500

4-3. Cartesian Coordinate of $Ce_2(\mu_2\text{-}O_{oxo})(H_2O)_{14}(H_2O)_{outer}$ (Dimer3)

O	-0.18946700	-0.14256600	0.18236000
O	-2.81705500	2.04865700	-1.35382100
O	-2.42324200	-2.30310700	0.21260400
O	-2.41158300	-0.50315500	2.34206600
O	-1.70639800	2.08059700	1.29650800
H	-2.25863600	0.13438000	3.09510800
H	-2.62507100	2.99366500	-1.09391200
H	-3.24407500	2.01379000	-2.25634700
H	-1.77343000	-2.89818600	0.68650400
H	-3.15238300	-2.84632700	-0.20306100
O	-1.45191800	-0.43017900	-2.27497500
O	-4.08015400	-0.66041600	-1.41865900
H	-1.97238200	-0.35391100	-3.12523000
H	-0.50509300	-0.67837000	-2.47124700
H	-4.02821800	-1.24151000	-2.23114200
H	-0.78585400	2.38316500	1.54098300
H	-4.74331500	0.70567500	1.71466600
O	-4.33220900	0.98704300	0.84889800
H	-4.90733000	1.65847500	0.38349100
H	-2.39233600	2.70112900	1.67497500
H	-2.62904800	-1.41394100	2.68813800
H	-5.03333700	-0.45492000	-1.20074500
Ce	-2.22027100	0.09937500	-0.01459800
Ce	1.90735400	-0.33850800	0.05299200
O	2.59828100	-0.60829100	-2.25024800
H	3.28267000	-0.05378300	-2.72552400
H	2.26212600	-1.33498400	-2.84959500
O	1.70040900	-1.61653100	2.10837200
H	1.76051300	-1.22494200	3.02548800
H	1.48749200	-2.59183400	2.15524300
O	4.02177100	0.72810500	0.15494500
H	4.23570200	1.72362400	-0.02428400
H	4.84642300	0.20486200	0.35472800
O	3.69367200	-2.03069300	0.11735000
H	3.93091100	-2.56759200	0.92555200
H	4.33167400	-2.21891600	-0.62834800
O	1.81836600	1.24386300	1.87695500
H	2.60968300	1.74854300	2.22202100
H	0.99444600	1.49104400	2.38774800
O	1.66639600	1.81728200	-1.06341600
H	1.36033100	2.65264400	-0.60929100
H	1.79647200	1.97904000	-2.04058200
O	1.08912700	-2.51341600	-0.65877100
H	1.68432600	-3.30065600	-0.81110800
H	0.13535700	-2.74804300	-0.83841500
O	4.57721200	3.15825000	-0.26859200
H	4.09456900	3.74202800	-0.90771200
H	5.36137900	3.62205200	0.12233800

4-4. Cartesian Coordinate of $Ce_3(\mu_2\text{-}O_{oxo})_3(\mu_3\text{-}O_{oxo})_2$ $(H_2O)_{12}$ (Trimer)

Ce	1.72235600	-0.86210400	-0.00882700
Ce	-0.10571700	1.94194000	0.00022400
Ce	-1.61590800	-1.05263400	0.01434000
O	0.12670300	-2.35370800	0.01315400
O	-2.09505800	1.09199500	0.03461000
O	1.97077100	1.30913800	-0.03945800
O	-0.02056700	-0.01356200	-1.27218100
O	0.01981700	0.00266500	1.27777700
O	2.54675400	-1.26221900	2.36435400
H	3.46671600	-1.52076800	2.64124600
H	1.97640100	-1.11693400	3.16593400
O	4.30018800	-0.53718700	-0.11343000
H	4.80948500	0.31420800	-0.15405700
H	4.91545200	-1.31536600	-0.08124800
O	2.44688800	-1.44606900	-2.37510100
H	1.83366900	-1.45380300	-3.15797400
H	3.37897500	-1.63261100	-2.66830400
O	3.19914100	-3.09384700	0.06459100
H	3.30946800	-3.63259700	0.89296100
H	3.30247800	-3.68344300	-0.72928100
O	-2.43719100	-1.45382000	-2.35377800
H	-2.03411300	-1.00489800	-3.14433500
H	-3.13002200	-2.10520400	-2.64640800
O	-4.29360800	-1.19776500	0.00363500
H	-4.83702500	-1.00011400	-0.80517500
H	-4.83926700	-1.03001300	0.81763100
O	-2.42998400	-1.45286800	2.38483400
H	-2.08651900	-0.95880400	3.17676300
H	-3.07853500	-2.15055400	2.67213000
O	-2.62344800	-3.44715700	0.03455700
H	-3.60471500	-3.59594400	0.01835100
H	-2.13499700	-4.31163100	0.03584600
O	0.02126000	2.74882700	2.41404000
H	0.07755800	2.12160000	3.18281000
H	0.02958600	3.69006800	2.73443600
O	1.22018500	4.20151300	-0.10352300
H	2.21393700	4.18347000	-0.09029400
H	0.90483100	5.14034900	-0.19789300
O	-1.65799600	4.05421400	0.06179100
H	-2.64411600	3.93063200	0.04409900
H	-1.44373400	5.02260100	0.13947500
O	-0.27269200	2.70346700	-2.42521700
H	-0.33971100	3.63791200	-2.75804300
H	-0.25754600	2.06520700	-3.18663800

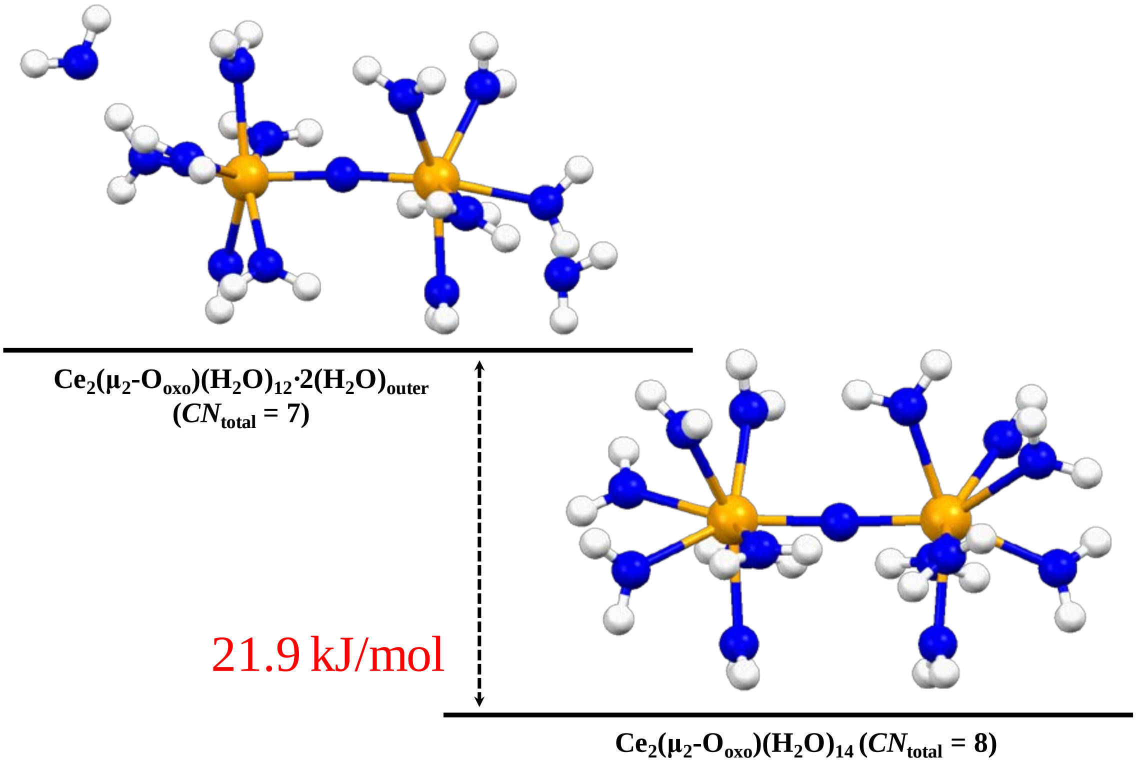
4-5. Cartesian Coordinate of $Ce_2(\mu_2\text{-}O_{oxo})(H_2O)_{14}$

O	-0.00644000	-0.02592400	0.13302600
O	3.14798800	-2.09721400	0.51868500
O	2.12985100	1.76732700	-1.69765100
O	1.90569900	2.17722700	1.08018100
O	1.80651000	-0.40504000	2.33782600
H	1.70226500	2.27437300	2.05323600
H	3.03907000	-2.58342500	1.38422600
H	3.70394100	-2.62921800	-0.11812600
H	1.47689000	2.52117400	-1.78558300
H	2.81080200	1.80518600	-2.42879400
O	1.33263300	-1.53624700	-1.76818300
O	3.86368700	-0.39234300	-1.66404600
H	1.89851000	-2.18584600	-2.27647500
H	0.36740200	-1.67311300	-1.98611300
H	3.75692600	-0.71670200	-2.60442000
H	0.93657400	-0.60588200	2.78895600
H	4.47260500	1.41499500	1.36350300
O	4.22254900	0.51845000	1.00019400
H	4.96167900	-0.14031000	1.13649800
H	2.55570100	-0.40879000	3.00018400
H	2.03950400	3.07244300	0.65711200
H	4.82602700	-0.20258500	-1.47210200
Ce	2.06739600	0.01110400	-0.03140800
Ce	-2.09060300	-0.01449700	0.02418600
O	-2.97263100	-0.83738800	-2.07938800
H	-3.65547000	-1.56194100	-2.18139600
H	-2.73519000	-0.45469900	-2.97247000
O	-1.96336900	2.03933700	1.31671500
H	-1.92896000	2.07253200	2.31510400
H	-1.84754400	2.95506400	0.93182200
O	-4.15604200	-1.09389000	0.72562900
H	-4.23824600	-2.06626400	0.94064500
H	-5.04271800	-0.63776300	0.78374100
O	-4.03746200	1.39258600	-0.47186200
H	-4.27997800	2.21820400	0.03579600
H	-4.72424200	1.19306100	-1.17002400
O	-1.84723900	-0.66878400	2.33455600
H	-2.59258400	-0.99912800	2.91400800
H	-0.98637400	-0.65132900	2.84498000
O	-1.79777000	-2.43511700	-0.04009900
H	-1.40507600	-2.96847800	0.70816200
H	-1.93129200	-3.01033700	-0.84633600
O	-1.51091900	1.61559800	-1.66190100
H	-2.18218200	2.20166900	-2.11557900
H	-0.58846200	1.81528600	-1.99121400

4-6. Cartesian Coordinate of $Ce_2(\mu_2\text{-}O_{oxo})(H_2O)_{12}\cdot 2(H_2O)_{outer}$

O	-0.02370300	-0.23100800	0.14918400
O	-2.36991500	0.93425300	2.48329100
O	-2.88768500	1.64345000	-1.64066000
O	-2.58630800	-1.21783600	-1.56863200
O	-2.20247400	-1.78593300	1.31798700
H	-2.61740800	-2.21285200	-1.46712000
H	-2.64112200	0.30025400	3.20984900
H	-2.25552800	1.85882200	2.85138400
H	-3.83035900	1.61440800	-1.97779900
H	-2.35147300	2.30478800	-2.16842700
O	-0.97524900	2.50193100	0.32320700
H	-1.44547000	3.37763800	0.19680300
H	-0.02321200	2.65402300	0.59248300
H	-1.42921500	-2.36976000	1.56954500
H	-4.99148200	-0.29159100	-0.24921800
O	-4.31617200	0.06334800	0.46414900
H	-4.78564000	0.41784700	1.27393500
H	-3.06602600	-2.20899800	1.59799100
H	-2.77334800	-0.95492300	-2.51590100
Ce	-2.01556500	0.32744500	0.19114000
Ce	2.02333100	-0.37475600	-0.07865600
O	3.19126500	1.31384400	-1.21187500
H	4.15968000	1.64329500	-1.03078300
H	2.76574500	1.83146600	-1.95434800
O	2.42281800	-2.66984000	-0.65572800
H	2.63109300	-3.40570000	-0.00939600
H	2.38130200	-3.02600300	-1.59048400
O	4.29149200	-0.85792800	0.55988500
H	4.87001000	-0.25339800	1.11050000
H	4.82280300	-1.62896000	0.20385300
O	1.85804300	-1.50668600	2.03516800
H	2.63816400	-1.85051600	2.56081900
H	0.99904600	-1.72735600	2.49957800
O	2.55676700	1.28719100	1.57160400
H	2.42866100	1.17004200	2.55743100
H	2.88761400	2.20944900	1.36744200
O	1.36305600	-0.58297000	-2.39709700
H	1.97945200	-0.49032500	-3.18139100
H	0.44355100	-0.83124600	-2.70435300
O	-5.94552100	-0.76373800	-1.24797500
H	-6.84320900	-0.37575900	-1.38153700
H	-5.77957800	-1.51942800	-1.86034000
O	5.53287700	2.11460900	-0.76999600
H	5.75884400	2.85873300	-0.16246700
H	6.34232400	1.70858600	-1.16221800

4-7. Comparison of Gibbs free energy between $Ce_2(\mu_2\text{-}O_{oxo})(H_2O)_{14}$ and $Ce_2(\mu_2\text{-}O_{oxo})(H_2O)_{12}\cdot 2(H_2O)_{outer}$



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