SUPPLEMENTARY MATERIAL

Molecular nanoparticles of cerium dioxide: structure-directing effect of halide ions†

Bradley Russell-Webster,[a] Khalil A. Abboud[a] and George Christou[*a]

Department of Chemistry, University of Florida, Gainesville, FL 32611-7200, USA

Syntheses

All the syntheses below have been reproduced multiple times. The yields are not optimized: at this stage, we have targeted well-formed crystalline solids from slow crystallizations to allow definitive characterization by single-crystal X-ray crystallography, rather than faster precipitation of products in higher yields as microcrystalline powders.

(pyH)$_3$(NH$_4$)[Ce$_{20}$O$_{18}$Cl$_{16}$(O$_2$CPh)$_{22}$] (1). To a solution of CeCl$_3\cdot$7H$_2$O (0.19 g, 0.50 mmol) in MeCN was added benzoic acid (0.12 g, 1.0 mmol) and pyridine (362 μL, 4.4 mmol). After an hour of stirring, the solution remained colorless but contained some white precipitate. At this point, solid (NH$_4$)$_2$[Ce(NO$_3$)$_6$] (0.055 g, 0.10 mmol) was added to give an orange solution that gradually turned purple over the course of an hour. After an hour with the precipitate still remaining, the stirring was halted and allowed to stand undisturbed at ambient temperature for four weeks during which time purple crystals of **1**.x(solv) slowly grew. The crystallographic sample was maintained in mother liquor; otherwise the crystals were collected by filtration, washed with MeCN and dried under vacuum; the yield was 10% based on Ce. Anal. Calcd (Found) for **1**·6H$_2$O (C$_{169}$H$_{144}$Ce$_{20}$Cl$_{16}$N$_4$O$_{68}$): C, 30.35 (30.25); H, 2.17 (2.13); N, 0.84 (0.63). We cannot rule out the possibility that the fourth cation is H$_3$O$^+$ rather than NH$_4^+$, given the large area of solvent disorder. For (pyH)$_3$(H$_3$O)[Ce$_{20}$O$_{18}$Cl$_{16}$(O$_2$CPh)$_{22}$]·5H$_2$O (C$_{169}$H$_{141}$Ce$_{20}$Cl$_{16}$N$_3$O$_{68}$): C, 30.51 (30.25); H, 2.14 (2.13); N, 0.63 (0.63). Selected IR data (cm^{-1}): 3429 (br), 3166 (br), 1594 (m), 1531 (m), 1403 (s), 1178 (w), 1144 (w), 1070 (w), 1025 (w), 852 (w), 720 (s), 676 (m), 565 (m), 535 (m), 465 (m).

[Ce$_6$O$_4$F(OH)$_3$(O$_2$CPh)$_{12}$(py)$_2$] (2). To a solution of anhydrous CeF$_3$ (0.099 g, 0.50 mmol) in MeCN was added benzoic acid (0.12 g, 1.0 mmol) and pyridine (362 μL, 4.4 mmol) and solid (NH$_4$)$_2$[Ce(NO$_3$)$_6$] (0.055 g, 0.10 mmol). The solution was then transferred to a Biotage Initiator microwave apparatus and heated at 80°C for an hour. The yellow solution was then filtered, and the filtrate maintained undisturbed at ambient temperature. Bright gold crystals of **2**·x(solv) slowly grew over four days. The crystallographic sample was maintained in mother liquor; otherwise the crystals were collected by filtration, washed with MeCN and dried under vacuum; the yield was 6% yield based on Ce. Anal. Calcd (Found) for **2**.MeCN (C$_{96}$H$_{76}$Ce$_6$FN$_3$O$_{31}$): C 43.89 (43.42); H 2.92 (2.78); N 1.60 (2.17); F 0.72 (0.87). Selected IR data (cm^{-1}): 3626 (w), 1595 (s), 1545 (s), 1491 (s), 1398 (s), 1175 (w), 1149 (w), 1069 (w), 1025 (w), 716 (m), 669 (m), 585 (m), 521 (m), 438 (m).

Single Crystal X-ray Crystallography

Crystallographic information files have been deposited at the Cambridge Crystallographic Data Centre with deposition codes **CCDC 1897929-1897930** for **1** and **2** respectively.

Crystal Structure data for **1·6H₂O**: X-Ray Intensity data were collected at 233 K on a Bruker DUO diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector. The structure was solved and refined in *SHELXTL2014*, using full-matrix least-squares refinement on F^2. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The structure was solved and refined in space group P2₁ which is clearly supported by the systematic absences. Space group P2₁/m was also considered but the data clearly do not have the mirror symmetry. Finally, the model that refined best is one refined as an inversion twin. The asymmetric unit consists of a Ce₂₀ cluster, three pyridinium cations, and a large area of disordered solvent. BVS calculations suggested the cluster to be 4- charge. Three protons were added in idealized positions to the three refined pyridinium cations. The fourth cation was concluded to be buried in the disordered solvent area, and since a fourth pyridinium was inconsistent with any electron density in the solvent area and is incompatible with the C,H,N analysis data, the options were NH_4^+ or H_3O^+, of which the former is considered most likely. They would be likely surrounded by hydrogen-bonded solvent molecules. Program SQUEEZE was run to determine the void size, and the suggested total number of electrons in it that would help determine the solvent in the unit cell. The large disordered solvent area was calculated to correspond to 2340 electrons per unit cell, which could be interpreted as ~53/cluster acetonitriles or a combination of pyridines and acetonitriles.

Crystal Structure data for **2·xMeCN**: X-Ray Intensity data were collected at 253 K on a Bruker DUO diffractometer using MoKα radiation (λ = 0.71073 Å) and an APEXII CCD area detector. Raw data frames were read by program SAINT[1] and integrated using 3D profiling algorithms. The resulting data were reduced to produce hkl reflections and their intensities and estimated standard deviations. The data were corrected for Lorentz and polarization effects and numerical absorption corrections were applied based on indexed and measured faces. The structure was solved and refined in *SHELXTL2014*, using full-matrix least-squares refinement on F^2. The non-H atoms were refined with anisotropic thermal parameters and all of the H atoms were calculated in idealized positions and refined riding on their parent atoms. The asymmetric unit consists of a half Ce6 cluster. All but one of the benzoate ligands are disordered and one of them is refined in three parts along with two partial acetonitrile molecules refined at 25% occupancy. The asymmetric unit consists of a half Ce6 cluster. All but one of the benzoate ligands are disordered and one of them is refined in three parts along with two partial acetonitrile molecules refined at 25% occupancy. Elemental analysis indicated the presence of a one F atom per Ce₆ cluster.

The four bridging atom positions (in the asymmetric unit) were obtained from a Difference Fourier Map and refined as oxygen atoms (O1, O2, O3 and O4). Their isotropic displacement parameters refined to values too high. Thus they were refined with partial site occupation factors and upon further refinement, a set of four electron density peaks appeared near these four oxygen atoms with longer distances to the Ce centers. These were also refined as partial oxygen positions; O1'-4'. The site occupation factor of O1-4 (with shorter Ce-O distances) and O1'-4' (with longer Ce-O distances) were dependently refined to values over 0.5. Judging by the shorter Ce-O distances, we expect the O1-4 set to be the oxido ligands and the O1'-O4' to be hydroxido ligands; bond distances Ce-O^{2-} are shorter than Ce-OH⁻ bond distances. The fact that both independently refined occupation factors of the oxido ligands (O1-4) and the hydroxido ligands (O1'-O4') refined to values higher than 0.5 (i.e., each 0.54, greater than the expected total of 1.0), and considering the fact that elemental analysis indicates the presence of one F per one Ce6 cluster, our conclusion is that a F atom and hydroxido oxygen can share the same position due to having similar size, charge and bonds to Ce that are significantly longer than Ce-O^{2-} bond distances. In the final refinement model, and after refining the site occupation factors of O1-4 and O1'-

4' dependently, we included a set of fluorine ligands sharing the same positions as the O1'-O4' by using EXYZ and EAPD commands. We fixed the site occupation factors of the O1-4 at 0.54 (as obtained from isotropic refinement of O1-4), and the site occupation factors of the O1'-4' at 0.345 and those of F1-4 at 0.115 to reflect the elemental analysis indicating the presence of one F per Ce6 cage. This gave a small improvement in the refinement: R1/wR2 = 2.99/7.37% vs 3.33/7.92% for the $\{Ce_6O_4(OH)_4\}$ core.

In the final cycle of refinement, 11057 reflections (of which 9655 are observed with $I > 2\sigma(I)$) were used to refine 451 parameters and the resulting R1, wR2 and S (goodness of fit) were 2.99 %, 7.37 % and 1.024, respectively. The refinement was carried out by minimizing the wR2 function using F2 rather than F values. R1 is calculated to provide a reference to the conventional R value but its function is not minimized.

Physical Measurements

Infrared spectra for complexes **1** and **2** collected in the solid state (KBr pellet) on a Nicolet iS5 FTIR spectrometer in the 400 – 4000 cm^{-1} range. UV-Vis spectra for complexes **1** and **2** were collected by dissolving solid samples in DCM over the range of 233 – 800 nm on an Evolution 201 with the temperature maintained at 25 °C during data collection with a PCCU1 module. Elemental analyses (C, H, N and F) were performed by Atlantic Microlab, Inc.

Supplementary Table S1. Crystal Data and Structure Refinement for **1** and **2**.

	1·Solv	**2**·MeCN
formula[a]	$C_{169}H_{132}N_4Cl_{16}Ce_{20}O_{62}$[b]/ $C_{169}H_{131}N_3Cl_{16}Ce_{20}O_{63}$[c]	$C_{94}H_{73}N_2F_1Ce_6O_{31}$
Fw, g mol^{-1}	6580.41[b]/6581.39[c]	2586.27
Space group	$P2_1$	$P\bar{1}$
a, Å	20.314 (5)	14.638 (9)
b, Å	24.463 (5)	14.726 (10)
c, Å	28.508 (6)	14.909 (10)
α, deg	90	60.518 (11)
β, deg	91.975 (5)	65.035 (11)
γ, deg	90	62.487 (10)
V, Å^3	14159 (5)	2409 (3)
Z	2	2
T, K	233	253
λ, Å	0.71073	0.71073
$\rho_{calc,}$ g cm^{-3}	1.539	1.811
μ, mm^{-1}	3.347	2.858
R1[d,e]	0.0582	0.0299
wR2[f]	0.1302	0.0737

[a] Excluding solvent molecules of crystallization. [b] Formula with NH_4^+ counterion. [c] Formula with H_3O^+ counterion [d] $I > 2\sigma(I)$. [e] $R1 = \Sigma(||F_o| - |F_c||) / \Sigma|F_o|$. [f] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (m*p)^2 + n*p]$, $p = [max(F_o^2,0) + 2* F_c^2]/3$, m and n are constants

**Supplementary Table S2**. Bond Valence Sums and Coordination Numbers (CN) for Ce Atoms in **1** and **2**.[a,b]

1					2			
Atom	Ce^{III}	Ce^{IV}	CN		Atom	Ce^{III}	Ce^{IV}	CN
Ce1	3.99	**3.51**	8		Ce1	4.29	**3.72**	9
Ce2	4.02	**3.53**	8		Ce2	4.74	**4.11**	8
Ce3	4.37	**3.70**	8		Ce3	4.72	**4.09**	9
Ce4	4.43	**3.75**	8					
Ce5	4.49	**3.80**	8					
Ce6	4.38	**3.71**	8					
Ce7	4.53	**3.88**	8					
Ce8	4.33	**3.71**	8					
Ce9	4.45	**3.81**	8					
Ce10	4.65	**3.98**	8					
Ce11	**3.06**	2.58	9					
Ce12	**3.06**	2.57	9					
Ce13	**2.59**	2.51	9					
Ce14	**3.00**	2.52	9					
Ce15	**3.00**	2.53	9					
Ce16	**3.03**	2.56	9					
Ce17	**2.95**	2.50	9					
Ce18	**2.94**	2.48	9					
Ce19	**2.85**	2.62	10					
Ce20	**2.95**	2.53	10					

[a]The bold values are the ones closest to the charge for which they are calculated; the oxidation state is thus the nearest integer to the bold value. [b] CN = coordination number.

Supplementary Table S3. Bond Valence Sums and Assignments for the O Atoms in **1**[a] and **2**[a,b].

1				2		
Atom	BVS	Assignment		Atom	BVS	Assignment
O1	1.78	O^{2-}		O1	2.05	O^{2-}
O2	1.77	O^{2-}		O2	2.06	O^{2-}
O3	1.70	O^{2-}		O3	2.08	O^{2-}
O4	1.93	O^{2-}		O4	2.09	O^{2-}
O5	1.89	O^{2-}		O1'	1.18	OH^- / F^-
O6	1.98	O^{2-}		O2'	1.19	OH^- / F^-
O7	1.97	O^{2-}		O3'	1.20	OH^- / F^-
O8	1.94	O^{2-}		O4'	1.21	OH^- / F^-
O9	1.95	O^{2-}				
O10	1.97	O^{2-}				
O11	1.93	O^{2-}				
O12	1.98	O^{2-}				
O13	1.96	O^{2-}				
O14	1.94	O^{2-}				
O15	1.99	O^{2-}				
O16	1.93	O^{2-}				
O17	2.00	O^{2-}				
O18	1.97	O^{2-}				

[a]An O BVS in the ~1.8-2.0, ~0.9-1.2, ~0.2-0.4 range indicates non, single- and double- deprotonation respectively. [b] Assignment of O^{2-} and OH^- to an O atom with BVS in the range ~1.60 – 1.70 is based on symmetry of the molecule, the symmetry equivalent partners of O atoms are assigned as being deprotonated.
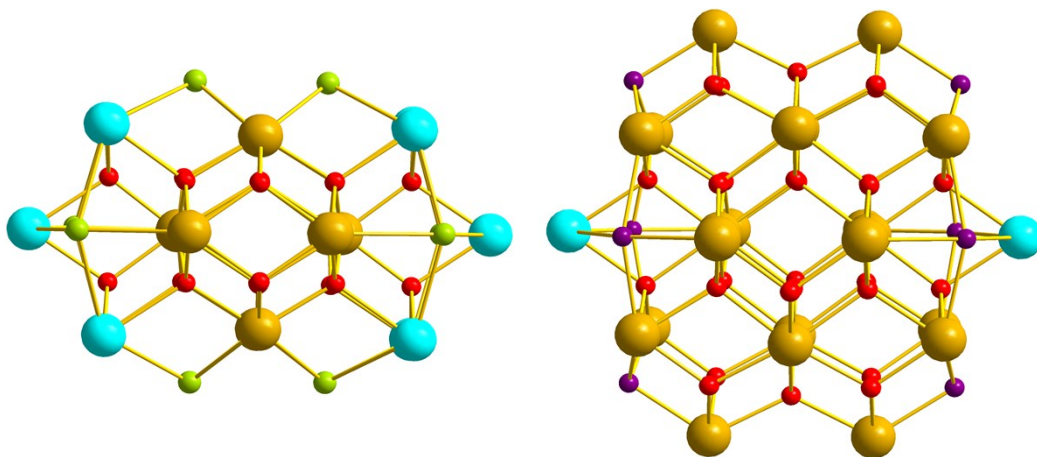

Fig S1 Structural comparison of the Ce_{20} anion of **1** with the previously synthesized Ce_{24}. Each compound adopts the fluorite structure with alternating Ce and O layers. The Ce_{24} adopts a five-layer A:B:C:B:A pattern where A = 2, B = 6, C = 8, whereas the Ce_{20} adopts a B:C:B pattern. The μ_2-Cl^- block the growth of the C layer on the Ce_{20}. Color code: Ce^{IV} gold, Ce^{III} sky blue, O red, OH purple, Cl green
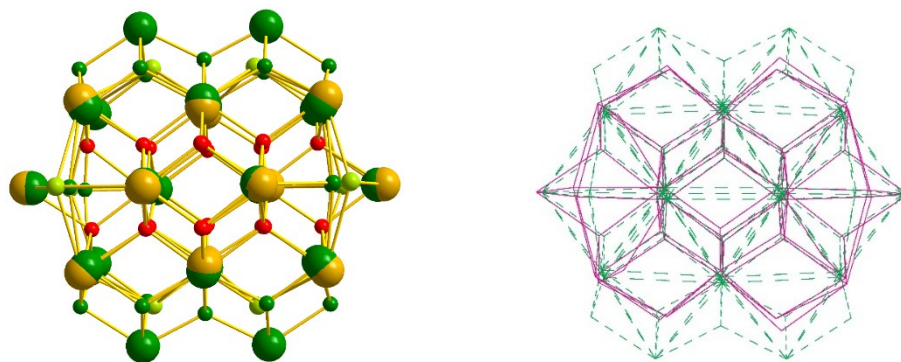
Fig S2 Root-mean-square difference plots of the core of the Ce_{20} anion of **1** overlaid with the Ce_{24}: **(left)** the Ce, O and Cl atoms of Ce_{20} are shown as gold, red and green, respectively. The Ce and additional O atoms of Ce_{24} are shown as dark green. **(right)** the Ce_{20} is shown in pink overlaid with the Ce_{24} in green.

Supplementary Table S4. The root-mean-square (R.M.S) difference between the Ce_{20} anion **1** and previously synthesized Ce_{24}

1	Ce_{24}	Deviation (Å)
Ce1	Ce6	0.194
Ce2	Ce6a	0.196
Ce3	Ce5	0.220
Ce4	Ce11	0.226
Ce5	Ce1c	0.205
Ce6	Ce5a	0.202
Ce7	Ce1a	0.064
Ce8	Ce1d	0.070
Ce9	Ce1	0.062
Ce10	Ce12	0.072
Ce11	Ce2a	0.246
Ce12	Ce9a	0.279
Ce13	Ce3	0.259
Ce14	Ce7	0.283
Ce15	Ce7a	0.282
Ce16	Ce9	0.271
Ce17	Ce2	0.223
Ce18	Ce3a	0.263
Ce19	Ce4a	0.186
Ce20	Ce4	0.184
Weighted R.M.S Deviation 0.213 Å		
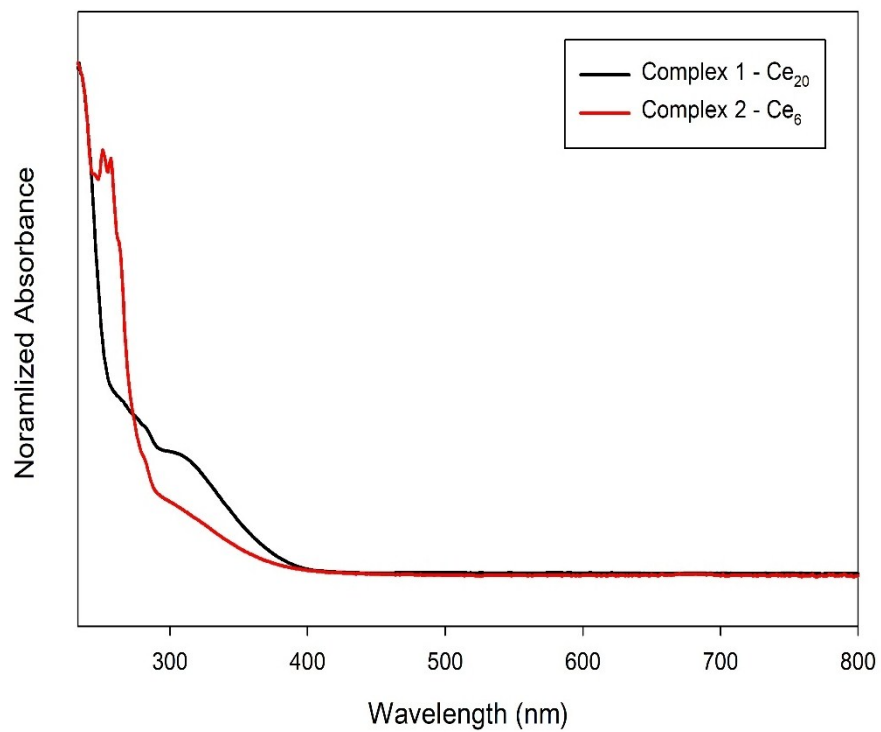
Fig S3 UV-Vis spectrum of complex **1** and complex **2**. Both samples were dissolved in DCM.
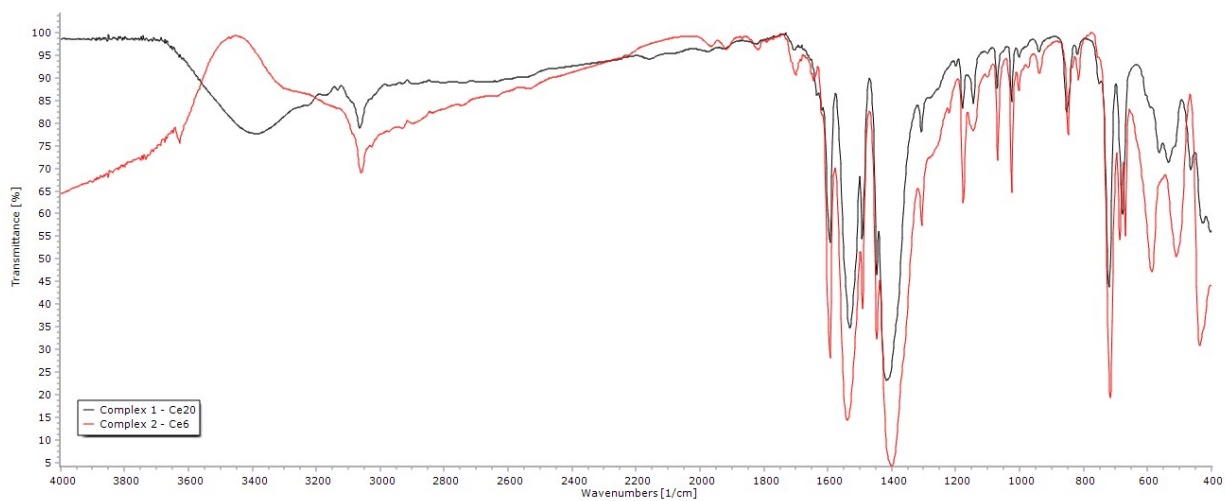
Fig S4 FTIR spectrum of complex **1** and complex **2**.