Electronic Supplementary Information for

Cerium oxide nanoclusters: Commensurate with concepts of polyoxometalate chemistry?

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Structural description of the precursor $[Ce_2(ib)_6(H_2O)_3]_n$ (**3**):

The crystal structure of precursor **3**, prepared from $Ce(NO_3)_3 \cdot 6H_2O$ and Hib in a water-ethanol solution, features single-stranded helical chains where $[Ce(O_2CCHMe_2)_3]$ and $[Ce(O_2CCHMe_2)(H_2O)_3]$ building units are bridged by two isobutyrate ligands. The helical pitch amounts to 16.414 Å, with a repetition unit of four Ce centers. There are two crystallographically independent Ce centers in the crystal structure of **3**, resulting in (1) a CeO_{10} environment defined by carboxylate oxygen donors of six isobutyrate ligands, four of them are chelating and the remaining two are bridging, (2) a CeO_9 environment defined by four carboxylate oxygen sites from two chelating isobutyrates, two carboxylate oxygen atoms from two bridging carboxylates and three water molecules. Bond distances range from 2.438(5) to 2.691(4) Å ($Ce–O_{carboxylate}$) and from 2.491(6) to 2.560(5) Å ($Ce–O_{water}$). The coordinated water molecules (O13, O14 and O15) in **3** form intra-chain O-H···O hydrogen bonds with the bridging carboxylate oxygen. BVS of 3.175/3.250 confirm a +III oxidation state for all Ce sites in **3**.

Further crystallography details

The structures of giant molecular metal oxide clusters with oxo-carboxylate ligands are typically highly disordered and have large voids partially occupied by diffused solvent molecules. This often results in low-resolution data and necessitates the use of restrains to optimize geometrical parameters and thermal displacement coefficients for ligands. The metal-oxygen core usually is not influenced by those manipulations and its geometry remains virtually the same.

One of the metal core positions in structure of **1** displays an electron density of about 1/6 of the value expected for a Ce atom, therefore a fully occupied Na was assigned to this position. Such coordination of sodium to oxo-carboxylate ligands is not very common; however, the existence of one Na atom per cluster has been also confirmed by elemental analysis. SIMU, DELU (displacement parameters), DFIX (geometrical parameters), and BUMP ("anti-bumping") restrains were used to stabilize the refinement and to obtain appropriate geometry for ligands. The part of residual electron density in voids indicated possible existence of a quarter of MeCN solvent molecule. The refinement with this solvent molecule (as well as an attempt to SQUEEZE[1] electron density from voids) has not improved the result, therefore the original model and intensity data were used for final outputs.

The structure of **2** was refined using SIMU, DELU, and DFIX restrains to obtain appropriate geometries for the ligands. The residual electron density in the voids did not indicate any solvent-like moieties. A refinement after using the SQUEEZE routine has not improved the result, therefore the non-modified model and intensity data were used for final outputs.

The structure of **3** was refined to R_1 = 0.0730 using SIMU, DELU, and DFIX restrains to obtain appropriate geometries for the ligands. The residual electron density in voids pointed to possible existence of diffused solvent: water and ethanol were two candidates based on the synthesis procedure. Use of the SQUEEZE routine significantly improved R_1 factor of the refinement and its result was in a good accord with existence of one ethanol solvent molecule per void. This solvent molecule was not included to connectivity table, but was added to the final formula to display true metric outputs.

1. A. L. Spek, *J. Appl. Cryst.* 2003, **36**, 7.

Table S1. Summary of crystallographic details, data collection, and refinement details for **1**–**3**

Compound	**2**	**1**	**3**
Empirical formula	$C_{124}H_{222}Ce_{22}O_{88}$	$C_{82}H_{155}Ce_{10}N_5NaO_{48}$	$C_{26}H_{54}Ce_2O_{16}$
Molecular weight / g mol^{-1}	6203.66	3403.30	902.93
T / K	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$	$P2_1/n$
a / Å	33.045(3)	30.2744(14)	14.6915(11)
b / Å	18.2348(11)	15.6022(7)	18.5748(14)
c / Å	32.962(2)	29.3014(14)	15.3352(12)
β / °	91.474(2)	118.854(1)	113.766(1)
V / Å^3	19855(2)	12122.2(10)	3830.0(5)
Z	4	4	4
ρ / g cm^{-3}	2.075	1.865	1.566
μ / mm^{-1}	5.009	3.756	2.408
Crystal size, mm^3	0.34 × 0.21 × 0.11	0.18 × 0.07 × 0.06	0.32 × 0.12 × 0.08
Index ranges	$-36 \le h \le 36$ $-20 \le k \le 20$ $-36 \le l \le 36$	$-40 \le h \le 40$ $-20 \le k \le 20$ $-39 \le l \le 38$	$-17 \le h \le 17$ $-19 \le k \le 22$ $-18 \le l \le 18$
Reflections collected	64946	122402	23450
Independent reflections	14310 [R(int) = 0.0724]	30147 [R(int) = 0.0468]	6742 [R(int) = 0.1351]
Completeness to theta	99.7 %	99.8 %	99.9 %
Data / restraints / parameters	14310 / 682 /1076	30147 / 439 / 1316	6742 / 0 / 382
Goodness-of-fit on F^2	1.090	1.113	0.938
Final R_1, wR_2	R_1 = 0.0678, wR_2 = 0.1796	R_1 = 0.0499, wR_2 = 0.1191	R_1 = 0.0562, wR_2 = 0.1410
R indices (all data)	R_1 = 0.1225, wR_2 = 0.2337	R_1 = 0.0756 wR_2 = 0.1386	R_1 = 0.0688, wR_2 = 0.1499
Largest diff. peak/hole, e Å^{-3}	3.158 / –2.671	3.458 / –2.272	1.810 / –2.018

Table S2. Bond valence sum calculations for Ce sites in compounds **1**–**3**

		Assignment
Compound **2**		
Ce1	4.987	Ce^{4+}
Ce2	4.731	Ce^{4+}
Ce3	4.704	Ce^{4+}
Ce4	4.655	Ce^{4+}
Ce5	4.875	Ce^{4+}
Ce6	4.922	Ce^{4+}
Ce7	4.726	Ce^{4+}
Ce8	4.080	Ce^{4+}
Ce9	3.683	Ce^{3+}
Ce10	3.867	Ce^{3+}
Ce11	3.664	Ce^{3+}
Compound **1**		
Ce1	4.904	Ce^{4+}
Ce2	2.970	Ce^{3+}
Ce3	4.608	Ce^{4+}
Ce4	4.794	Ce^{4+}
Ce5	4.887	Ce^{4+}
Ce6	4.285	Ce^{4+}
Ce7	4.819	Ce^{4+}
Ce8	4.469	Ce^{4+}
Ce9	4.471	Ce^{4+}
Ce10	4.446	Ce^{4+}
Compound **3**		
Ce1	3.175	Ce^{3+}
Ce2	3.250	Ce^{3+}