$Ce_2[MoO_5][MoO_4]$ and $Ce_5[MoO_4]_8$: Two New Cerium Oxomolybdates, Each Exhibiting a Special Structural Feature

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$Ce_2[MoO_5][MoO_4]$ crystallizes monoclinically in space group $P2_1/c$ (a = 2241.98(9), b = 712.95(3), c = 2044.19(8) pm, β = 116.936(2)°, Z = 16). Besides eight crystallographically different Ce^{3+} cations with coordination numbers ranging from seven *plus* one to ten, its structure contains two isolated oxomolybdate(VI) species, namely $[MoO_4]^{2-}$ tetrahedra and $[MoO_5]^{4-}$ trigonal bipyramids and square pyramids. The oxygen polyhedra around the Ce^{3+} cations build up a three-dimensional $^3_\infty\{[Ce_2O_9]^{12-}\}$ network by vertex-, edge-, and face-connections with the Mo^{6+} cations residing in tetrahedral, square-pyramidal, and trigonal-bipyramidal voids therein. $Ce_5[MoO_4]_8$ also crystallizes monoclinically in space group $P2_1/c$ (a = 1133.14(5), b = 1704.96(7), c = 1406.21(6) pm, β = 90.749(2)°, Z = 4). In its structure eight isolated $[MoO_4]^{2-}$ tetrahedra are present, which display an overall negative charge of -16. To maintain electroneutrality, mixed-valency of the five crystallographically independent cerium cations must be considered. A thorough bond-valence analysis reveals cerium at the Ce1 site as tetravalent, while the other four cerium cations prove to be trivalent. The polyhedra around all cerium cations form chains with a V-shaped profile along [100] *via* vertex-, edge-, and face-connections to result in a sawblade pattern. These chains are interlocked into sheets parallel to the (001) plane and linked by the Mo^{6+} cations to form a three-dimensional network.

Key words: Cerium, Oxomolybdates, Crystal Structure, Mixed Valency

Introduction

Not too many oxomolybdates(VI) of cerium are known in the literature so far. Besides the crystal structures of two cerium(III) compounds, namely $Ce_6Mo_{10}O_{39}$ [1] and $Ce_2Mo_4O_{15}$ [2], which can be described by the structured formulae $Ce_6[MoO_4]_8[Mo_2O_7]$ and $Ce_2[MoO_4]_2[Mo_2O_7]$, respectively, only the existence of Ce_2MoO_6 [3] has been reported, although considerable doubt arose on both the published crystal system and the lattice parameters of the latter [4]. Regarding cerium(IV) oxomolybdates(VI), only triclinic $Ce[MoO_4]_2$ has been reported [5], and besides its lattice parameters no description of the crystal structure has been given. Thus, the two title compounds, $Ce_2Mo_2O_9$ and $Ce_5Mo_8O_{32}$, enlarge the family of cerium oxomolybdates(VI) very considerably. Furthermore, both compounds exhibit each a special structural feature, which can be seen clearly in the case of $Ce_2Mo_2O_9$ if written with the structured formula $Ce_2[MoO_5][MoO_4]$. Its crystal structure consists of both isolated $[MoO_4]^{2-}$ tetrahedra and isolated $[MoO_5]^{4-}$ units, which are an almost unknown feature for oxomolybdates so far. One exception, however, is their existence in the structure of $K_4[MoO_5]$ [6], which crystallizes isotypically with the respective oxotungstates $K_4[WO_5]$ and $Rb_4[WO_5]$ [6] representing the only compounds containing isolated $[WO_5]^{4-}$ units. $Ce_5[MoO_4]_8$, the structured formula of $Ce_5Mo_8O_{32}$, reveals that if all molybdenum cations are hexavalent, one out of five cerium cations needs to be tetravalent, while the others can be considered as Ce^{3+} cations. Thus, $Ce_5[MoO_4]_8$ represents the first reported mixed-valent cerium(III, IV) oxomolybdate(VI) according to $Ce^{IV}Ce_4^{III}[MoO_4]_8$.

Experimental Section

Synthesis of $Ce_2[MoO_5][MoO_4]$

An attempt to synthesize iodide derivatives of cerium oxomolybdate (*e. g.* $CeI[MoO_4]$) using elemental cerium

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(Ce: 99.9 %, ChemPur, Karlsruhe, Germany), cerium dioxide (CeO_2: 99.9 %, ChemPur, Karlsruhe, Germany), elemental iodine (I_2: 99.9 %, Alfa Aesar, Karlsruhe, Germany), and molybdenum trioxide (MoO_3: *p. a.*, Merck, Darmstadt, Germany) according to the following equation:

$$CeO_2 + Ce + I_2 + 2\,MoO_3 \longrightarrow 2\,CeI[MoO_4]$$

in evacuated silica ampoules at 820 °C for seven days did not lead to the desired product, but to red, transparent needle-shaped single crystals of $Ce_2[MoO_5][MoO_4]$. Since bronze-colored MoO_2 [7] could be identified as one of the by-products, the following reaction can be assumed:

$$CeO_2 + Ce + 3\,MoO_3 \longrightarrow Ce_2[MoO_5][MoO_4] + MoO_2$$

All resulting iodine-containing by-products were water soluble, while $Ce_2[MoO_5][MoO_4]$ remained stable when exposed to air and humidity.

Synthesis of $Ce_5[MoO_4]_8$

Due to an oxygen break-in into a fused silica ampoule containing elemental cerium, cerium dioxide, cerium tribromide ($CeBr_3$: 99.9 %, Aldrich, Taufkrichen, Germany) and molybdenum trioxide for an attempt to synthesize cerium(III) bromide oxomolybdate(VI) according to:

$$3\,CeO_2 + Ce + 2\,CeBr_3 + 6\,MoO_3 \longrightarrow 6\,CeBr[MoO_4]$$

(reaction temperature: 820 °C, reaction time: 7 d), dark-brown, transparent, coarse, air- and water-resistant single crystals of $Ce_5[MoO_4]_8$ emerged from the reaction mixture. To maintain electroneutrality, one out of five cerium cations in the empirical formula must be tetravalent, thus the following equation for its formation is assumed:

$$6\,CeO_2 + 2\,Ce + 2\,O_2 + 2\,CeBr_3 + 16\,MoO_3 \\ \longrightarrow 2\,Ce_5[MoO_4]_8 + 3\,Br_2$$

and supported by the fact, that elemental bromine (Br_2) was observed during the reaction.

Due to the fact that both title compounds emerged merely as by-products, the possibilities to perform extended analyses besides single crystal X-ray structure determination were rather limited. Attempts to obtain phase-pure samples of both $Ce_2Mo_2O_9$ and $Ce_5[MoO_4]_8$ have not yet been successful.

X-Ray structure determination

Intensity data sets for single crystals of both $Ce_2[MoO_5]$-$[MoO_4]$ and $Ce_5[MoO_4]_8$ were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromatized MoK_α radiation (wavelength: λ = 71.073 pm). A numerical absorption correction was performed with the help of the program HABITUS [8]. The structure solutions and refinements were carried out utilizing the program package SHELX-97 [9]. Details of the data collections and structure refinements [10] are summarized in Table 1, interatomic distances of $Ce_2[MoO_5][MoO_4]$ can be found in Table 2, and those of $Ce_5[MoO_4]_8$ together with the results of bond-valence calculations [11] are displayed in Table 3. Due to the large number of atomic positions in the crystal structure of both compounds (52 for $Ce_2[MoO_5][MoO_4]$ and 45 for $Ce_5[MoO_4]_8$), atomic parameters are not presented in the printed paper but can be obtained along with further details of the crystal structure investigation from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-423024 for $Ce_2[MoO_5][MoO_4]$ and CSD-423025 for $Ce_5[MoO_4]_8$.

Table 1. Crystal structure data for $Ce_2[MoO_5][MoO_4]$ and $Ce_5[MoO_4]_8$.

	$Ce_2[MoO_5][MoO_4]$	$Ce_5[MoO_4]_8$
Crystal system, space group	monoclinic, $P2_1/c$ (no. 14)	
Formula units Z	16	4
Lattice constants		
a, pm	2241.96(8)	1133.14(2)
b, pm	712.97(2)	1704.96(4)
c, pm	2044.19(7)	1406.21(3)
β, deg	116.936(2)	90.749(2)
Calcd. density D_x, g cm^{-3}	5.62	4.84
Molar volume V_m, cm^{3}mol^{-1}	109.64	408.98
$F(000)$, e	4352	3528
Index range hkl	±29, ±9, ±26	±15, ±22, ±18
θ range, deg	3.0–27.6	1.8–28.2
Absorption coeff., μ, mm^{-1}	15.7	11.9
Data corrections	background, polarization and Lorentz factors; numerical absorption correction (HABITUS [8])	
Scattering factors	International Tables, Vol. C [10]	
Collected / unique refls	12328 / 6698	53960 / 6700
parameters	470	407
R_{int} / R_σ	0.055 / 0.072	0.116 / 0.055
R_1 for (n) reflections with $\lvert F_o \rvert \geq 4\sigma(F_o)$	0.043 (n = 4638)	0.034 (n = 5249)
R_1 / wR_2 for all reflections	0.082 / 0.088	0.055 / 0.068
Goodness of fit (GoF)	1.083	1.030
Extinction coefficient g	0.00012(1)	0.00160(3)
Residual electron density, $\rho_{min/max}$, e$^-$ $\times 10^{-6}$ pm^{-3}	1.92 / −1.93	1.62 / −1.62

Results and Discussion

Structure of $Ce_2[MoO_5][MoO_4]$

$Ce_2[MoO_5][MoO_4]$ crystallizes monoclinically in space group $P2_1/c$ (a = 2241.98(9), b = 712.95(3), c = 2044.19(8) pm, β = 116.936(2)°) with sixteen

Distance	*d* (pm)	Distance	*d* (pm)	Distance	*d* (pm)
Ce1–O15	246.0(8)	Ce2–O9	237.0(8)	Mo1–O1	175.3(8)
–O15′	250.9(8)	–O13	243.4(9)	–O2	181.2(8)
–O12	254.3(8)	–O12	250.2(8)	–O3	182.9(8)
–O9	255.3(8)	–O33	251.7(9)	–O4	189.0(8)
–O22	257.6(8)	–O10	252.0(8)	–O5	194.9(9)
–O11	261.7(8)	–O13′	256.7(8)	$\bar{d}$(Mo1–O)	184.7
–O8	264.3(8)	–O34	258.8(8)	Mo2–O6	176.6(8)
–O35	269.3(8)	–O24	262.3(8)	–O7	179.6(8)
–O11′	270.4(9)	–O34′	265.5(9)	–O8	181.3(8)
–O22′	270.6(9)			–O9	186.8(8)
				–O10	201.3(8)
$\bar{d}$(Ce1–O)	260.0	$\bar{d}$(Ce2–O)	253.1	$\bar{d}$(Mo2–O)	186.6
Ce3–O5	241.9(9)	Ce4–O5	238.2(8)	Mo3–O11	177.8(8)
–O25	242.5(8)	–O10	243.8(8)	–O12	180.4(8)
–O4	247.5(9)	–O30	247.5(9)	–O13	181.3(8)
–O17	249.8(8)	–O7	256.1(8)	–O14	185.9(8)
–O32	250.6(8)	–O24	257.6(8)	–O15	202.2(8)
–O1	251.4(9)	–O2	260.9(9)	$\bar{d}$(Mo3–O)	185.5
–O28	255.2(8)	–O36	264.1(9)	Mo4–O16	174.9(9)
–O4′	263.1(8)	–O27	267.9(8)	–O17	176.6(7)
–O1′	269.4(9)	–O32	272.5(9)	–O18	185.0(8)
				–O19	187.5(9)
				–O20	203.9(8)
$\bar{d}$(Ce3–O)	252.4	$\bar{d}$(Ce4–O)	256.5	$\bar{d}$(Mo4–O)	185.6
Ce5–O19	234.9(9)	Ce6–O23	242.2(8)	Mo5–O21	171.8(9)
–O28	244.8(9)	–O18	243.0(9)	–O22	176.1(8)
–O19′	246.0(8)	–O3	243.0(8)	–O23	176.2(8)
–O31	250.9(8)	–O20	243.8(8)	–O24	179.7(7)
–O3	253.5(9)	–O6	253.2(8)	$\bar{d}$(Mo5–O)	176.0
–O18	255.2(8)	–O16	255.0(9)	Mo6–O25	173.5(8)
–O4	261.7(8)	–O26	264.5(9)	–O26	176.7(8)
–O26	266.1(8)	–O27	272.8(8)	–O27	178.5(8)
				–O28	178.6(9)
$\bar{d}$(Ce5–O)	251.6	$\bar{d}$(Ce6–O)	252.2	$\bar{d}$(Mo6–O)	176.8
Ce7–O8	234.6(8)	Ce8–O14	231.3(8)	Mo7–O29	171.8(8)
–O15	240.6(8)	–O2	236.6(10)	–O30	174.0(9)
–O20	250.5(8)	–O20	249.5(7)	–O31	174.9(9)
–O14	252.6(8)	–O10	254.1(9)	–O32	181.2(9)
–O21	254.0(9)	–O6	261.4(9)	$\bar{d}$(Mo7–O)	175.5
–O29	254.8(8)	–O36	265.1(8)	Mo8–O33	170.6(9)
–O35	255.2(8)	–O7	266.4(9)	–O34	176.5(8)
–O23	258.4(8)	–O30	293.4(9)	–O35	178.2(8)
				–O36	178.6(8)
$\bar{d}$(Ce7–O)	250.1	$\bar{d}$(Ce8–O)	257.3	$\bar{d}$(Mo8–O)	176.0

Table 2. Selected interatomic distances (pm) for $Ce_2[MoO_5][MoO_4]$ with estimated standard deviations in parentheses.

formula units per unit cell. The crystal structure contains eight crystallographically different Ce^{3+} cations with coordination numbers from seven *plus* one to ten showing a wide variety of irregular polyhedra (Fig. 1). The interatomic distances between the Ce^{3+} cations and the surrounding O^{2-} anions are covering a range from 231 to 273 pm (Table 2), which is a very common interval as seen in numerous compounds comprising Ce^{3+} cations and complex oxoanions (*e. g.* $CeTaO_4$: $d(Ce^{3+}\text{–}O^{2-})$ = 233 – 269 [12]) as well as in A-type Ce_2O_3 ($d(Ce^{3+}-O^{2-})$ = 234 – 269 [13]). Even the slightly longer distance of 293 pm to the eighth oxide anion in the coordination sphere of $(Ce8)^{3+}$ is not to be considered particularly long, since similar distances are also found in a few structures such as in $Ce_6[MoO_4]_8[Mo_2O_7]$ [1] or in $Ce[AsO_4]$ [14], in which the longest bonding $Ce^{3+}\text{–}O^{2-}$ distances are 290 and 294 pm, respectively. The coordination number around four of the eight crystallographically distinguishable Mo^{6+} cations is five, realized in a distorted square pyramid in case of $(Mo1)^{6+}$ and trigonal bipyramids for the other

Table 3. Selected interatomic distances (pm) and results of the bond-valence calculations [11] to determine the formal charge of the cerium cations for $Ce_5[MoO_4]_8$ with estimated standard deviations in parentheses.

Distance	d (pm)	V_i[a]	Distance	d (pm)	V_i[a]	Distance	d (pm)	V_i[a]
Ce1–O27	225.6(6)	0.61	Ce2–O14	235.8(7)	0.48	Ce3–O22	241.9(6)	0.42
–O16	227.4(6)	0.57	–O28	236.9(5)	0.47	–O18	242.9(7)	0.41
–O8	228.9(6)	0.56	–O7	240.8(6)	0.43	–O32	246.0(5)	0.38
–O11	233.1(6)	0.50	–O29	242.9(6)	0.41	–O4	247.9(6)	0.37
–O1	234.8(6)	0.49	–O12	246.0(6)	0.38	–O25	249.0(6)	0.36
–O2	238.5(6)	0.45	–O30	247.3(6)	0.37	–O26	250.2(6)	0.35
–O19	240.8(6)	0.42	–O21	248.3(6)	0.37	–O15	251.7(5)	0.34
–O24	259.1(6)	0.28	–O20	272.1(6)	0.22	–O30	254.5(6)	0.32
	$\Sigma =$	3.88		$\Sigma =$	3.13		$\Sigma =$	2.95
Ce4–O5	245.8(6)	0.39	Ce5–O31	239.7(5)	0.44	$\bar{d}$(Ce1–O)	235.6	
–O3	246.2(6)	0.38	–O23	242.3(6)	0.42	$\bar{d}$(Ce2–O)	246.3	
–O20	247.1(6)	0.38	–O9	248.9(6)	0.36	$\bar{d}$(Ce3–O)	248.0	
–O28	250.7(6)	0.35	–O24	250.4(6)	0.35	$\bar{d}$(Ce4–O)	256.0	
–O17	250.8(6)	0.35	–O10	251.8(6)	0.34	$\bar{d}$(Ce5–O)	253.4	
–O6	252.8(6)	0.33	–O16	253.9(6)	0.32			
–O32	262.4(5)	0.27	–O4	255.9(9)	0.31			
–O31	272.0(6)	0.22	–O3	284.1(8)	0.16			
–O12	276.1(5)	0.20						
	$\Sigma =$	2.87		$\Sigma =$	2.70			

Distance	d (pm)	Distance	d (pm)	Distance	d (pm)	Distance	d (pm)
Mo1–O1	175.0(6)	Mo3–O9	173.9(6)	Mo5–O17	173.7(6)	Mo7–O25	172.1(6)
–O2	175.6(6)	–O10	176.0(6)	–O18	175.2(6)	–O26	173.9(6)
–O3	176.6(6)	–O11	177.4(6)	–O19	176.9(6)	–O27	177.1(6)
–O4	177.5(6)	–O12	179.0(6)	–O20	178.2(6)	–O28	181.4(5)
$\bar{d}$(Mo1–O)	176.2	$\bar{d}$(Mo3–O)	176.6	$\bar{d}$(Mo5–O)	176.0	$\bar{d}$(Mo7–O)	176.1
Mo2–O5	175.0(5)	Mo4–O13	171.9(6)	Mo6–O21	174.4(6)	Mo8–O29	174.2(6)
–O6	175.1(6)	–O14	173.1(7)	–O22	174.6(6)	–O30	174.6(6)
–O7	175.2(6)	–O15	174.7(6)	–O23	175.0(6)	–O31	178.3(6)
–O8	180.6(6)	–O16	182.5(5)	–O24	178.9(6)	–O32	178.4(5)
$\bar{d}$(Mo2–O)	176.5	$\bar{d}$(Mo4–O)	175.6	$\bar{d}$(Mo6–O)	175.7	$\bar{d}$(Mo8–O)	176.4

[a] Calculation of the formal charge: $V_i = \sum_j \exp\left(\frac{R_0 - R_{ij}}{b}\right)$ with $R_0(Ce^{3+})$ = 2.031 Å, b = 0.449; $R_0(Ce^{4+})$ = 2.028 Å, b = 0.443.

three molybdenum(VI) cations (Fig. 2). The Mo^{6+}–O^{2-} bond lengths are in an interval of 175 – 204 pm. For $(Mo1)^{6+}$ one short (175 pm) and four longer distances (181 – 194 pm) are found (Table 2) with the tightly bonded oxygen atom at the top of the pyramid and the other four building up its square bottom face. The other three pentacoordinated molybdenum(VI) cations exhibit four Mo^{6+}–O^{2-} bond lengths between 175 and 187 pm, each with one longer distance in the region of 201 – 204 pm for every case (Table 2). These distances are consistent with those in other compounds containing Mo^{6+} cations with coordination numbers of five, such as $Cu[MoO_4]$ ($d(Mo^{6+}$–$O^{2-})$ = 174 – 204 pm) [15]. The oxygen polyhedra around $(Mo5)^{6+}$–$(Mo8)^{6+}$ form tetrahedral *ortho*-oxomolybdate units with Mo^{6+}–O^{2-} distances from 172 to 181 pm (Table 2) and bond angles in the range of 105 – 118° with the exception of the $[(Mo6)O_4]^{2-}$ tetrahedra, which shows a wider range (100 – 131°) and thus, a greater distortion (Fig. 3). The molybdenum–oxygen bond lengths are in good agreement with those in other compounds comprising *ortho*-oxomolybdate units (*e. g.* $La_2[MoO_4]_3$: $d(Mo^{6+}$–$O^{2-})$ = 173 – 182 pm [16]). Though uncommon, the aforementioned highly irregular O–Mo–O angles are not unknown, as proven by the crystal structure of $Hg[MoO_4]$ [17], in which these angles range between 97 and 144°. Since the oxomolybdate units are isolated in the crystal structure, a closer look at the interconnection of the oxygen polyhedra around the cerium cations is helpful for understanding the structure. These polyhedra form a complicated and cluttered three-dimensional network by edge- and vertex-connections.

Very often, a structure comprising complex ions can be described in an easy and understandable way, if these ions are shrunk to their centers of gravity. The arrangement of these centers can then be compared to already known simple structure types. The crystal structure of *Ln*F$[MoO_4]$ (*Ln* = Sm–Tm) [18] *e. g.* comprises both isolated $[F_2Ln_2]^{4+}$ cations and $[MoO_4]^{2-}$ anions, for which the structured formula $[F_2Ln_2]$-$[MoO_4]_2$ allocates an AB_2 structure type, which could in this case be identified as a distorted variation of

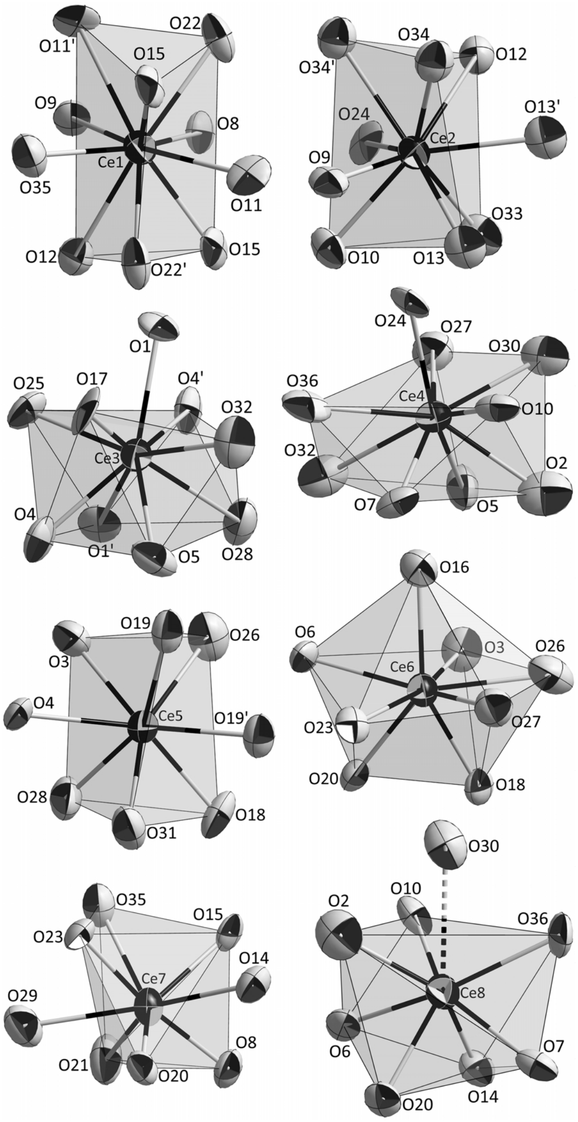

Fig. 1. Coordination polyhedra around the eight crystallographically independent Ce^{3+} cations in the crystal structure of $Ce_2[MoO_5][MoO_4]$ (ellipsoid representation at the 95 % probability level).

AlB_2 [19]. In case of $Ce_2[MoO_5][MoO_4]$ the ratio of cerium cations to oxomolybdate anions is 1 : 1, which can be potentially ascribed a simple AB structure type. Unfortunately, the coordination numbers of the Ce^{3+} cations as well as those of the oxomolybdate units vary between six and seven, hence no simple AB structure type can be identified. In Fig. 4 a view of the crystal structure of $Ce_2[MoO_5][MoO_4]$ along the *b* axis is displayed. It is striking that all oxomolybdate units of similar types are arranged in rows along [010] with the Ce^{3+} cations located in between.

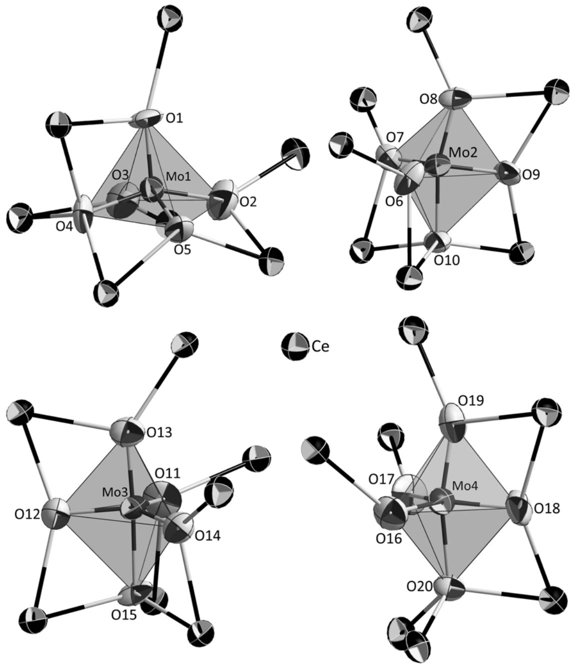

Fig. 2. Cationic coordination around the four different $[MoO_5]^{4-}$ units in the crystal structure of $Ce_2[MoO_5]$-$[MoO_4]$ (ellipsoid representation at the 95 % level).

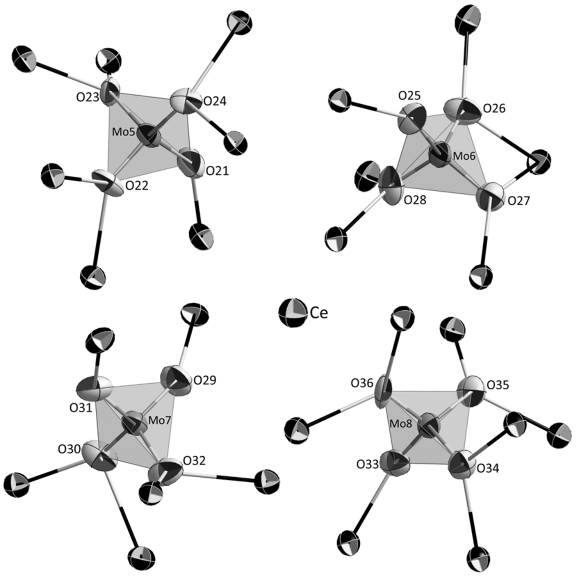

Fig. 3. Cationic coordination around the four different $[MoO_4]^{2-}$ tetrahedra in the crystal structure of $Ce_2[MoO_5]$-$[MoO_4]$ (ellipsoid representation at the 95 % level).

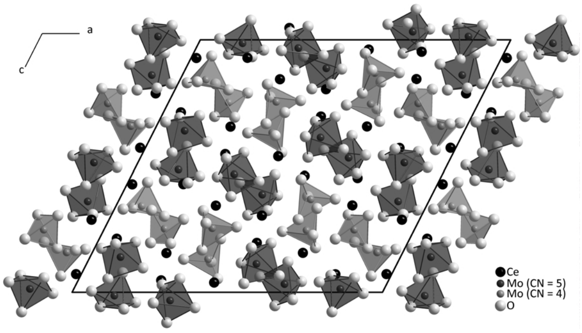

Fig. 4. View at the crystal structure of $Ce_2[MoO_5][MoO_4]$ along [010].

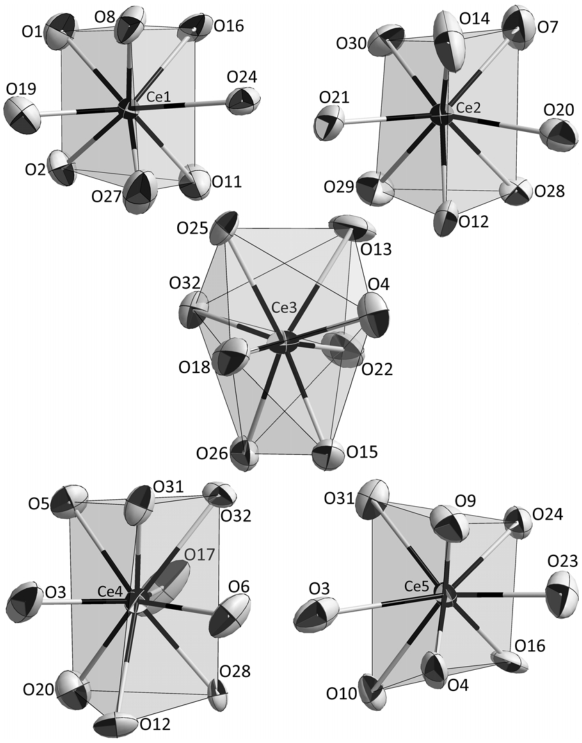

Fig. 5. Coordination polyhedra around the five crystallographically independent cerium cations in the crystal structure of $Ce_5[MoO_4]_8$ (ellipsoid representation at the 95 % level).

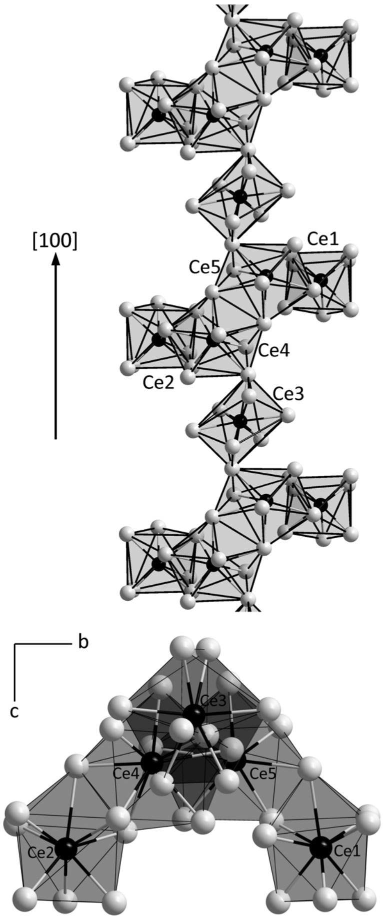

Fig. 6. Chain of vertex-, edge-, and face-shared oxygen polyhedra around the cerium cations $^1_\infty\{[Ce_5O_{32}]^{48-}\}$ along [100] in a sawblade-like arrangement (top) displaying a V-shaped profile (bottom) in the crystal structure of $Ce_5[MoO_4]_8$.

Structure of $Ce_5[MoO_4]_8$

$Ce_5[MoO_4]_8$ also crystallizes monoclinically in space group $P2_1/c$ (a = 1133.14(5), b = 1704.96(7), c = 1406.21(6) pm, β = 90.749(2)°) with four formula units in the *pseudo*-orthorhombic unit cell. In the crystal structure five cerium cations can be distinguished crystallographically, one of them being tetravalent, while the other four remain trivalent to maintain the overall electroneutrality. The coordination numbers vary between eight and nine resulting in bi- (for Ce1, Ce2, and Ce5) and tricapped trigonal prisms (for Ce4) as well as trigonal dodecahedra (for Ce3, see Fig. 5). The interatomic distances between Ce1 and its surrounding oxide anions range from 226 to 251 pm and thus are significantly shorter than those of the other cerium cations with values of 236 – 284 pm (Table 3). Hence, Ce1 can be considered as the site for the tetravalent cerium cation, while the others need to be just trivalent. This assumption is also supported by bond-valence calculations [11], in which the formal charge of Ce1 is calculated to be +3.88, while the formal charges of the Ce2–Ce5

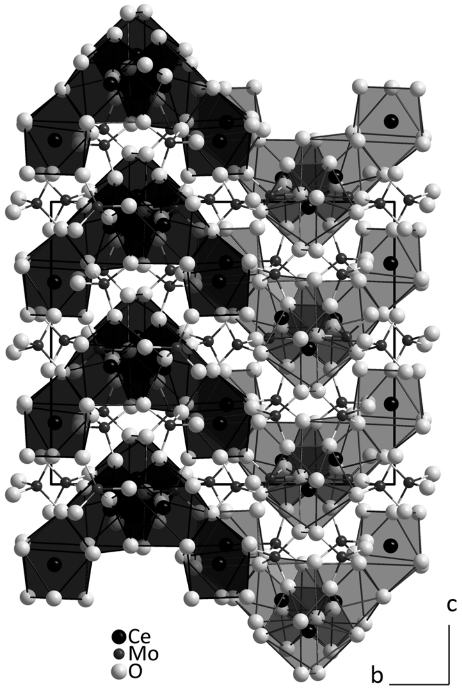

Fig. 7. View at the crystal structure of $Ce_5[MoO_4]_8$ along [100] with special emphasis on the sawblade-shaped $^1_\infty\{[Ce_5O_{32}]^{48-}\}$ chains recognizable by their V-shaped profiles. Herein, "black" chains are interlocked with "grey" ones.

cations range between +2.70 and +3.13 (Table 3). Furthermore, the short Ce(IV)–O distances are consistent with those in other compounds containing tetravalent cerium cations, such as $Ce[TeO_3]_2$ ($d(Ce^{4+}–O^{2-})$ = 223 – 257 pm) [20] or CeO_2 ($d(Ce^{4+}–O^{2-})$ = 233 pm [21].

First attempts of the structure solution were carried out in the orthorhombic space group *Pccn* reducing the number of crystallographically distinguishable cerium cations to three. However, the Ce^{4+} and one of the Ce^{3+} cations would be located at the same *Wyckoff* position in the orthorhombic super group. A *translationengleiche* symmetry reduction of *index* 2 into the direct subgroup $P2_1/c$ represented a suitable solution, leaving the Ce^{4+} cations all ordered at one exclusive position, well separated from its symmetry-equivalent Ce^{3+} congener in the orthorhombic supergroup. The symmetry reduction is also supported by significantly improved residual values as well as balanced displacement parameters. All eight crystallographically independent Mo^{6+} cations represent the centers of isolated *ortho*-oxomolybdate tetrahedra. As in $Ce_2[MoO_5][MoO_4]$, the molybdenum–oxygen bond lengths within the $[MoO_4]^{2-}$ units range between 172 and 183 pm, while their bond angles are closer to the ideal tetrahedral angle with values from 99 to 116° than in the afore described cerium(III) oxomolybdate(VI). The oxygen polyhedra around the cerium cations form a chain along [100] according to $^1_\infty\{[Ce_5O_{32}]^{48-}\}$ *via* vertex-, edge-, and face-connections. The separated chains show a sawblade-like arrangement (Fig. 6, top) with a V-shaped profile (Fig. 6, bottom). These $^1_\infty\{[Ce_5O_{32}]^{48-}\}$ chains are interlocked along the *b* axis in an *up-down-up-down* manner to form wave-shaped layers parallel to the (001) plane of the crystal structure of $Ce_5[MoO_4]_8$, although no direct linkages between the chains *via* oxygen atoms are present. These layers are interconnected by the eight Mo^{6+} cations to build up the three-dimensional crystal structure (Fig. 7). Since this crystal structure provides positions which are suitable for one tetravalent and four trivalent cations, exchanges of those with other appropriate elements (*e. g.* Zr^{4+}, Hf^{4+}, Pr^{4+}, and La^{3+}, Pr^{3+}, *etc.*) are the next logical step and will be pursued in the future.

Conclusion

Two new cerium oxomolybdates have emerged as unexpected by-products during the attempted syntheses of halide derivatives of cerium(III) oxomolybdates(VI), and their crystal structures have been determined. Besides Ce^{3+} cations and $[MoO_4]^{2-}$ tetrahedra, the structure of $Ce_2[MoO_5][MoO_4]$ consists of isolated $[MoO_5]^{4-}$ units, which is an extremely rare feature in the chemistry of oxomolybdates(VI). On the other hand, $Ce_5[MoO_4]_8$ comprises exclusively $[MoO_4]^{2-}$ tetrahedra in the anionic part of its structure, but to maintain electroneutrality, one out of the five crystallographically independent cerium cations was found to be tetravalent among the trivalent remainders.

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