A New Example of the Structure Type $A_2[Z_2R_4X_9]$: Synthesis and Crystal Structure of $Na_2[(ON)Ce_4Cl_9]$

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**A New Example of the Structure Type $A_2[\{Z_2R_4\}X_9]$:
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SHORT COMMUNICATION

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A New Example of the Structure Type $A_2[\{Z_2R_4\}X_9]$: Synthesis and Crystal Structure of $Na_2[\{(ON)Ce_4\}Cl_9]$

Christian M. Schurz^[a], Monika Meyer, Gerd Meyer^{[b]*}, and Thomas Schleid^{[a]*}*Dedicated to Professor Gerd Becker on the Occasion of his 70th Birthday***Keywords:** Cerium, Oxide Nitride Chlorides, Crystal Structures

First single crystals of $Na_2[\{(ON)Ce_4\}Cl_9]$ were obtained during synthesis attempts for the cerium nitride chloride Ce_2NCl_3 ($= \{N_2Ce_4\}Cl_6$). With a molar ratio of 8 : 10 : 3 for Ce, $CeCl_3$ and NaN_3 along with an excess of the flux NaCl, the mixture obviously contained a small amount of $CeOCl$ that led to the formation of $Na_2[\{(ON)Ce_4\}Cl_9]$. It crystallizes in the monoclinic space group $P2_1/m$ (no. 11) with two formula units in the unit cell with

dimensions of $a = 813.21(6)$ pm, $b = 1146.13(9)$ pm, $c = 942.86(7)$ pm and $\beta = 107.504(5)^\circ$. As the dominating structural feature $\{ZCe_4\}^{9.5+}$ tetrahedra are fused via *trans*-oriented edges to generate ${}^\infty\{ZCe_{4/2}\}^{3.5+}$ chains ($Z = \frac{1}{2} O + \frac{1}{2} N$) just as in the structurally isotypic compounds $A_2[\{Z_2R_4\}X_9]$ ($A = Na, K$; $R = Pr, Nd, Gd$; $X = Cl, Br$; $Z = O, O/N$).

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Introduction

In rare-earth metal cluster complex chemistry, there are a few main-group elements, oxygen, nitrogen and sometimes carbon, which act as endohedral atoms Z for tetrahedral clusters, $\{ZR_4\}$ [1]. The formula type $\{OR_4\}X_6$ ($X = Cl, Br, I$) with isolated $\{OR_4\}$ tetrahedra embedded in the cluster complex $[\{OR_4\}X_{18}]^{8-}$ is observed for alkaline-earth and the *pseudo*-alkaline-earth rare-earth elements $R = Ca, Sr, Ba, Sm, Eu$, and Yb and may be considered as salts [2]. $\{OR_4\}$ tetrahedra are also seen in $\{ZLa_4\}Br_7$ [3] with two or three excess electrons depending on whether nitrogen or oxygen atoms are considered as endohedral atoms. An example for an isolated tetrahedral cluster centered by a carbon atom was recently found for $\{CCe_4\}Cl_8$ [4] and for the oligomer $\{C_{10}Sc_{24}\}I_{30}$ [5].

Chains of edge-connected $\{ZR_4\}$ tetrahedra have been observed for the ternary compounds ZR_2X_3 , i.e. $\{ZR_{4/2}\}X_3$ with the structure of the tetrahedral chain analogous to that of SiS_2 , for $R = La, Ce, Pr, Nd, Gd$ and $Z = N$ [6]. Similar $\{ZR_{4/2}\}$ zig-zag chains, running along [010] of the monoclinic unit cell as the

dominating structural feature, are also present in the quaternary compounds $A_2\{Z_2R_4\}X_9$ which were observed so far with $A = Na, K$; $R = Pr, Nd, Gd$; $X = Cl, Br$; $Z = O, O/N$, not in all possible combinations [7, 6c]. We were now able to expand the number of rare-earth element (R) examples to cerium with $Na_2[\{(ON)Ce_4\}Cl_9]$.

One problem with these compounds is the nature of Z. It can be an oxygen and/or nitrogen atom. In all cases there are excess electrons, two if Z equals N and three with $Z = O$, which attest for the metallic lustre of the respective compounds. Under-occupation of the A sites has also been discussed [7c]. Mixed oxide/nitride occupation is known for quite a while, the first example perhaps have been single crystals of $Sm_{10}Si_6O_{24}N_2$ [8].

Results and Discussion

The new cluster complex chloride $Na_2[\{(ON)Ce_4\}Cl_9]$, which most likely contains a mixed occupation of oxygen and nitrogen atoms encapsulated in cerium tetrahedra, crystallizes in space group $P2_1/m$ of the monoclinic system with $a = 813.21(6)$ pm, $b = 1146.13(9)$ pm, $c = 942.86(7)$ pm, $\beta = 107.504(5)^\circ$ and $Z = 2$ (see Table 1 for the atomic coordinates and U_{eq} values). Considering bond lengths of $CeCl_3$ ($d(Cl^- - Ce^{3+}) = 296 - 297$ pm) [9], Ce_2NCl_3 ($d(N^{3-} - Ce^{3+}) = 234$ pm for $CN(N^{3-}) = 4$; $d(Cl^- - Ce^{3+}) = 287 - 339$ pm) [10], Ce_3NCl_6 ($d(N^{3-} - Ce^{3+}) = 226 - 243$ pm for $CN(N^{3-}) = 4$; $d(Cl^- - Ce^{3+}) = 281 - 331$ pm) [11], $Ce_4NS_3Cl_3$ ($d(N^{3-} - Ce^{3+}) = 229 - 238$ pm for $CN(N^{3-}) = 4$; $d(Cl^- - Ce^{3+}) = 294 - 332$ pm) [12], CeN ($d(N^{3-} - Ce^{3+}) = 251$ pm for $CN(N^{3-}) = 6$) [13], Ce_2O_3 ($d(O^{2-} -$

Ce^{3+}) = 234 – 243 pm for $\text{CN}(\text{O}^{2-}) = 4$ and 269 pm for $\text{CN}(\text{O}^{2-}) = 6$ [14], NaCl ($d(\text{Cl}^- - \text{Na}^+) = 282$ pm) [15] and $\text{Na}_2[\{(\text{ON})\text{R}_4\}\text{Cl}_9]$ ($\text{R} = \text{Nd}, \text{Gd}$; $d(\text{Cl}^- - \text{Na}^+) = 272 - 304$ pm) [7c, 6c], the distances fall into a plausible range between 287 and 338 pm for $\text{Cl}^- - \text{Ce}^{3+}$ as well as 230 – 238 pm for $\text{O}^{2-}/\text{N}^{3-} - \text{Ce}^{3+}$ and 274 – 308 pm for $\text{Cl}^- - \text{Na}^+$ bonds (see Table 2).

Table 1 Atomic coordinates and equivalent isotropic thermal displacement coefficients ($U_{\text{eq}}^{\text{a)}}$ /pm²) for $\text{Na}_2[\{(\text{ON})\text{Ce}_4\}\text{Cl}_9]$

atom		x/a	y/b	z/c	U_{eq}
Na ^{b)}	4f	0.2277(4)	0.9885(4)	0.4285(3)	535(13)
Ce1	2e	0.59441(4)	$1/4$	0.82845(4)	98(1)
Ce2	2e	0.61698(4)	$1/4$	0.21976(4)	109(1)
Ce3	4f	0.27813(3)	0.04458(2)	0.95034(3)	137(1)
O/N ^{c)}	4f	0.5613(4)	0.1243(3)	0.0150(4)	119(9)
Cl1	2e	0.2508(2)	$1/4$	0.1415(2)	206(3)
Cl2	2e	0.2245(2)	$1/4$	0.7406(2)	201(3)
Cl3	2e	0.6436(3)	$1/4$	0.5334(2)	362(4)
Cl4	4f	0.8938(2)	0.4013(1)	0.8769(1)	221(3)
Cl5	4f	0.5088(2)	0.9970(1)	0.3033(2)	325(3)
Cl6	4f	0.9104(2)	0.0904(1)	0.3169(2)	299(3)

^{a)} $U_{\text{eq}} = 1/3[U_{33} + 1/\sin^2\beta(U_{11} + U_{33} + 2 U_{13} \cos\beta)]$,

^{b)} site occupation probability: 97(1) %,

^{c)} refined molar ratio O : N = 56(7) % : 44(7) %.

Table 2 Selected internuclear distances in $\text{Na}_2[\{(\text{ON})\text{Ce}_4\}\text{Cl}_9]$

	d/pm		d/pm	d/pm
Ce1–O/N	235.1 (2×)	Ce3–O/N	230.2	238.0
Ce1–Cl2	287.0	Ce3–Cl4	294.5	305.5
Ce1–Cl4	291.1 (2×)	Ce3–Cl6	296.2	
Ce1–Cl3	292.7	Ce3–Cl1/2	301.4	302.1
Ce1–Cl5	310.4 (2×)	Ce3–Cl5	333.7	338.3
Ce2–O/N	234.2 (2×)	O/N–O/N	288.2	300.3
Ce2–Cl1	284.4			
Ce2–Cl3	289.9	Na–Cl6	273.8	307.6
Ce2–Cl6	292.6 (2×)	Na–Cl5	278.5	287.2
Ce2–Cl5	319.7 (2×)	Na–Cl3/4	291.1	292.5

(insert Fig_1 here)

Figure 1 View of $[\text{ZCe}_4]^{9.5+}$ tetrahedra fused via *trans*-oriented edges to form $1/\infty \{[\text{ZCe}_{4/2}^e]^{3.5+}\}$ chains ($\text{Z} = 1/2 \text{ O} + 1/2 \text{ N}$) in the crystal structure of $\text{Na}_2[\{(\text{ON})\text{Ce}_4\}\text{Cl}_9]$.

As the dominating structural feature $[(\text{O}_x\text{N}_y)\text{Ce}_4]^{9.5+}$ tetrahedra (the charge of 9.5+ refers to $x = y = 0.5$) are *trans*-edge connected to form zig-zag shaped $1/\infty \{[\text{ZCe}_{4/2}^e]^{3.5+}\}$ chains, which run along the *b*-axis (Fig. 1). While $(\text{Ce}1)^{3+}$ and $(\text{Ce}2)^{3+}$ with a common edge are located at the 2*e* site with symmetry *m*, the $(\text{Ce}3)^{3+}$ cation is placed at the 4*f* position with lower symmetry (1) and build the second connecting edge with itself. The crystallographically unique Na^+ cation and the $(\text{O}^{2-}/\text{N}^{3-})$ anion are located at the 4*f* site, as well as three of the chloride anions (Cl4, Cl5, Cl6), while all further chloride anions (Cl1, Cl2, Cl3) occupy the Wyckoff position 2*e*. Each Ce^{3+} cation is surrounded by an anionic trigonal-prismatic

coordination sphere (2 $\text{O}^{2-}/\text{N}^{3-}$ and 4 Cl^- anions) with two (Ce1 and Ce2) and, respectively, three caps (Ce3) of chloride anions.

(insert Fig_2 here)

Figure 2 View at the highly distorted $[\text{NaCl}_6]^{5-}$ octahedron with three next nearest chloride anions (distances in pm).

(insert Fig_3 here)

Figure 3 View of the three-dimensional framework of the crystal structure of $\text{Na}_2[\{(\text{ON})\text{Ce}_4\}\text{Cl}_9]$ with its $1/\infty \{[\text{ZCe}_{4/2}^e]^{3.5+}\}$ chains ($\text{Z} = 1/2 \text{ O} + 1/2 \text{ N}$) and its $1/\infty \{[\text{NaCl}_{4/2}^e \text{Cl}_{1/2}^c \text{Cl}_{1/1}^t]^{3-}\}$ layers.

As expected from the already known compounds of the $\text{Na}_2[\{Z_2\text{R}_4\}\text{Cl}_9]$ structure type ($\text{R} = \text{Pr}, \text{Nd}, \text{Gd}$; $\text{Z} = \text{O}, \text{O/N}$), the $[\text{NaCl}_6]^{5-}$ octahedra are highly distorted and the thermal displacement parameters of sodium show only a weak attraction between Na^+ and three next nearest chloride anions (Fig. 2). The (Cl1)[−] and (Cl2)[−] anions do not take part in the linkage of the three-dimensional framework. They have, however, an influence on the distortion of the $[\text{NaCl}_6]^{5-}$ octahedra, which are fused to $1/\infty \{[\text{NaCl}_{4/2}^e \text{Cl}_{1/2}^c \text{Cl}_{1/1}^t]^{3-}\}$ layers (superscripts: e = edge-connecting, c = corner-connecting, t = terminal).

Finally, the whole structure is assembled to $1/\infty \{[\text{ZCe}_{4/2}^e]^{3.5+}\}$ chains that are directly interconnected by (Cl3)[−] and (Cl4)[−] as well as by (Cl5/6)[−]– Na^+ –(Cl5/6)[−] bridges (Fig. 3).

Experimental Section

$\text{Na}_2[\{(\text{ON})\text{Ce}_4\}\text{Cl}_9]$ was obtained by heating a mixture of cerium, cerium trichloride and sodium azide in a molar ratio of 8 : 10 : 3 designed to produce Ce_2NCl_3 [10] along with an excess of the flux sodium chloride at 850 °C for seven days. Small amounts of cerium oxide chloride in cerium trichloride led to transparent orange-yellow single crystals of $\text{Na}_2[\{(\text{ON})\text{Ce}_4\}\text{Cl}_9]$, of which one was characterized by single crystal X-ray diffraction (κ -CCD, Bruker-Nonius). Essential information about the structure solution and refinement for $\text{Na}_2\text{Ce}_4\text{ONCl}_9$ is given in reference [16]. Further details may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (Fax: (+49)7247-808-666; E-mail: crysdata@fizkarlsruhe.de), on quoting the depository number CSD-421558. A half-quantitative measurement with an electron-beam microprobe (Camebax, Cameca) by using the energy-dispersive technique approximately confirms the molar ratio of Na : Ce : Cl = 2 : 4 : 9 in $\text{Na}_2[\{(\text{ON})\text{Ce}_4\}\text{Cl}_9]$.

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