A New Example of the Structure Type A2[Z2R4X9]: Synthesis and Crystal Structure of Na2[(ON)Ce4Cl9]
Christian Schurz, Monika Meyer, Gerd Meyer, Thomas Schleid

To cite this version:

HAL Id: hal-00552469
https://hal.science/hal-00552469
Submitted on 6 Jan 2011

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.
A New Example of the Structure Type A2[\{Z2R4\}X9]: Synthesis and Crystal Structure of Na2[\{(ON)Ce4\}Cl9]

<table>
<thead>
<tr>
<th>Journal:</th>
<th>Zeitschrift für Anorganische und Allgemeine Chemie</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID:</td>
<td>zaac.201000111</td>
</tr>
<tr>
<td>Wiley - Manuscript type:</td>
<td>Communication</td>
</tr>
<tr>
<td>Date Submitted by the Author:</td>
<td>03-Mar-2010</td>
</tr>
</tbody>
</table>
| Complete List of Authors: | Schurz, Christian; Universität Stuttgart, Institut für Anorganische Chemie  
Meyer, Monika  
Meyer, Gerd; Universität zu Köln, Institut für Anorganische Chemie  
Schleid, Thomas; Universität Stuttgart, Institut fuer Anorganische Chemie |
| Keywords: | Cerium, Oxide Nitride Chlorides, Crystal Structure |
A New Example of the Structure Type $A_2[(Z_2R_4)X_9]$: Synthesis and Crystal Structure of $Na_2[(\text{ON})Ce_4]Cl_4$  

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 $Na_2[(\text{ON})Ce_4]Cl_4$ were obtained during synthesis attempts for the cerium nitride chloride $Ce_2NCl_5 (= (N_2Ce_4)Cl_4)$. With a molar ratio of 8 : 10 : 3 for Ce, CeCl_4 and NaCl, along with an excess of the flux NaCl, the mixture obviously contained a small amount of CeOCl that led to the formation of $Na_2[(\text{ON})Ce_4]Cl_4$. 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, $\{ZCe_4\}_{4/2}^{3+}$ tetrahedra are fused via trans-oriented edges to generate $\{ZCe_4\}_{4/2}^{3+}$ chains (Z = $^{1/2}$ O + $^{1/2}$ N) just as in the structurally isotypic compounds $A_2[Z_2R_4]X_9$ ($A = Na, K; R = Pr, Nd, Gd; X = Cl, Br; Z = O, O/N$).

---

**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 $\{OR_4\}_X$ ($X = Cl, Br, I$) with isolated $\{OR_4\}$ tetrahedra embedded in the cluster complex $\{OR_4\}_{X_9}$ 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 $\{C_{10}Se_{24}\}I_{30}$ [5].

Chains of edge-connected $\{ZR_4\}$ tetrahedra have been observed for the ternary compounds $ZR_5X_3$, i.e. $\{ZR_2\}X_3$ 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 $\{ZR_2\}$ 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 $Na_2[(\text{ON})Ce_4]Cl_4$.

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 $Sm_{10}Si_{24}O_{24}N_2$ [8].

**Results and Discussion**

The new cluster complex chloride $Na_2[(\text{ON})Ce_4]Cl_4$, 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 and $\beta = 107.504(5)^\circ$ and $Z = 2$ (see Table 1 for the atomic coordinates and $U_{eq}$ values). Considering bond lengths of $CeCl_3$ ($d(\text{Cl}–\text{Ce}^{3+}) = 296 – 297$ pm) [9], $Ce_2NCl_3$ ($d(\text{N}^{2–}\text{–Ce}^{3+}) = 234$ pm for CN($N^{2–}$) = 4; ($d(\text{Cl}–\text{Ce}^{3+}) = 287 – 339$ pm) [10], $Ce_2NCl_6$ ($d(\text{N}^{2–}\text{–Ce}^{3+}) = 226 – 243$ pm for CN($N^{2–}$) = 4; ($d(\text{Cl}–\text{Ce}^{3+}) = 281 – 331$ pm) [11], $Ce_4NSiCl_4$ ($d(\text{Cl}–\text{Ce}^{3+}) = 229 – 238$ pm for CN($N^{2–}$) = 4; ($d(\text{Cl}–\text{Ce}^{3+}) = 294 – 332$ pm) [12], $CeN$ ($d(\text{N}^{2–}\text{–Ce}^{3+}) = 251$ pm for CN($N^{2–}$) = 6) [13], $Ce_2O_3$ ($d(\text{O}^{2–}\text{–Ce}^{3+}) = 230$ pm for CN($O^{2–}$) = 4) [14].
lower symmetry (1) and build the second connecting axis (Fig. 1). While (Ce1)
(x = y = 0.5) are crystal structure of Na

Ce1–Cl5 310.4 (2×) Ce3–Cl5 333.7 338.3
Ce1–Cl4 291.1 (2×) Ce3–Cl6 296.2
Ce1–Cl2 287.0 Ce3–Cl4 294.5 305.5
Ce1–O/N 235.1 (2×) Ce3–O/N 230.2 238.0
Cl6

Cl5 4
Cl4 4
Cl3 2
Cl2 2

Ce2–O/N 234.2 (2×) 0.1415(2)  206(3)
Ce2–Cl2 289.9 Na–Cl6 273.8 307.6
Ce2–Cl4 292.6 (2×) Na–Cl5 278.5 287.2
Ce2–Cl6 319.7 (2×) Na–Cl3/4 291.1 292.5

The distances fall into a range between 287 and 338 pm for Cl–Ce

As expected from the already known compounds of the Na[\{Z2R2\}Cl6]
structure type (R = Pr, Nd, Gd; Z = O, O/N), the [NaCl6]

Ce2–O/N 234.2 (2×) 0.1415(2)  206(3)
Ce2–Cl2 289.9 Na–Cl6 273.8 307.6
Ce2–Cl4 292.6 (2×) Na–Cl5 278.5 287.2
Ce2–Cl6 319.7 (2×) Na–Cl3/4 291.1 292.5

Finally, the whole structure is assembled to \(\{Z\text{Ce}^{3+}\}_{2/2}\) chains that are directly interconnected by (Cl3) and (Cl4) as well as by (Cl5/6) – Na+ – (Cl5/6)
brides (Fig. 3).

Experimental Section

Na2\[\{ONCe\}\] was obtained by heating a mixture of cerium, cerium trichloride and sodium azide in a molar ratio of 8 : 10 : 3 designed to produce Ce2NCl10 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 Na2\[\{ONCe\}\], of which one was characterized by single crystal X-ray diffraction (n-CCD, Bruker-Nonius). Essential information about the structure solution and refinement for Na2CeONCl6 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: crysdatal@fizkarlsruhe.de), on quoting the depository number CSD-421558. A half-quantitative measurement with an electron-beam microprobe ( Cameba, Cameca) by using the energy-dispersive technique approximately confirms the molar ratio of Na : Ce : Cl = 2 : 4 : 9 in Na2\[\{ONCe\}\].

Acknowledgement

This work has been supported by the Universities of Stuttgart and Cologne as well as by the Deutsche Forschungsgemeinschaft. Initial work as performed by Dr. Monika Meyer [17] (now: Dr. Monika Tautz) was done at the University of Hannover.


[16] An intensity data set was recorded at room temperature with a κ-CCD diffractometer using Mo-Kα radiation (graphite monochromator: λ = 71.01 pm). Crystal data: a = 813.21(6) pm, b = 1146.13(9) pm, c = 942.86(7) pm, β = 107.504(5)°, Vm = 252.35 cm³/mol; Dx = 3.786 g/cm³; monoclinic, P21/m (no. 11), Z = 2; F(000) = 844, θ max = 28.3° (±h = 10, ±k = 15, ±l = 12), 17446 measured reflections, 2178 symmetrically independent, correction for absorption (µ = 12.12 mm–1) with the program HABITUS (W. Herrndorf and H. Bärnighausen, Karlsruhe 1993, Gießen 1996); Rint = 0.057, Rw = 0.024; structure determination and refinement with the program system SHELX-97 (G. M. Sheldrick, Göttingen 1997), scattering factors from International Tables, Vol. C (1992); R value for 2089 reflections with IF > 4σ(Fo): R1 = 0.025; R values for all 2178 reflections: R1 = 0.027, wR2 = 0.058, GooF = 1.116.


Received: ((will be filled in by the editorial staff))
Published online: ((will be filled in by the editorial staff))
C. M. Schurz, M. Meyer, G. Meyer*, Th. Schleid*

A New Example of the Structure Type $A_2[[Z_4R_4]X_9]$:
Synthesis and Crystal Structure of $Na_2[[((ON)Ce_4]Cl_9]

Page No. – Page No.
View of \([ZCe4]^9.5+\) tetrahedra fused via trans-oriented edges to form \([ZCe^3.5+]\) chains \((Z = 1/2\ O + 1/2\ N)\) in the crystal structure of Na2\([(ON)Ce4]Cl9\).
View at the highly distorted [NaCl6]5– octahedron with three next nearest chloride anions (distances in pm).

170x119mm (600 x 600 DPI)
View of the three-dimensional framework of the crystal structure of Na2[(ON)Ce4]Cl9 with its $\{Z\text{Ce }3.5^+\}$ chains ($Z = 1/2 \text{ O } + 1/2 \text{ N}$) and its $\{\text{NaCl Cl Cl }3^–\}$ layers.

170x113mm (600 x 600 DPI)