Syntheses and Crystal Structures of \( \text{RE}_2\text{As}_4\text{O}_9 \) (\( \text{RE} = \text{Nd}, \text{Sm} \)):
Oxo-Arsenates(III) according to \( \text{RE}_4(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8) \) Exhibiting
the Cyclic \( \text{As}_4\text{O}_8^{4-} \) Anion

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Dedicated to Professor Gerhard Thiele on the occasion of his 70th birthday

Single crystals of light violet \( \text{Nd}_2\text{As}_4\text{O}_9 \) and yellow \( \text{Sm}_2\text{As}_4\text{O}_9 \) were obtained from the reactions of the respective lanthanide oxides with \( \text{As}_2\text{O}_3 \) in a \( \text{NaCl} \) flux at 850 \( ^\circ \text{C} \) in sealed silica ampoules. According to the structure determination, the triclinic compounds (\( P\overline{1}, Z = 2, \text{Nd}/\text{Sm}: a = 686.32(9)/680.92(9), b = 763.06(8)/756.4(1), c = 954.8(1)/951.2(1) \text{ pm}, \alpha = 96.83(1)/96.66(2)^\circ, \beta = 103.78(2)/103.67(2)^\circ, \gamma = 104.40(1)/104.35(2)^\circ, R_1 = 0.0184/0.0282 \) (all data)) have to be formulated as \( \text{RE}_4(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8) \) emphasizing the presence of both \( \text{As}_2\text{O}_5^{4-} \) and cyclic \( \text{As}_4\text{O}_8^{4-} \) anions. The \( \text{As}_4\text{O}_8^{4-} \) anions show \( C_i \) symmetry and connect layers of the composition \( \{2\text{∞}[\text{RE}_2(\text{As}_2\text{O}_5)]\}_4^{+} \) along the [001] direction. The lanthanide ions are in nine- and eightfold coordination, respectively.

**Key words:** Lanthanides, Arsenites, cyclo-Tetraarsenite Anion

Introduction

There has been considerable increase in the knowledge of rare earth compounds containing complex oxo-anions throughout the last years [1]. The lively interest that these compounds have attracted can be attributed to their diverse properties, ranging from magnetic and spectroscopic phenomena to the features of open framework structures. Among the plethora of compounds that has been synthesized the oxoselenenates(IV) (selenites) seem to be of vital importance [2]. One reason is that the crystal structures of selenites are frequently non-centrosymmetric and that the non-linear optical effects (NLO) arising from the lack of inversion symmetry are strong due to the high polarizability of the anions [3 – 6]. Recently we have used the \( \text{SeO}_3^{2-} \) ion successfully to combine rare earth and transition metal ions in solid state compounds aiming at new magnetic and luminescent properties [7, 8]. We now extended our efforts towards oxo-arenates(III) (arsenites) because these anions are isomorphous with the selenite ions but their higher charge allows for other compositions. Unfortunately no simple arsenates(III) of the rare earth elements are known up to now, and only the \( \text{O}^{2-} \) and \( \text{Cl}^{-} \) containing species \( \text{RE}_3\text{OCl}(\text{AsO}_3)_2 \) (\( \text{RE} = \text{La}, \text{Sm}, \text{Gd} \)) have been reported [9]. Here we present the syntheses of the first compounds in the systems \( \text{RE}_2\text{O}_3/\text{As}_2\text{O}_3 \) and their unusual crystal structure.

Experimental Section

For the syntheses of \( \text{RE}_2\text{As}_4\text{O}_9 \) (\( \text{RE} = \text{Nd}, \text{Sm} \)) the oxides \( \text{RE}_2\text{O}_3 \) (\( \text{RE} = \text{Nd}, \text{Sm} \)) and \( \text{As}_2\text{O}_3 \) as well as \( \text{NaCl} \) as a flux were sealed in silica tubes. The molar ratio \( \text{RE}_2\text{O}_3/\text{As}_2\text{O}_3/\text{NaCl} \) was 1:2:5. In a resistance furnace the ampoules were fired in a first step to 350 \( ^\circ \text{C} \). After keeping this temperature for 24 h, it was raised to 850 \( ^\circ \text{C} \) within 35 h. After 24 h at this temperature the furnace was cooled down slowly at a rate of 10 \( ^\circ \text{C}/\text{h} \). The reaction products contained plate shaped single crystals of the arsenites which are light violet in the case of neodymium and yellow for samarium. For each compound some crystals were glued on glass fibres and checked by orientation images taken on an image plate diffractometer (STOE IPDS). They showed the same triclinic unit cell, and for the best specimen of the neodymium and samarium compound, respectively, intensity data were
Empirical formula
Nd$_2$As$_4$O$_9$  Sm$_2$As$_4$O$_9$

Lattice parameters
\[
\begin{align*}
a & = 686.32(9) \text{ pm} & a & = 680.92(9) \text{ pm} \\
b & = 763.06(8) \text{ pm} & b & = 756.4(1) \text{ pm} \\
c & = 954.8(1) \text{ pm} & c & = 951.2(1) \text{ pm} \\
\alpha & = 96.83(1)^\circ & \alpha & = 96.66(2)^\circ \\
\beta & = 103.78(2)^\circ & \beta & = 103.67(2)^\circ \\
\gamma & = 104.49(1)^\circ & \gamma & = 104.35(2)^\circ
\end{align*}
\]

Cell volume
461.9(1) Å$^3$  453.2(1) Å$^3$

No. of formula units
2  2

Crystal system — Triclinic —
Space group — P\bar{1} (No. 2) —
Diffractometer — Stoe IPDS-I —
Radiation — Mo-K$_\alpha$ (graphite-monochrom., $\lambda = 71.07$ pm) —
Temperature 153 K 153 K

Data range
$3.3^\circ < 2\theta < 52.1^\circ$

Index range
$-8 \leq h \leq 8$  $-8 \leq k \leq 8$  $-11 \leq l \leq 11$

$\phi$-Range: increment
$0^\circ < \phi < 312^\circ$; 2.0$^\circ$

No. of images
156  160

Exposure time
3 min  7 min

Detector distance
70 mm  70 mm

Data corrections — Polarization/Lorentz —
Absorption correction — Numerical [12, 13] —

$\mu$
253.64 cm$^{-1}$  273.51 cm$^{-1}$

No. of collected reflections
5706  5779

No. of unique reflections
1689  1669

No. of reflections with $I_o > 2\sigma(I)$
1411  1254

$R_{int}/R_\sigma$
0.0371 / 0.0345  0.0613 / 0.0593

Scattering factors — Intern. Tables, Vol. C —

Goodness of fit
922  956

$R_1$: $wR_2$ $l > 2\sigma(I)$
0.0184; 0.0353  0.0282; 0.0639

$R_1$: $wR_2$ (all data)
0.0262; 0.0364  0.0452; 0.0689

Extinction coefficient
0.0010(1)  —

CSD$^a$
415762  415763

Results and Discussion

The oxo-arsenates(III) RE$_2$As$_4$O$_9$ (RE = Nd, Sm) are the first representatives of compounds in the systems RE$_2$O$_3$/As$_2$O$_3$ with RE being a rare earth element. Interestingly, in the crystal structures no simple AsO$_3^{3-}$ ions were found but diarsenite groups, As$_2$O$_5^{4-}$, and the unusual tetrameric cyclic As$_4$O$_8^{4-}$ anions. Thus, the compounds are to be written as to Nd$_4$(As$_2$O$_5$)$_2$(As$_4$O$_8$) and Sm$_4$(As$_2$O$_5$)$_2$(As$_4$O$_8$). The occurrence of As$_2$O$_5^{4-}$ ions is a well known feature in the crystal chemistry of o xoarsenates(III) [14], and in both compounds under discussion the anions show

Table 1. Crystallographic data of Nd$_4$(As$_2$O$_5$)$_2$(As$_4$O$_8$) and Sm$_4$(As$_2$O$_5$)$_2$(As$_4$O$_8$)

$^a$ Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen. The data can be obtained on quoting the given CSD number.

Fig. 1. The cyclo-tetraarsenate(III) anion As$_4$O$_8^{4-}$ in the crystal structures of RE$_2$(As$_2$O$_5$)$_2$(As$_4$O$_8$) (RE = Nd, Sm). The anion has C$_2$ symmetry and the bridging oxygen atoms O23 and O12 are situated slightly apart from the plane that is spanned by the four arsenic atoms. The bond distances (in pm) are given for the neodymium compound (cf. Table 3).
essentially the distances and angles as previously described. The largest distances As-O within the group are found to be bridging oxygen atoms with values around 187 pm (Table 2), and the angles As-O-As are about 136°.

The distances As-O to the terminal oxygen atoms vary between 171 and 178 pm, and the remarkable differences can be attributed to the different coordination of these atoms by the lanthanide ions. The angles O-As-O cover a large range from 89° up to 105°, again in good agreement with previous findings.

The most interesting feature of the crystal structure of the new compounds is the tetrameric cycloarsenite anion, As$_4$O$_9$$^{4-}$. To the best of our knowledge only one compound with a cyclo-tetraarsenite anion has been reported, namely the mineral stenhuggarite, CaFe$_5$B$_2$As$_5$O$_7$ [15]. In this mineral, however, the anion has a very different shape compared to the findings presented here: It shows the arsenic atoms in a tetrahe-

dral array ($S_4$ symmetry), while in the present case all arsenic atoms lie in a plane and the anion has C$_1$ symmetry (Fig. 1). The bridging oxygen atoms within the tetramer are only slightly shifted from that plane by 14 pm (O334) and 57 pm (O324), respectively. The angles As-O-As are about 136° and the distances As-O to the bridging oxygen atoms range from 178 to 184 pm.

The terminal and the bridging oxygen atoms form an-
Fig. 2. Coordination of the $\text{As}_2\text{O}_5^{4-}$ groups by $\text{RE}^{3+}$ ions in the crystal structures of $\text{RE}_2(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8)$ (RE = Nd, Sm). Distances are given in pm.

Fig. 3. Crystal structure of $\text{RE}_2(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8)$ (RE = Nd, Sm). Layers of the composition $\{\frac{2}{\text{RE}_2(\text{As}_2\text{O}_5)_2}\}^{4+}$ are stacked in the [001] direction and linked by $\text{As}_4\text{O}_8^{4-}$ ions. In the [010] direction open channels are formed that incorporate the lone electron pairs of the arsenic atoms.

Fig. 4. Coordination of the $\text{RE}(1)^{3+}$ (on top) and $\text{RE}(2)^{3+}$ ions (at bottom) in the crystal structures of $\text{RE}_4(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8)$ (RE = Nd, Sm).
ing tridentate (Fig. 4). The \([\text{REO}_9]\) polyhedron has the shape of a distorted tricapped trigonal prism. \(\text{RE}(2)^{3+}\) is surrounded by four monodentate and one chelating \(\text{As}_2\text{O}_5^{4-}\) groups as well as by two monodentate \(\text{As}_4\text{O}_8^{4-}\) ions leading to a square anti-prismatic \([\text{REO}_8]\) polyhedron (Fig. 4).

As often observed in crystal structures involving ions with \(s^2\) configuration, a prominent stereochemical influence of the lone electron pairs is observed. In the structures of \(\text{Nd}_4(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8)\) and \(\text{Sm}_4(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8)\) this leads to open channels along the [010] direction which obviously incorporate the electron pairs (Fig. 3).

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Note. During the preparation of the manuscript it turned out that the samarium compound \(\text{Sm}_4(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8)\) has been synthesized independently at the same time by the group of Prof. Th. Schleid, University Stuttgart, Germany [16].