

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 As_2O_3 in a NaCl flux at 850 °C in sealed silica ampoules. According to the structure determination, the triclinic compounds ($P\bar{1}$, $Z = 2$, Nd/Sm: $a = 686.32(9)/680.92(9)$, $b = 763.06(8)/756.4(1)$, $c = 954.8(1)/951.2(1)$ pm, $\alpha = 96.83(1)^\circ/96.66(2)^\circ$, $\beta = 103.78(2)^\circ/103.67(2)^\circ$, $\gamma = 104.40(1)^\circ/104.35(2)^\circ$, $R1 = 0.0184/0.0282$ (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 $\{\frac{2}{\infty}[\text{RE}_2(\text{As}_2\text{O}_5)]_2\}^{4+}$ 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 oxoselenates(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 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-arsenates(III) (arsenites) because these anions are isomorphous with the selenite ions but their higher charge allows for other compositions. Unfortunately no simple arsen-

ates(III) of the rare earth elements are known up to now, and only the O^{2-} and 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 RE_2O_3 ($\text{RE} = \text{Nd}, \text{Sm}$) and As_2O_3 as well as 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 °C. After keeping this temperature for 24 h, it was raised to 850 °C within 35 h. After 24 h at this temperature the furnace was cooled down slowly at a rate of 10 °C/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	<i>a</i> = 686.32(9) pm <i>b</i> = 763.06(8) pm <i>c</i> = 954.8(1) pm α = 96.83(1)° β = 103.78(2)° γ = 104.40(1)°	<i>a</i> = 680.92(9) pm <i>b</i> = 756.4(1) pm <i>c</i> = 951.2(1) pm α = 96.66(2)° β = 103.67(2)° γ = 104.35(2)°
Cell volume	461.9(1) Å ³	453.2(1) Å ³
No. of formula units	2	2
Crystal system	— Triclinic —	
Space group	— <i>P</i> $\bar{1}$ (No. 2) —	
Diffractometer	— Stoe IPDS-I —	
Radiation	— Mo-K α (graphite-monochrom., λ = 71.07 pm) —	
Temperature	153 K	153 K
Data range	3.3° < 2 θ < 52.1°	3.3° < 2 θ < 52.1°
Index range	−8 ≤ <i>h</i> ≤ 8 −8 ≤ <i>k</i> ≤ 8 −11 ≤ <i>l</i> ≤ 11	−8 ≤ <i>h</i> ≤ 8 −9 ≤ <i>k</i> ≤ 9 −11 ≤ <i>l</i> ≤ 11
φ -Range; increment	0° < φ < 312°; 2.0°	0° < φ < 320°; 2.0°
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] —	
μ	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>I</i> _o > 2 σ (<i>I</i>)	1411	1254
<i>R</i> _{int} / <i>R</i> _{σ}	0.0371 / 0.0345	0.0613 / 0.0593
Structure solution and refinement	— SHELXS-86, SHELXL-97 [10, 11] —	
Scattering factors	— Intern. Tables, Vol. C —	
Goodness of fit	0.922	0.956
<i>R</i> 1; <i>wR</i> 2 <i>I</i> _o > 2 σ (<i>I</i>)	0.0184; 0.0353	0.0282; 0.0639
<i>R</i> 1; <i>wR</i> 2 (all data)	0.0262; 0.0364	0.0452; 0.0689
Extinction coefficient	0.0010(1)	—
CSD ^a	415762	415763

Table 1. Crystallographic data of Nd₄(As₂O₅)₂(As₄O₈) and Sm₄(As₂O₅)₂(As₄O₈)

^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.

collected with the same diffractometer. The structure was solved applying direct methods [10] and refined introducing anisotropic displacement factors for all atoms [11]. Absorption effects have been treated numerically [12, 13]. Crystallographic data and details of the measurement are summarized in the Tables 1–3.

Results and Discussion

The oxo-arsenates(III) RE₂As₄O₉ (RE = Nd, Sm) are the first representatives of compounds in the systems RE₂O₃/As₂O₃ with RE being a rare earth element. Interestingly, in the crystal structures no simple AsO₃^{3−} ions were found but diarsenite groups, As₂O₅^{4−}, and the unusual tetrameric cyclic As₄O₈^{4−} anions. Thus, the compounds are to be written as to Nd₄(As₂O₅)₂(As₄O₈) and Sm₄(As₂O₅)₂(As₄O₈). The occurrence of As₂O₅^{4−} ions is a well known feature in the crystal chemistry of oxoarsenates(III) [14], and in both compounds under discussion the anions show

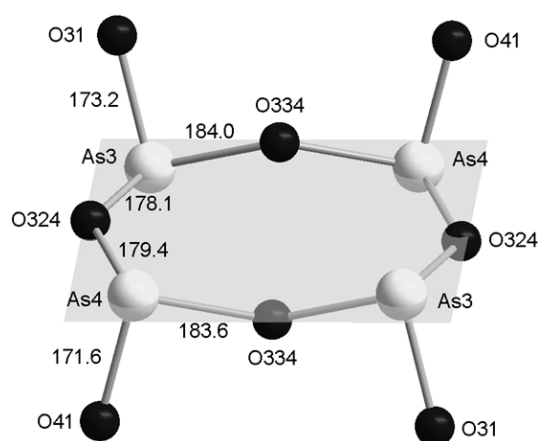


Fig. 1. The *cyclo*-tetraarsenate(III) anion As₄O₈^{4−} in the crystal structures of RE₄(As₂O₅)₂(As₄O₈) (RE = Nd, Sm). The anion has C_i symmetry and the bridging oxygen atoms O23 and O12 are situated slightly apart from the plane that is spanned by the four arsenic atoms. The bond distances (in pm) are given for the neodymium compound (*cf.* Table 3).

Table 2. Atomic positions and equivalent displacement parameters for Nd₄(As₂O₅)₂(As₄O₈) and Sm₄(As₂O₅)₂(As₄O₈)

Atom ^b	x	y	z	U _{eq} /Å ² ^a
Nd1	0.25047(4)	0.05597(4)	0.87918(3)	0.01540(9)
Sm1	0.25282(9)	0.05674(8)	0.87941(6)	0.0116(2)
Nd2	0.22066(4)	0.53204(4)	0.90397(3)	0.01530(9)
Sm2	0.22167(9)	0.53193(8)	0.90514(6)	0.0118(2)
As1	0.24977(7)	0.92264(8)	0.21539(6)	0.0157(1)
As1	0.2470(2)	0.9214(2)	0.2148(1)	0.0119(3)
O112	0.1387(5)	0.1060(6)	0.1478(5)	0.0189(9)
O112	0.135(1)	0.105(1)	0.1487(9)	0.015(2)
O12	0.0004(5)	0.7775(6)	0.1738(4)	0.0190(9)
O12	1.00(1)	0.7778(9)	0.1747(8)	0.010(2)
O13	0.3414(5)	0.8707(6)	0.0607(4)	0.0182(8)
O13	0.341(1)	0.870(1)	0.0599(9)	0.014(2)
As2	0.30713(7)	0.35188(8)	0.20842(6)	0.0151(1)
As2	0.3068(2)	0.3530(2)	0.2086(1)	0.0117(3)
O21	0.4091(5)	0.3332(5)	0.0539(4)	0.0179(8)
O21	0.409(1)	0.331(1)	0.0535(9)	0.013(2)
O22	0.1263(5)	0.4578(6)	0.1299(4)	0.0172(8)
O22	0.126(1)	0.460(1)	0.1277(9)	0.014(2)
As3	0.17701(8)	0.77089(8)	0.55776(7)	0.0191(1)
As3	0.1793(2)	0.7696(2)	0.5599(1)	0.0145(3)
O31	0.2250(5)	0.7498(6)	0.7406(5)	0.0198(9)
O31	0.226(1)	0.748(1)	0.7444(9)	0.015(2)
O324	0.1010(6)	0.3182(7)	0.4975(6)	0.032(1)
O324	0.100(2)	0.323(1)	0.498(1)	0.029(2)
O334	0.1831(5)	0.0126(6)	0.6099(5)	0.0204(8)
O334	0.181(1)	0.012(1)	0.6122(9)	0.016(2)
As4	0.31848(8)	0.23732(8)	0.57753(7)	0.0185(1)
As4	0.3191(2)	0.2383(2)	0.5779(1)	0.0146(3)
O41	0.3710(5)	0.3337(6)	0.7591(4)	0.0177(8)
O41	0.3769(1)	0.335(1)	0.7614(9)	0.017(2)

^a $U_{eq} = 1/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aba^*b^*\cos\gamma + 2U_{13}aca^*c^*\cos\beta + 2U_{23}bcb^*c^*\cos\alpha]$ [17]; ^b all atoms occupy the site 2i.

essentially the distances and angles as previously described. The largest distances As-O within the group are found to the bridging oxygen atoms with values around 187 pm (Table 2), and the angles As-O-As are about 118°. 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 *cyclo*-arsenite anion, As₄O₈⁴⁻. To the best of our knowledge only one compound with a *cyclo*-tetraarsenite anion has been reported, namely the mineral stenhuggarite, CaFeSbAs₂O₇ [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-

Table 3. Selected distances/pm and angles/° Nd₄(As₂O₅)₂(As₄O₈) and Sm₄(As₂O₅)₂(As₄O₈).

Nd1	-O21	236.5(4)	Sm1	-O21	233.5(8)
	-O12	237.9(4)		-O12	234.3(8)
	-O13	242.9(4)		-O13	240.6(8)
	-O334	246.7(4)		-O334	243.8(8)
	-O31	248.8(4)		-O31	247.6(8)
	-O41	257.8(4)		-O41	255.2(8)
	-O112	258.5(3)		-O112	255.3(8)
	-O13	262.0(3)		-O13	259.0(7)
	-O112	285.7(4)		-O112	287.1(8)
Nd2	-O22	234.8(3)	Sm2	-O22	232.8(8)
	-O12	238.7(4)		-O31	236.1(7)
	-O21	240.6(3)		-O12	236.6(7)
	-O31	241.0(4)		-O21	238.6(7)
	-O22	248.3(4)		-O22	243.9(7)
	-O41	249.5(4)		-O41	248.3(8)
	-O21	257.6(4)		-O21	255.7(8)
	-O13	265.1(4)		-O13	262.9(8)
As1	-O12	171.6(3)	As1	-O12	170.9(7)
	-O13	177.8(4)		-O13	177.8(8)
	-O112	186.1(4)		-O112	185.0(8)
As2	-O22	171.9(4)	As2	-O22	172.1(8)
	-O21	178.3(4)		-O21	178.3(8)
	-O112	188.0(4)		-O112	188.6(8)
As3	-O31	173.2(4)	As3	-O31	174.3(8)
	-O324	178.1(4)		-O324	177.8(10)
	-O334	184.0(4)		-O334	183.5(8)
As4	-O41	171.6(4)	As4	-O41	172.5(8)
	-O324	179.4(4)		-O324	180.7(10)
	-O334	183.6(4)		-O334	184.5(8)
O12-As1-O13		105.3(2)	O12-As1-O13		106.1(3)
O12-As1-O1112		89.2(2)	O12-As1-O1112		88.5(4)
O13-As1-O1112		95.7(2)	O13-As1-O1112		96.2(4)
As1-O112-As2		118.2(2)	As1-O112-As2		117.7(4)
O22-As2-O21		94.6(2)	O22-As2-O21		94.3(4)
O22-As2-O112		98.6(2)	O22-As2-O112		98.2(4)
O21-As2-O112		90.9(2)	O21-As2-O112		90.6(3)
O31-As3-O324		99.2(2)	O31-As3-O324		99.4(4)
O31-As3-O334		89.9(2)	O31-As3-O334		89.4(4)
O324-As3-O334		95.7(2)	O324-As3-O334		95.8(4)
As3-O324-As4		136.4(3)	As3-O324-As4		135.6(5)
As3-O334-As4		136.8(2)	As3-O334-As4		135.6(5)
O41-As4-O324		100.7(2)	O41-As4-O324		101.3(4)
O41-As4-O334		91.0(2)	O41-As4-O334		90.7(4)
O324-As4-O334		101.2(2)	O324-As4-O334		101.4(4)

dral array (S₄ symmetry), while in the present case all arsenic atoms lie in a plane and the anion has C_i 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-

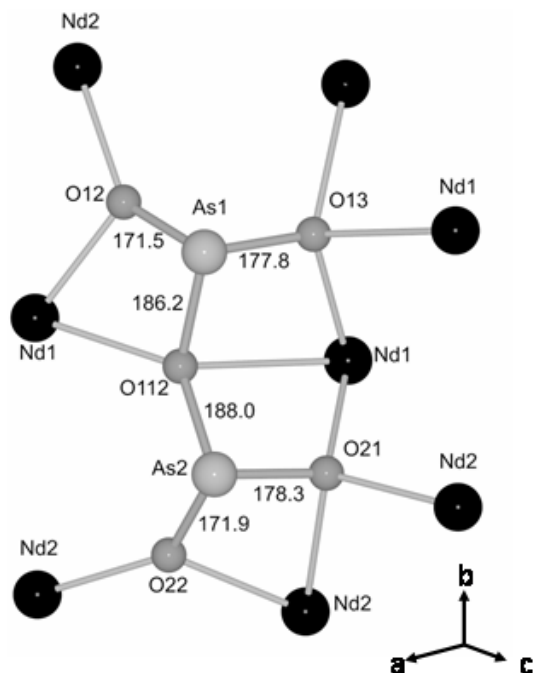


Fig. 2. Coordination of the $\text{As}_2\text{O}_5^{4-}$ groups by RE^{3+} ions in the crystal structures of $\text{RE}_4(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8)$ (RE = Nd, Sm). Distances are given in pm.

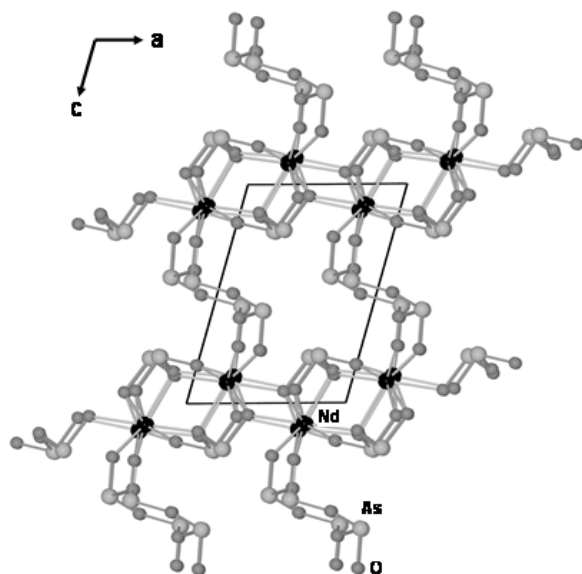


Fig. 3. Crystal structure of $\text{RE}_4(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8)$ (RE = Nd, Sm). Layers of the composition $\{2[\text{RE}_2(\text{As}_2\text{O}_5)]_2\}^{4+}$ are stacked in the [001] direction and linked by $\text{As}_4\text{O}_8^{4-}$ ions. In the [010] direction open channels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

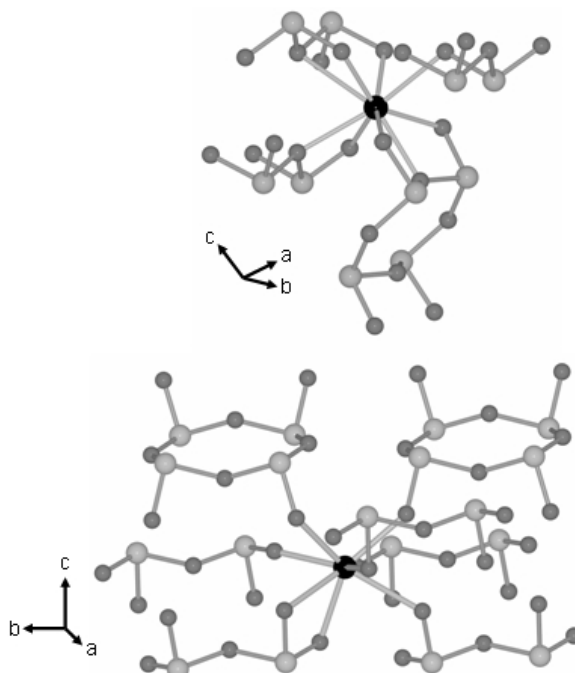


Fig. 4. Coordination of the $\text{RE}(1)^{3+}$ (on top) and $\text{RE}(2)^{3+}$ ions (at bottom) in the crystal structures of $\text{RE}_4(\text{As}_2\text{O}_5)_2(\text{As}_4\text{O}_8)$ (RE = Nd, Sm).

gles with the arsenic atoms that are either around 100° or around 90° . These distances and angles are similar to the findings for the *cyclo*-tetraarsenite anion in $\text{CaFeSbAs}_2\text{O}_7$, despite of the different shape of the individual anions.

In the crystal structure of the two arsenites, the RE^{3+} ions are linked by the $\text{As}_2\text{O}_5^{4-}$ groups to layers of the composition $\{2[\text{RE}_2(\text{As}_2\text{O}_5)]_2\}^{4+}$. Within the layers, the diarsenite groups are coordinated by eight RE^{3+} ions, and also the bridging oxygen atoms of the anion are involved in the RE^{3+} coordination (Fig. 2). This leads to relatively short RE^{3+} - RE^{3+} distances of 367 pm for the neodymium and 363 pm for the samarium compound. The $\{2[\text{RE}_2(\text{As}_2\text{O}_5)]_2\}^{4+}$ layers are stacked in the [001] direction, and are connected by the *cyclo*-tetraarsenite anions (Fig. 3).

In this way the latter are coordinated by six RE^{3+} ions *via* the terminal oxygen atoms and two of the four bridging oxygen atoms. For the two crystallographically different RE^{3+} ions, $\text{RE}(1)^{3+}$ and $\text{RE}(2)^{3+}$, coordination numbers of nine and eight arise. $\text{RE}(1)^{3+}$ is surrounded by three $\text{As}_2\text{O}_5^{4-}$ ions and one $\text{As}_4\text{O}_8^{4-}$ group, the diarsenite ions being mono-, di-, and tri-dentate, and the *cyclo*-tetraarsenite anions be-

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].

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