



Article Sc₂[Se₂O₅]₃: The First Rare-Earth Metal Oxoselenate(IV) with Exclusively [Se₂O₅]²⁻ Anions

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Abstract: The scandium oxodiselenate(IV) $Sc_2[Se_2O_5]_3$ was synthesized via solid-state reactions between scandium sesquioxide (Sc_2O_3) and selenium dioxide (SeO_2) with thallium(I) chloride (TICl) as fluxing agent in molar ratios of 1:4:2. Evacuated fused silica ampoules were used as reactions vessels for annealing the mixtures for five days at 800 °C. The new scandium compound crystallizes in the triclinic space group $P\overline{1}$ with the lattice parameters a = 663.71(5) pm, b = 1024.32(7) pm, c = 1057.49(8) pm, $\alpha = 81.034(2)^{\circ}$, $\beta = 87.468(2)^{\circ}$, $\gamma = 89.237(2)^{\circ}$ and Z = 2. There are two distinct Sc^{3+} positions, which show six-fold coordination by oxygen atoms as $[ScO_6]^{9-}$ octahedra (d(Sc-O) = 205-212 pm). Three different $[Se_2O_5]^{2-}$ anions provide these oxygen atoms with their terminal ligands (O^t). Each of the six selenium(IV) central atoms exhibit a stereochemically active lone pair of electrons, so that all $[Se_2O_5]^{2-}$ anions consist of two ψ^1 -tetrahedral $[SeO_3]^{2-}$ subunits $(d(Se-O^t) = 164-167 \text{ pm}, d(Se-O^b) = 176-185 \text{ pm}, <math>\sphericalangle(O-Se-O) = 93-104^{\circ}$) sharing one bridging oxygen atom (O^b) with $\sphericalangle(Se-O^b-Se) = 121-128^{\circ}$. The vibrational modes of the complex anionic $[Se_2O_5]^{2-}$ entities were characterized via single-crystal Raman spectroscopy.

Keywords: scandium; lone-pair; oxoselenate; complex anions; Raman spectroscopy; solid-state reactions

1. Introduction

Owing to their potential as materials with an inorganic antenna effect [1] within energy transfer processes for lighting applications, many rare-earth metal(III) oxoselenates(IV) were published with different structural characteristics in the past decades. So even the pure rare-earth metal(III) oxoselenates(IV) with the simple formula $RE_2[SeO_3]_3$ ($\equiv RE_2Se_3O_9$; RE = Sc, Y, La–Lu) [2–12] show a cornucopia of structure and space-group types. For the smallest rare-earth metal, scandium $Sc_2[SeO_3]_3$ crystallizes in a hexagonal crystal structure in space group $P6_3/m$ [3]. In contrast, the $RE_2[SeO_3]_3$ -type phases with lanthanum and cerium show an orthorhombic structure in space-group Pnma [2,4]. The next two lanthanides, praseodymium and neodymium, exhibit for their RE_2 [SeO₃]₃ compounds the monoclinic crystal system with the space group $P2_1/n$ [2,8]. All further rare-earth metals(III) (RE = Y, Sm–Lu) [6,7,10] adopt the same triclinic crystal structure for their RE_2 [SeO₃]₃-type representatives with space-group $P\overline{1}$. Besides this formula type, representatives containing oxygen atoms not bonded to the Se⁴⁺ cations are known with the formula $RE_2O[SeO_3]_2$ $(\equiv RE_2Se_2O_7; RE = Y, Sm-Tm)$ [13–16]. Most of the compounds crystallize in the tetragonal $Tb_2O[SeO_3]_2$ structure-type [16], but the newest experimental research shows that monoclinic $Sm_3O_2Sm[SeO_3]_4$ ($\equiv Sm_2Se_2O_7$) is also accessible [15]. All these compounds exhibit the same basic module, which is responsible for the crystal structure, and these basic modules are oxygen-centered $[ORE_4]^{10+}$ tetrahedra, which are interconnected in different ways. Furthermore, in the literature is a rare-earth metal(III) oxoselenate(IV) known with two 'free' oxygen atoms per formula unit

and the composition $Sc_2O_2[SeO_3]$ [17,18]. This formula type $RE_2O_2[SeO_3]$ ($\equiv RE_2SeO_5$) was long postulated from *Oppermann* et al. [19–23] in various RE_2O_3/SeO_2 systems. Nevertheless, no single crystals were available to confirm this crystal structure, so it was only assumed via powder diffraction methods [19–23]. Only one representative, including rare-earth metals, is known so far in the literature, which exhibits complex anionic $[Se_2O_5]^{2-}$ units. $Sm_2[SeO_3][Se_2O_5]_2$ ($\equiv Sm_2Se_5O_{13}$) [24] contains only two of these anions, while with the title compound the first rare-earth metal(III) oxoselenate(IV) was accessible with exclusively these sort of anions. The aim of the synthesis was a TISc[SeO_3]_2, however, which should be structurally similar to the alkali-metal scandium oxoselenates(IV) $ASc[SeO_3]_2$ (A = Na-Cs) [25] known in the literature. This paper describes the crystal structure of the new title compound $Sc_2[Se_2O_5]_3$ as well as the vibrational modes of the $[Se_2O_5]^{2-}$ groups via single-crystal Raman measurements.

2. Materials and Methods

For the synthesis of the scandium oxodiselenate(IV) $Sc_2[Se_2O_5]_3$ a mixture of Sc_2O_3 (ChemPur: 99.9%), SeO₂ (ChemPur: 99.9%) and TICI (Alfa Aesar: 'pure') in a molar ratio of 1:4:2 was used. The target product was thus $TlSc[SeO_3]_2$ according to the known alkali-metal scandium oxoselenates(IV) $ASc[SeO_3]_2$ (A = Na-Cs) [25]. The chemicals were stored and handled in a glove box (GS Glove-Box Systems) under an argon atmosphere. The reactants were filled into glassy fused silica ampoules, which were evacuated to 10^{-3} mbar and torch sealed. Afterwards, the reaction vessels were heated up over 8 h to 800 °C and tempered for five days at this temperature. The furnace was cooled down to 500 $^{\circ}$ C within 99 h, and held at this temperature for another 2 h, before it was completely cooled down within 4 h to room temperature. The crude product was checked for its water- and air-stability. Afterwards it was washed with demineralized water to remove most of the fluxing agents (SeO₂ and TlCl). Some colorless, plate-like crystals were selected and characterized via X-ray structure analysis. For this purpose, the crystals were measured at room temperature on a κ-CCD X-ray diffractometer (Bruker Nonius, Karlsruhe, Germany) with graphite-monochromatized Mo-K α radiation ($\lambda = 71.07$ pm). A numerical absorption correction was carried out with the program HABITUS [26], but the structure solution and refinement was performed with the program SHELX-97 [27,28]. In Table 1 the crystallographic data of Sc₂[Se₂O₅]₃ are summarized, while Table 2 contains the atomic positions and their equivalent isotropic displacement coefficients. The interatomic distances and bond angles are shown in Table 3.

The reflections in the X-ray powder pattern (Figure 1) exhibit a low intensity due to the poor crystallinity of the product, therefore a good evaluation and characterization was not possible (Figure 1). However, scandium oxoselenate(IV) $Sc_2[SeO_3]_3$ and some residual thallium(I) chloride TICl could be identified as by-products. In addition, the powder pattern shows reflections of another side phase, which could not be determined so far. Hence, a successful synthesis of the phase pure title compound $Sc_2[Se_2O_5]_3$ was not successful yet.

The single-crystal Raman measurements were operated on a XploRa device (Horiba, Bensheim, Germany) from 200–1000 cm⁻¹ to detect the vibrational modes of the complex anionic $[Se_2O_5]^{2-}$ anions. Further details of the crystal structure investigations can be obtained at the Fachinfomrationszentrum Karlsruhe, 76334 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de, http://www.fiz-karlsruhe.de/requestfordepositeddata.html) for the depository number CSD-433355 of Sc₂[Se₂O₅]₃.

Empirical Formula	$\mathbf{Sc}_{2}[\mathbf{Se}_{2}\mathbf{O}_{5}]_{3} \ (\equiv \mathbf{Sc}_{2}\mathbf{Se}_{6}\mathbf{O}_{15})$	
Crystal system	triclinic	
Space group	<i>P</i> 1 (no. 2)	
Lattice parameters		
a/pm	663.71(5)	
b/pm	1024.32(7)	
c/pm	1057.49(8)	
α/deg	81.034(2)	
β/deg	87.468(2)	
γ/deg	89.237(2)	
Number of formula units (Z)	2	
Calculated density (D_x in g/cm ³)	3.762	
Molar volume ($V_{\rm m}$ in cm ³ /mol)	188.58(9)	
Diffractometer	κ-CCD (Bruker Nonius)	
Wavelength (λ in pm)	71.07 (Mo Kα)	
Index range $(\pm h_{\max}, \pm k_{\max}, \pm l_{\max})$	8/13/13	
Number of e^- per unit cell (<i>F</i> (000))	732	
Absorption coefficient (μ in mm ⁻¹)	16.426	
Number of collected vs. unique reflections	31217/3256	
Data-set residuals (R_{int}/R_{σ})	0.084/0.036	
Structure residuals (R_1/wR_2)	0.034/0.074	
Goodness of fit (GooF)	1.058	
Extinction coefficient (g)	0.0101(5)	
Residual electron density (max./min. in $e^{-} 10^{-6} pm^{-3}$)	1.318/-1.267	
CSD-number	433,355	

Table 1. Crystallographic data of $Sc_2[Se_2O_5]_3$ and their determination.

Table 2. Atomic coordinates and equivalent isotropic displacement coefficients (U_{eq}/pm^2) for Sc₂[Se₂O₅]₃ (all atoms occupy the general 2*i* site)

Atom	x/a	y/b	zlc	U _{eq} ¹
Sc1	0.16448(9)	0.58715(7)	0.26677(7)	145(2)
Sc2	0.31102(9)	0.06071(7)	0.28974(7)	143(2)
Se1	0.22321(5)	0.77750(4)	0.51356(4)	173(1)
Se2	0.31368(5)	0.30185(4)	0.49159(4)	156(1)
Se3	0.14680(5)	0.33785(4)	0.08075(4)	197(1)
Se4	0.34062(5)	0.46713(4)	0.80898(4)	189(1)
Se5	0.20134(5)	0.01376(4)	0.77299(4)	171(1)
Se6	0.32216(5)	0.85034(4)	0.04488(4)	173(1)
O1	0.3565(4)	0.8834(3)	0.4083(3)	257(6)
O2	0.1123(4)	0.6849(3)	0.4203(3)	241(6)
O3	0.4252(4)	0.6720(3)	0.5744(3)	229(6)
O4	0.2120(4)	0.4093(3)	0.3801(3)	245(6)
O5	0.2599(4)	0.1567(3)	0.4489(3)	210(6)
O6	0.3013(4)	0.2435(3)	0.1727(3)	288(7)
07	0.1988(4)	0.4927(3)	0.1010(3)	289(7)
O8	0.2873(4)	0.3302(3)	0.9362(3)	354(8)
O9	0.1421(4)	0.4542(3)	0.7240(3)	308(7)
O10	0.4805(4)	0.6157(3)	0.2594(3)	241(6)
O11	0.0055(4)	0.0288(3)	0.2913(3)	289(7)
O12	0.3733(4)	0.9148(3)	0.7186(3)	227(6)
O13	0.1454(4)	0.9259(3)	0.9300(3)	346(8)
O14	0.3719(4)	0.9735(3)	0.1228(3)	288(7)
O15	0.1445(4)	0.7649(3)	0.1370(3)	229(6)

¹ defined as temperature factor according to: $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{13}hla^*c^* + 2U_{12}hka^*b^* + 2U_{23}hlb^*c^*)].$

Se5-O13-Se6

Sc1-O4	204.7(3)	Sc2011	205.7(3)
Sc1-O2	205.1(3)	Sc1-O1	206.7(3)
Sc1-09	207.9(3)	Sc1-O6	207.9(3)
Sc1-O15	210.9(3)	Sc1-O5	209.1(3)
Sc1O10	211.8(3)	Sc1012	211.0(3)
Sc1-07	213.3(3)	Sc1014	212.1(3)
Se1-O1	166.1(3)	Se2–O4	164.4(3)
Se1–O2	167.0(3)	Se1-O5	166.7(3)
Se1–O3	178.9(3)	Se1–O3	184.6(3)
Se306	164.3(3)	Se409	164.5(3)
Se1-O7	167.6(3)	Se1O10	165.6(3)
Se1-08	176.7(3)	Se1–O8	181.3(3)
Se5-011	165.2(3)	Se6014	165.5(3)
Se1012	166.0(3)	Se1015	166.3(6)
Se1013	178.7(3)	Se1013	180.6(3)
O1-Se1-O3	098.52(13)	O3-Se2-O4	095.05(13)
O2-Se1-O3	101.80(14)	O3-Se2-O5	101.58(14)
O1-Se1-O2	102.67(14)	O4-Se2-O5	103.23(14)
O6-Se3-O8	095.50(15)	O8-Se4-O10	093.04(15)
O7-Se3-O8	099.83(15)	O8-Se4-O9	098.24(16)
O6-Se3-O7	105.18(15)	O9-Se4-O10	104.03(15)
O11-Se5-O13	096.13(15)	O13-Se6-O15	093.44(13)
O12-Se5-O13	100.96(15)	O13-Se6-O14	102.13(15)
O11-Se5-O12	102.11(14)	O14-Se6-O15	103.96(15)
Se1-O3-Se2	121.32(14)	Se308Se4	126.31(18)

Table 3. Selected interatomic distances (d/pm) and angles ($\langle \langle \rangle^{\circ}$) in the crystal structure of Sc₂[Se₂O₅]₃.



127.48(17)

Figure 1. Measured powder pattern of the title compound (black) with the reference of Sc₂[Se₂O₅]₃ (red), $Sc_2[SeO_3]_3$ (green), and TlCl (blue) from single crystal data.

3. Results and Discussion

The new scandium oxodiselenate(IV) $Sc_2[Se_2O_5]_3$ ($\equiv Sc_2Se_6O_{15}$) crystallizes in the triclinic space group $P\overline{1}$ (no. 2) with the lattice parameters a = 663.71(5) pm, b = 1024.32(7) pm, c = 1057.49(8) pm, $\alpha = 81.034(2)^\circ$, $\beta = 87.468(2)^\circ$, $\gamma = 89.237(2)^\circ$, and Z = 2 (Table 1). In the crystal structure, two distinct Sc^{3+} cations exist (Table 2). Both of them are six-fold coordinated by oxygen atoms as $[ScO_6]^{9-}$ octahedra, which belong to six terminally attached $[Se_2O_5]^{2-}$ units (Figure 2). The $Sc^{3+}-O^{2-}$ distances range in the area of 204 to 212 pm (Table 3). These correlate well with them known from the scandium oxoselenate(IV) $Sc_2[SeO_3]_3$ (d = 201-220 pm) [3].



Figure 2. Coordination sphere of the two crystallographically distinct Sc^{3+} , which are six-fold coordinated by oxygen atoms as $[ScO_6]^{9-}$ octahedra ((**top left**) and (**bottom left**)). The oxygen atoms themselves belong to six terminally attached $[Se_2O_5]^{2-}$ anions. Symmetry related atoms are shown with an a(x, y, z) or b(-x, -y, -z) and a thermal ellipsoid representation with probability factor of 95% (**left**).

Moreover, three different complex anionic $[Se_2O_5]^{2-}$ groups occur in the crystal structure (Figure 3), showing different dihedral angles between the two (O,O,O)-faces ((O1,O2,O3)–(O3,O4,O5) = 121.2°; (O6,O7,O8)–(O8,O9,O10) = 146.0°; (O11,O12,O13)–(O13,O14,O15) = 152.2°). The Se⁴⁺–O²⁻ distances are located in an interval from 164 to 167 pm (Table 3), this is slightly smaller than those in downeyite-type SeO₂ (d = 171-173 pm) [29]. In contrast, the Se⁴⁺–(O^b)²⁻ distances are significantly

longer with 177 to 185 pm. Similar distances were found in the first known lanthanoid(III) oxoselenate(IV) with $[Se_2O_5]^{2-}$ units, $Sm_2[SeO_3][Se_2O_5]_2$ ($\equiv Sm_2Se_5O_{13}$, d = 164-184 pm) [24] namely. The $[ScO_6]^{9-}$ octahedra are interconnected via the terminally grafting $[Se_2O_5]^{2-}$ units resulting in the three-dimensional network of $Sc_2[Se_2O_5]_3$ (Figure 4). The displacements of the Se⁴⁺ cations from their triangular (O,O,O)-plane are for all three complex anionic $[Se_2O_5]^{2-}$ anions very much alike. These displacements range from 77.3 pm (Se1), 78.3 pm (Se3), 79.4 pm (Se6), 79.5 pm (Se5), 79.7 pm (Se2), to 82.0 pm (Se4). Also the Se–O^b–Se angles are located in a small area with (Se1)–(O3)^b–(Se2) = 121.3°, (Se3)–(O8)^b–(Se4) = 126.3°, and (Se5)–(O13)^b–(Se6) = 127.5°.



Figure 3. Configuration of the three different $[Se_2O_5]^{2-}$ groups in the crystal structure of triclinic $Sc_2[Se_2O_5]_3$. These consist of two via vertex interconnected ψ^1 -tetrahedral $[SeO_3]^{2-}$ subunits with different tilting angles between their two (O,O,O)-faces. In addition, the cationic coordination sphere of the $[Se_2O_5]^{2-}$ anions is shown (thermal ellipsoid representation with probability factor of 95%). Note that none of the bridging oxygen atoms (O3, O8, and O13) has a coordinative contacts to the Sc^{3+} cations.



Figure 4. All $[ScO_6]^{9-}$ octahedra are interconnected by terminally attached $[Se_2O_5]^{2-}$ anions to form the three-dimensional network of triclinic $Sc_2[Se_2O_5]_3$.

Raman-spectroscopic measurements of Sc₂[Se₂O₅]₃ single crystals show typically modes, known from free $[SeO_3]^{2-}$ units with ψ^1 -tetrahedral shape and ideal C_{3v} symmetry. These modes belong to two symmetric vibrations with A_1 at 810 and 425 cm⁻¹ and E at 740 and 375 cm⁻¹ according to Siebert [30]. By the influence of the crystal field these bands of the $[SeO_3]^{2-}$ anions split up into wide areas. The symmetric stretching modes are located in the range of 890–790 cm⁻¹ (v_s) and the anti-symmetric stretching modes occur between 760 and 660 cm⁻¹ (v_{as}). According to these, also the bending modes have an expanded area with the symmetric bending mode between 510 and 420 cm⁻¹ (δ_s) and anti-symmetric bending mode from 410 up to 330 cm⁻¹ [30]. The complex anionic oxodiselenate(IV) units generate one more stretching mode resulted from the slightly longer $Se^{4+}-(O^b)^{2-}$ bond by about 10 to 15 pm expanded. This mode is located between 650 and 550 cm⁻¹ [12] and seems to be specific for $[Se_2O_5]^{2-}$ anions (v_{SeOB}). In the Raman spectrum three signals can be detected in this area with $\nu = 578$, 606 and 632 cm⁻¹. For the symmetric stretching mode (ν_s) two signals appear at 901 and 934 cm⁻¹ and for the anti-symmetric stretching mode (v_{as}) three at 739, 800, and 811 cm⁻¹. In the area of the symmetric bending mode v = 420-550 cm⁻¹ (δ_s) four signals can be found at 435, 469, 523, and 539 cm^{-1} . At smaller wavenumbers between 208 and 387 cm^{-1} , the anti-symmetric bending modes as well as lattices vibrations are located. Seven signals at 208, 235, 274, 292, 322, 347, and 387 cm^{-1} become obvious in these areas (Figure 5). For the characterization of these modes modern articles were used as references [11,18,31–33].



Figure 5. Single-crystal Raman spectrum of $Sc_2[Se_2O_5]_3$ in the area from 200 to 1000 cm⁻¹. The different stretching and bending modes of the complex anionic $[Se_2O_5]^{2-1}$ units are shown.

4. Conclusions

Unlike yttrium, its heavier congener in group III of the periodic table of the elements, scandium hardly forms compounds suitable as hosts for doping with appropriate lanthanoid(III) cations (e.g., Eu³⁺ or Tb³⁺) for luminescence materials. Its small ionic radius (r:(Sc³⁺) = 74.5 pm for C.N. = 6 [34]) and its preference for octahedral coordination figures explain this finding plausibly, whereas yttrium (r:(Y³⁺) = 101.9 pm for C.N. = 8 [34]) ranges within the heavy lanthanoid compartment (Dy³⁺, Ho³⁺, or Er³⁺) under these circumstances, without being a 4*f* element. So even with nice [SeO₃]²⁻ pyramids as building blocks with a lone-pair of electron at the Se⁴⁺ cations, scandium(III) oxoselenate(IV) derivatives are unable to host Ln^{3+} cations, as long as they contain only six-fold coordinated Sc³⁺ cations, e.g., Sc₂[SeO₃]₃ [3], Sc₂O₂[SeO₃] [17,18] and our new example Sc₂[Se₂O₅]₃. However this changes, whenever the Sc³⁺ cations reside in coordination polyhedra with higher coordinated Sc³⁺ cations in pentagonal bipyramids, Eu³⁺ cations can replace these partially (1–5%), which leads to red luminescent materials in the case of ScF[SeO₃]:Eu³⁺ [17]. The tight [ScO₅F₂]⁹⁻ polyhedra provoke a slight red-shift of the Eu³⁺-centered luminescence, however, as compared to the YF[SeO₃]:Eu³⁺ example [10] with Eu³⁺ in the eight-fold coordination of [YO₆F₂]¹¹⁻ polyhedra.

Supporting Materials: The CIF of the title compound can be downloaded directly with the publication, containing all crystallographic data.

Author Contributions: Stefan Greiner and Thomas Schleid conceived and designed the experiments; Stefan Greiner performed the experiments; Stefan Greiner and Thomas Schleid analyzed the data; Thomas Schleid contributed reagents/materials/analysis tools; Stefan Greiner wrote the paper and Thomas Schleid polished it.

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Conflicts of Interest: The authors declare no conflict of interest.

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