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$CsTmCl_2[SeO_3]$: a quinary phase in the system $CsCl/TmOCl/SeO_2$

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Abstract

$CsTmCl_2[SeO_3]$ was prepared by reaction of a stoichiometric mixture of Tm_2O_3, $TmCl_3$, SeO_2 and CsCl in an evacuated torch-sealed silica tube at 830°C for 7 days as colourless single crystals (monoclinic, $P2_1/n$; $a = 658.92(5)$, $b = 689.26(6)$, $c = 1752.5(1)$ pm, $\beta = 99.093(7)^\circ$, $Z = 4$; κ-CCD, $R_{\text{all}} = 0.035$, GooF$\,=1.090$). The structure is characterized by layers parallel to (001) consisting of parallel zigzag strands $^1_\infty\{[TmO^e_{4/2}O^t_{1/1}Cl^t_{2/1}]^{5-}\}(\equiv^1_\infty\{[TmO_3Cl_2]^{5-}\})$ with both chloride anions occupying apical positions in the pentagonal bipyramid $[TmO_5Cl_2]$ (d(Tm–O)$\,=225$–240 pm, d(Tm–Cl)$\,=261$ pm, 2×). Four of the five equatorial oxygen atoms are utilized to share *trans*-edges, whereas one remains terminal and is syndiotactically ordered along the chain direction [010]. Within the layers these different chains are held together by Se^{4+} cations via both an edge and a vertex of a trigonal $[SeO_3]^{2-}$ pyramid. The Cs^+ coordination sphere can be described as a (2+1)-capped trigonal prism ($d(Cs-Cl) = 336-385$ pm, 6×) with all three oxygen atoms ($d(Cs-O) = 320$, 383 and 407 pm) being the triangular face of a single $[SeO_3]^{2-}$ anion. The crystal structure is strongly influenced by the stereochemical lone-pair effect at the Se^{4+} cations reflected by the formation discrete of ψ^1-tetrahedral $[SeO_3E]^{2-}$ groups (E=non-binding electron pair) with Se–O distances of 166, 170 and 171 pm.

Keywords: Caesium; Thulium; Chlorides; Oxoselenates(IV); Crystal structure

1. Introduction

Since the discovery of rare-earth selenates by Berzelius in 1818 [1], only hydrated and hydrogen-selenite compounds have been described in majority. However, many authors characterized more recently anhydrous selenates(IV) of lanthanides (e.g., $La_2[SeO_3]_3$, $Er_2[SeO_3]_3$, $Gd_3[SeO_3]_4F$) by means of single crystal data [2–5]. Mixed metal phases containing both lanthanides and alkali or transition metals have not been reported much, although Berrigan [6], Harrison [7], and Morris [8] have described some of them such as $Cu_3ErClO_2[SeO_3]_2$, $CuLa_2[SeO_3]_4$, and $NaLa[SeO_3]_2$, respectively. The structure of the last two compounds is based on chains of $[LaO_{10}]$ polyhedra sharing edges and vertices with the $[SeO_3]^{2-}$ groups to form an infinite two-dimensional layer which contains half of the selenium atoms. The characteristic bonding geometry of the Se^{4+} cations with respect to nearby oxygen atoms in these materials and other selenium(IV)-containing phases [9–12] is found to be pyramidal. For a more general introduction on oxoselenates(IV) of the lanthanides, we highly recommend a most recent review article by Wickleder [13]. In this paper, we report the synthesis of a new quinary compound ($CsTmCl_2[SeO_3]$) by direct solid-state reaction and its layered crystal structure with all selenium within the layers.

2. Experimental

$CsTmCl_2[SeO_3]$ was prepared by solid-state reactions of stoichiometric quantities of Tm_2O_3 (Auer-Remy, 99.99%), $TmCl_3$ (Auer-Remy, 99.99%), SeO_2 (Alfa, puratronic, 99.99%) and CsCl (E. Merck, suprapur; 99.99%). The solid components of the starting materials were heated together at 830°C for 7 days in evacuated sealed silica tubes. After this period, the furnace was cooled down slowly with about 0.1°C/min to 400°C and then switched off. Two different major phases were observed, one of which consisted of colourless needle-shaped crystals of $Tm_2[SeO_3]_3$, and the other of colourless flat ones of $CsTmCl_2[SeO_3]$, both stable in air and

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light. The title compound was characterized and its structure determined by single-crystal X-ray diffraction using a κ-CCD diffractometer with Mo$K\alpha$ radiation ($\lambda = 71.07\,\mathrm{pm}$). The monoclinic unit cell dimensions were determined using 2309 unique reflections. Systematic absences typical for a 2_1 screw axis ($0k0, k = 2n+1$) and a diagonal glide plane ($h0l, h+l = 2n+1$) could be observed. Data collection parameters are listed in Table 1 in agreement with the centrosymmetric space group $P2_1/n$. All calculations were made using a program system SHELX-97 [14]. The positions of the heavy atoms (Cs and Tm) were obtained from a phase set derived by direct methods. Difference Fourier cycling was then used to find the remaining atoms. The program X-SHAPE [15] was applied for the numerical absorption correction, and finally the program DIAMOND [16] for the visualization of the crystal structure. The final refinement converged to $R_1 = 3.5\%$, w$R_2 = 8.1\%$, and a Goodness of Fit of 1.090 for all 2309 reflections. Positional and anisotropic thermal displacement parameters obtained in the final full-matrix least-squares refinement are listed in Table 2. Selected bond distances and angles for $\mathrm{CsTmCl_2[SeO_3]}$ are summarized in Table 3.

Table 1
Crystallographic data for $\mathrm{CsTmCl_2[SeO_3]}$ and their determination

Formula	$\mathrm{CsTmCl_2SeO_3}$
Crystal system	Monoclinic
Space group	$P2_1/n$ (no. 14), $Z = 4$
Unit cell parameters	$a = 658.92(5)$ pm $b = 689.26(6)$ pm $c = 1752.5(1)$ pm $\beta = 99.093(7)^\circ$
Calculated density ($D_x/\mathrm{g\,cm^3}$)	4.223
Molar volume ($V_\mathrm{m}/\mathrm{cm^3\,mol^{-1}}$)	118.322
Diffractometer	κ-CCD (Nonius, Delft/NL)
Radiation	Mo$K\alpha$ (graphite monochromator; $\lambda = 71.07$ pm)
Temperature	298 K
2θ range	$6^\circ \leqslant 2\theta \leqslant 60^\circ$
Index range	$-9 \leqslant h \leqslant 9,\ -9 \leqslant k \leqslant 9,\ -24 \leqslant l \leqslant 24$
$F(000)$	864
Absorption coefficient (μ)	$21.09\,\mathrm{mm^{-1}}$
Absorption correction	Numerical, after crystal shape optimization with the program X-SHAPE [15]
Collected reflections	18536
Unique reflections	2309
R_int/R_σ	0.055/0.028
Reflections with $\lvert F_\mathrm{o}\rvert \geqslant 4\sigma \lvert F_\mathrm{o}\rvert$	2176
Structure solution and refinement	Program system SHELX-97 [14]
Scattering factors	International Tables, Vol. C [20]
R_1/R with $\lvert F_\mathrm{o}\rvert \geqslant 4\sigma \lvert F_\mathrm{o}\rvert$	0.035/0.032
wR_2/Goodness of fit (GooF)	0.081/1.090
Extinction (g)	0.0023(2)
Residual electron density ($\rho/\mathrm{e^-\,10^6\,pm}$)	max: 2.20, min: −2.22

Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoteing the depository number CSD-412448.

3. Results and discussion

The structure of $\mathrm{CsTmCl_2[SeO_3]}$ is illustrated in Fig. 1. There are eight different unique atoms in the unit cell, all of which occupy the same general Wyckoff position (4e). The thulium cations have seven nearest neighbours (five oxygen, $d(\mathrm{Tm{-}O}) = 225{-}240$ pm and two chlorine atoms $d(\mathrm{Tm{-}Cl}) = 261$ pm) in an approximate pentagonal bipyramid $[\mathrm{TmO_5Cl_2}]$ with both chloride anions occupying the apical positions. Five oxygen atoms (one O1, two O2 and two O3) serve to fuse the $[\mathrm{TmO_5Cl_2}]$ polyhedra with four nearby selenate

Table 2
Atomic coordinates and anisotropic thermal displacement parameters for $\mathrm{CsTmCl_2[SeO_3]}$

Atom	x/a	y/b	z/c
Cs	0.19304(8)	0.20950(8)	0.94572(3)
Tm	0.11872(3)	0.32123(3)	0.25820(1)
Cl1	0.4854(3)	0.1895(3)	0.6101(1)
Cl2	0.1802(3)	0.3386(3)	0.4089(1)
Se	0.06818(8)	0.18288(8)	0.70761(3)
O1	0.2818(6)	0.1733(6)	0.7722(3)
O2	0.4194(6)	0.4958(6)	0.2366(3)
O3	0.4219(6)	0.1455(6)	0.2443(3)

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cs	285(2)	688(4)	393(3)	103(2)	120(2)	84(2)
Tm	112(1)	108(1)	299(2)	−4(1)	41(1)	0(1)
Cl1	386(9)	466(10)	288(8)	13(7)	53(7)	−44(8)
Cl2	254(8)	680(13)	313(8)	−75(8)	44(6)	−33(8)
Se	120(2)	157(3)	262(3)	5(2)	54(2)	0(2)
O1	92(17)	253(22)	333(23)	−11(16)	43(15)	−2(14)
O2	168(18)	124(18)	455(26)	26(17)	72(17)	42(15)
O3	141(17)	88(17)	604(29)	20(16)	101(18)	3(15)

Table 3
Selected interatomic distances (d/pm) and angles (∢/deg) for $\mathrm{CsTmCl_2[SeO_3]}$

Cs–O1	319.6	Tm–O1	227.2	Se–O1	166.2
Cs–O3	382.9			Se–O2	170.1
Cs–O2	407.7	Tm–O2	226.1	Se–O3	171.4
		Tm–O2′	239.9		
Cs–Cl1	345.0			O1–Se–O2	103.5
Cs–Cl1′	359.5	Tm–O3	225.1	O1–Se–O3	103.8
Cs–Cl1″	385.0	Tm–O3′	238.1	O2–Se–O3	90.2
Cs–Cl2	335.5	Tm–Cl1	260.6		
Cs–Cl2′	338.9	Tm–Cl2	261.1		
Cs–Cl2″	361.3				

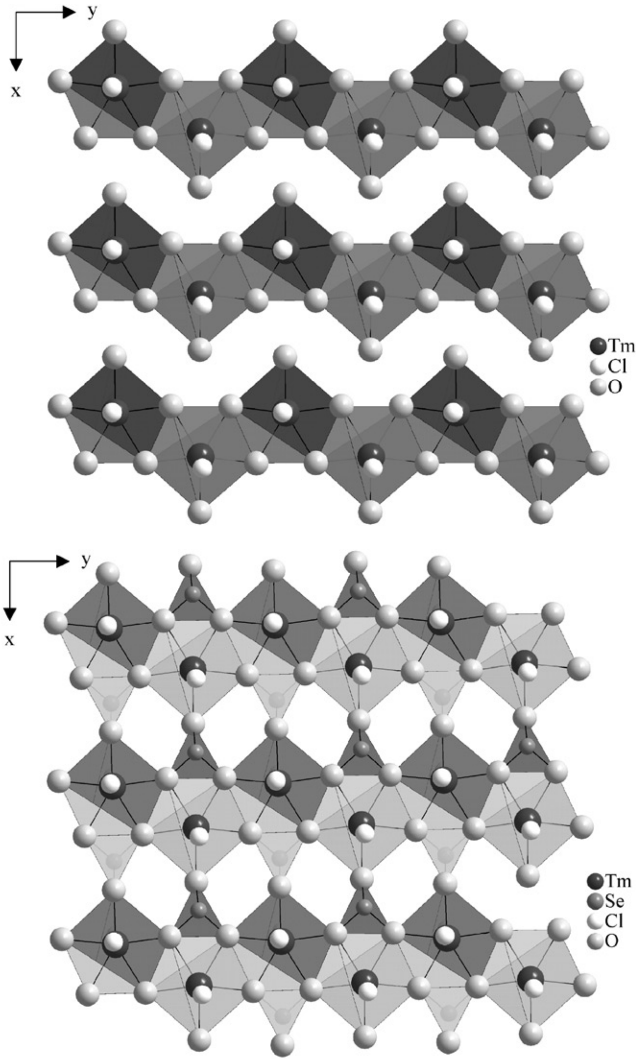

Fig. 1. Structure of $\mathrm{CsTmCl_2[SeO_3]}$ viewed along [001]; only the parallel ${}^1_\infty\{[\mathrm{TmO_3Cl_2}]^{5-}\}$ chains (*above*) and the corresponding ${}^2_\infty\{[\mathrm{TmCl_2(SeO_3)}]^{2-}\}$ layers (*below*) are represented.

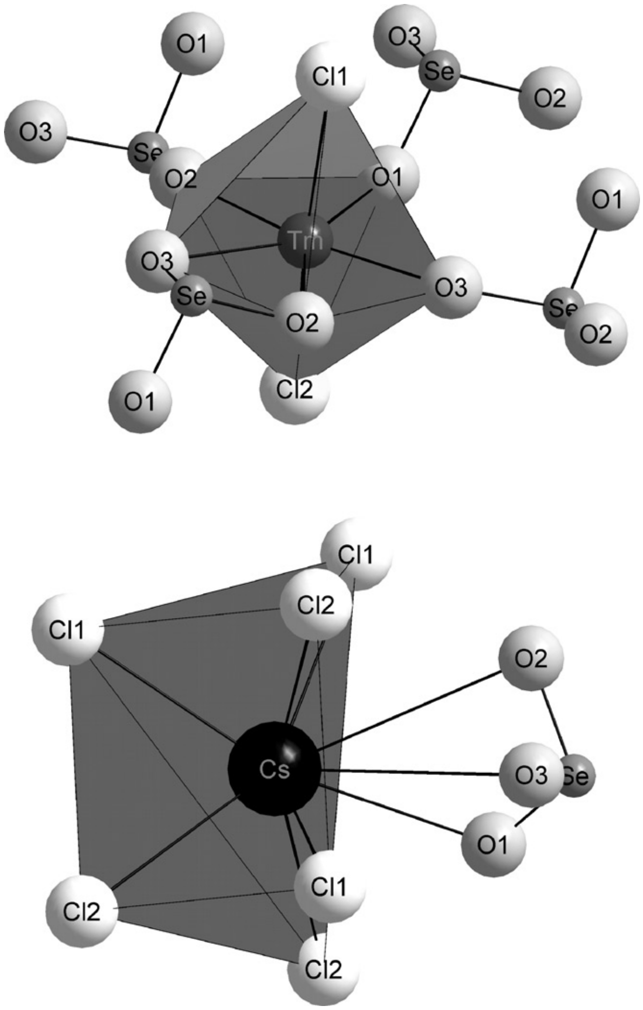

Fig. 2. Pentagonal bipyramid of oxygen and chlorine about $\mathrm{Tm^{3+}}$ showing four attached $[\mathrm{SeO_3}]^{2-}$ groups (*above*), and distorted tricapped trigonal prism coordination of oxygen and chlorine about $\mathrm{Cs^+}$ (*below*) in $\mathrm{CsTmCl_2[SeO_3]}$.

(IV) groups via edge and corner sharing (Fig. 2, *above*). The caesium cation is ninefold coordinated in the shape of a tricapped trigonal prism. The caps are consisting only of the three oxygen atoms of one single selenate group located approximately normal to a rectangular face of the prism (Fig. 2, *below*). This coordination sphere is smaller compared to that one observed in e.g., $\mathrm{CsTe_2O_6}$ (CN = 18, $d(\mathrm{Cs{-}O}) = 315\,\mathrm{pm}\ (6\times) + 370\,\mathrm{pm}\ (12\times)$) [17], but this can be explained by the fact that six large $\mathrm{Cl^-}$ anions are involved. The $[\mathrm{SeO_3}]^{2-}$ groups adopt their usual Ψ^1 pyramidal geometry ($d(\mathrm{Se{-}O}) = 166{-}172\,\mathrm{pm}$) with the $\mathrm{Se^{4+}}$ lone-pair electrons presumably occupying the fourth tetrahedral vertex. The O–Se–O bond angles show a few particular distortions (values of 90° for the O2–Se–O3 angle versus 104° for the O1–Se–O2 and O1–Se–O3 ones) but are well within the range observed for the above-mentioned selenates (IV). Furthermore, five cations (three $\mathrm{Tm^{3+}}$ terminal, one $\mathrm{Tm^{3+}}$ and one $\mathrm{Cs^+}$ edge-spanning each) complete the coordination sphere about the trigonal pyramidal $[\mathrm{Se(O1)(O2)(O3)}]^{2-}$ anion (Fig. 3) and the distance between the central cation of the pyramid ($\mathrm{Se^{4+}}$) and the plane containing O1, O2, O3 is about 80 pm. The main structural feature in $\mathrm{CsTmCl_2[SeO_3]}$ emphasizes either chains or layers which contain $[\mathrm{TmO_5Cl_2}]$ polyhedra and all selenium atoms, interleaved with caesium layers. The packing of these polyhedral building units which can be visualized in terms of parallel infinite anionic zigzag strands ${}^1_\infty\{[\mathrm{TmO^{e}_{4/2}O^{t}_{1/1}Cl^{t}_{2/1}}]^{5-}\}(\equiv {}^1_\infty\{[\mathrm{TmO_3Cl_2}]^{5-}\})$ propagating parallel to the [010] direction (Fig. 1, *above*). The $[\mathrm{SeO_3}]^{2-}$ groups are grafted onto the $[\mathrm{TmO_5Cl_2}]$ polyhedra, linking different ${}^1_\infty\{[\mathrm{TmO_3Cl_2}]^{5-}\}$ strands via one edge (O2–O3) and one vertex (O1) to form layers parallel to the (001) plane such that a two-dimensional framework described as ${}^2_\infty\{[\mathrm{TmCl_2(SeO_3)}]^{2-}\}$ formed

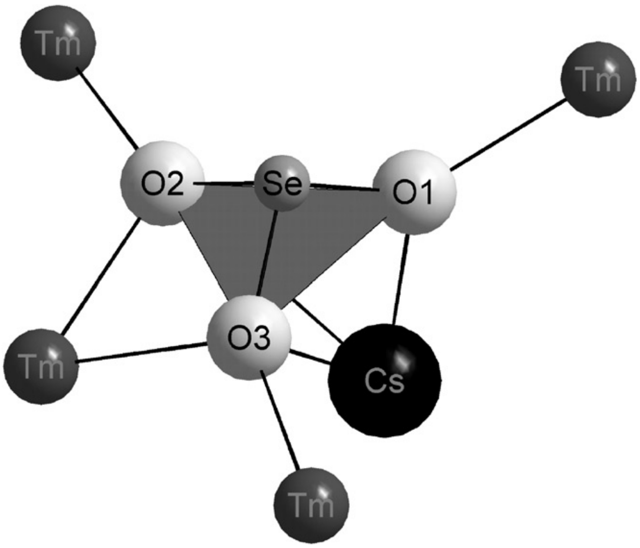

Fig. 3. Coordination sphere about the trigonal pyramidal $[SeO_3]^{2-}$ anion consisting of five cations (four Tm^{3+} and one Cs^+).

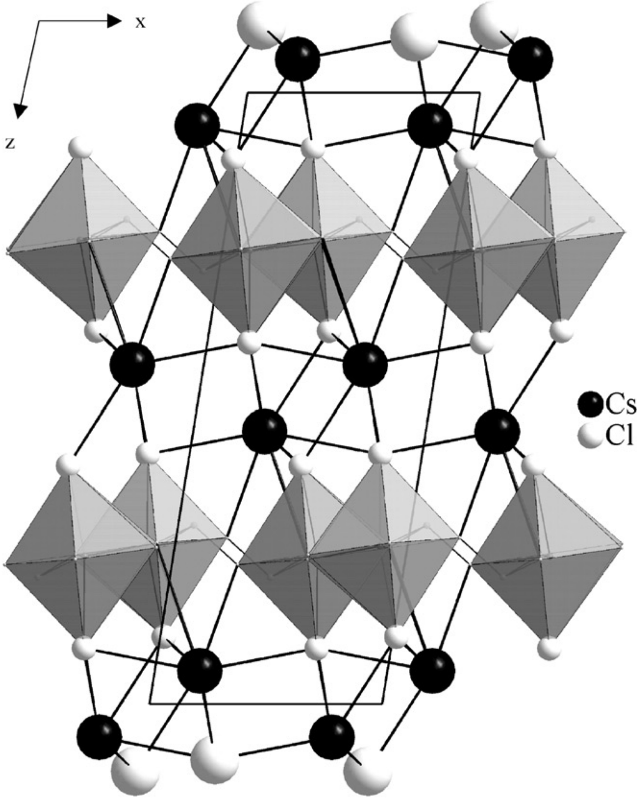

Fig. 4. Packing diagram of $CsTmCl_2[SeO_3]$ viewed down [010] in a $[TmO_5Cl_2]$ polyhedra representation. Caesium and chlorine atoms are represented by spheres of an arbitrary radius.

by complex chains is observed (Fig. 1, *below*). The layers built up by the pentagonal bipyramids $[TmO_5Cl_2]$ and the $[SeO_3E]$ tetrahedra, exhibit remarkable similarities with the one formed by the bicapped trigonal prisms $[MO_8]$ (M= Nd, Sm) and analogous $[SeO_3E]$ groups in the crystal structures of $Nd(HSeO_3)(SeO_3) \cdot 2H_2O$ [18] and $Sm(HSeO_3)(SeO_3) \cdot 2H_2O$ [19]. This sharing of edges and corners with the $[SeO_3]^{2-}$ groups was previously observed in $CuLa_2[SeO_3]_4$ and $NaLa[SeO_3]_2$ as well, with the difference that only half of the selenium atoms in the latter are located within the sheets [7, 8]. The O2 and O3 that fuse $[SeO_3E]$ groups with the $[TmO_5Cl_2]$ polyhedra via an edge are at a distance of 238 and 240 pm, respectively, apart from the Tm^{3+} cations, whereas O1 that bridges the two groups via a vertex is only 227 pm away, indicating a strong association between the parallel chains along [001] (Fig. 1, *below*). Half of the selenium atoms in $CsTmCl_2[SeO_3]$ have their lone-pair electrons oriented above the anionic layer and the other half below it for centrosymmetric reasons. The position of the Cs^+ cations when connecting neighbouring layers along the c direction is essentially the same as the one of Na^+ in $NaLa[SeO_3]_2$ (see Fig. 4 compare to Fig. 4 in Ref. [8]).

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