

NdClSeO₃ and ErClSeO₃: First Chloride-Selenites of the Rare Earth Elements

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Dedicated to Professor Albrecht Mewis on the occasion of his 60th birthday

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Violet single crystals of NdClSeO₃ (*Pnma*, $Z = 8$, $a = 1115.3(2)$, $b = 535.19(6)$, $c = 1356.8(1)$ pm, $R_{\text{all}} = 0.0281$) were obtained from the reaction of Nd₂O₃, NdCl₃, and SeO₂ in evacuated silica ampoules. The analogous procedure using Er₂O₃ and ErCl₃ led to pink single crystals of ErClSeO₃ (*Pnma*, $Z = 4$, $a = 721.8(1)$, $b = 692.2(1)$, $c = 874.3(2)$ pm, $R_{\text{all}} = 0.0305$). The crystal structure of NdClSeO₃ contains two crystallographically different neodymium ions. Nd(2)³⁺ is coordinated by four oxygen atoms and four chloride ions while eight oxygen atoms and one Cl⁻ ion are connected to Nd(1)³⁺. The linkage of the polyhedra leads to a three-dimensional structure. In the structure of ErClSeO₃ the Er³⁺ ion is coordinated by two Cl⁻ ions, three O-monodentate SeO₃²⁻ and one O,O-chelating SeO₃²⁻ groups. The [ErO₅Cl₂] polyhedra can be seen as pentagonal bipyramids, which are connected in the [010] direction *via* opposite edges of oxygen atoms to infinite chains. These are further linked *via* chloride ions to give a three-dimensional network. In both crystal structures a prominent stereochemical activity of the lone electron pairs of the selenite ions can be observed.

Introduction

Besides the fundamental crystal chemical interest on selenites of rare earth elements these compounds have attracted attention because they often crystallize with acentric space groups and thus are candidates to show unique physical properties. Among the compounds known so far the number of acentric crystal structures is higher for the mixed anionic species. The fluoride selenites M₃(SeO₃)₄F (M = Nd, Sm, Gd) (space group *P6₃mc*) [1], the acidic perchlorate selenite (H₃O)Nd(HSeO₃)(SeO₃)(ClO₄) (space group *P2₁*) [2] and the diselenite nitrate Y(Se₂O₅)(NO₃) (space group *P2₁2₁2₁*) [3] may serve as examples. The existence of acentric fluoride selenites encouraged us to investigate also chloride selenites. Recently, Oppermann *et al.* reported the phase diagram of the system SmOCl/SeO₂. According to these investigations three compounds exist, namely SmClSeO₃, SmClSe₂O₅, and SmSe₃O₇Cl [4]. They have been prepared *via* solid state reactions of SmOCl and SeO₂ and characterized by means of X-ray powder diffraction and IR spectroscopy. However, crystal

structures are not known up to now. This is also true for the compounds of the other rare earth elements, whereas the chloride selenite of trivalent bismuth, BiClSeO₃, has been shown to be trimorphic [5]. Only one of these phases (α -BiClSeO₃) has been characterized and shown to exhibit acentric symmetry (orthorhombic, space group *P2₁2₁2₁*) and a strong SHG effect [6]. Furthermore, the structures of several oxide chloride selenites have been reported recently, namely M₃O₂Cl(SeO₃)₂ (M = Tb, Er) [7], Tb₅O₄Cl₃(SeO₃)₂ [8], M₄O₃Cl₂(SeO₃)₂ (M = Tb, Er) and Sm₉O₈Cl₃(SeO₃)₄ [9]. Our attempts to prepare chloride selenites now afforded NdClSeO₃ and ErClSeO₃ in single crystalline form so that structural data can be given here for the first time.

Experimental Section

The chlorides NdCl₃ and ErCl₃ were obtained according to literature procedures [10]. The chloride selenites NdClSeO₃ and ErClSeO₃ can be prepared in single phase form by the reaction of the respective chlorides, oxides and SeO₂ in the appropriate molar ratio. The formation of

Compound	NdClSeO ₃	ErClSeO ₃
Lattice parameter	<i>a</i> = 1115.3(2) pm <i>b</i> = 535.19(6) pm <i>c</i> = 1356.8(1) pm	<i>a</i> = 721.8(1) pm <i>b</i> = 692.2(1) pm <i>c</i> = 874.3(1) pm
Molar volume	61.0 cm ³ /mol	65.8 cm ³ /mol
No. of formula units	8	4
Crystal system	orthorhombic	orthorhombic
Space group	<i>Pnma</i> (No. 62)	<i>Pnma</i> (No. 62)
Measuring device	Stoe IPDS I	Stoe IPDS I
Radiation	Mo-K _α (graphite monochrom., λ = 71.07 pm)	
Temperature	20 °C	20 °C
Theta range	5° < 2θ < 54°	5° < 2θ < 56°
Index range	-14 ≤ <i>h</i> ≤ 14, -7 ≤ <i>k</i> ≤ 7, -17 ≤ <i>l</i> ≤ 17	-9 ≤ <i>h</i> ≤ 9, -8 ≤ <i>k</i> ≤ 9, -11 ≤ <i>l</i> ≤ 11
Rotation angle; φ increment	0° < φ < 250°; 2°	0° < φ < 200°; 2°
No. of exposures	125	100
Exposure time	5 min	5 min
Detector distance	60	60
Data corrections	Polarization and Lorentz factors	
Absorption correction	numerical [14]	
μ	230.9 cm ⁻¹	280.0 cm ⁻¹
Measured reflections	8538	3852
Unique reflections	979	569
— with <i>I</i> ₀ > 2σ(<i>I</i>)	854	500
No. of variables	68	35
<i>R</i> _{int}	0.0797	0.0619
Structure determinations	SHELXS-86 und SHELXL-93 [15]	
Scattering factors	Intern. Tables, Vol. C [16]	
Extinction coefficient	0.0054(3)	0.031(2)
Goodness of fit (obs/all)	1.027/0.980	1.223/1.169
<i>R</i> ₁ ; <i>wR</i> ₂ (<i>I</i> ₀ > 2σ(<i>I</i>))	0.0225; 0.0523	0.0250; 0.0668
<i>R</i> ₁ ; <i>wR</i> ₂ (all data)	0.0281; 0.0509	0.0305; 0.0684
Min./max. electron density/eÅ ⁻³	-1.234/1.041	-1.694/1.773
Deposition number	CSD 412754	CSD 412755

Table 1. Crystallographic data and their determination.

Table 2. Atomic positions and equivalent displacement parameters (in pm²) for NdClSeO₃.

Atom	Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} · 10 ⁻¹
Nd1	4c	0.57067(3)	1/4	0.40022(3)	9.6(1)
Nd2	4c	0.42911(3)	1/4	0.14447(3)	9.6(1)
Se1	4c	0.75915(6)	1/4	0.97100(5)	8.5(2)
O11	8d	0.2581(3)	0.9946(7)	0.1090(3)	11.7(7)
O12	4c	0.9143(3)	1/4	0.9739(4)	15(1)
Se2	4c	0.65344(6)	1/4	0.68323(5)	8.8(2)
O21	8d	0.4421(3)	0.9966(7)	0.2923(3)	12.7(7)
O22	4c	0.6574(4)	1/4	0.5607(4)	16(1)
Cl1	4c	0.4774(2)	1/4	0.9303(1)	15.6(4)
Cl2	4c	0.6692(1)	1/4	0.2025(1)	14.8(4)

$$U_{\text{eq}} = \frac{1}{3}[U_{11} + U_{22} + U_{33}] \text{ [17].}$$

single crystals is enhanced when an excess of the trichlorides is used as flux. The mixtures of the educts were sealed in silica tubes which were placed in a furnace. The temperature was raised to 300 °C with 20 °/h and then held for 24 h. Finally, the furnace was heated to 800 °C

Table 3. Selected distances (pm) and angles (degrees) for NdClSeO₃.

Nd1-O22	238.2(5)	Se1-O11 (2×)	171.1(4)
Nd1-O12	244.2(5)	Se1-O12	173.1(5)
Nd1-O21 (2×)	245.7(4)		
Nd1-O11 (2×)	250.1(3)	Se2-O21 (2×)	172.9(4)
Nd1-O12 (2×)	286.1(2)	Se2-O22	166.4(5)
Nd1-Cl2	289.9(2)		
Nd2-O11 (2×)	239.5(3)	Nd2-Cl1-Nd2 (2×)	112.94(4)
Nd2-O21 (2×)	242.6(4)	Nd2-Cl1-Nd2	122.96(6)
Nd2-Cl2	279.1(2)		
Nd2-Cl1	295.6(2)	Nd2-Cl2-Nd1	84.12(5)
Nd2-Cl1 (2×)	304.5(1)		

and slowly (5 °C/h) cooled to 30 °C. The chloride selenites show the color of the respective rare earth ion, *e. g.* violet for Nd and pink for Er. The compounds are sensitive to moisture and turn cloudy after a while when exposed to air. Single crystals have been selected in a glove box and mounted into glass capillaries. The reflection intensities were collected on an image plate diffractometer

Table 4. Atomic positions and equivalent displacement parameters (in pm²) for ErClSeO₃.

Atom	Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} · 10 ⁻¹
Er	4c	0.10522(6)	1/4	0.46012(5)	10.9(2)
Cl	4c	0.4411(4)	1/4	0.3168(1)	24.0(6)
Se1	4c	0.7100(1)	1/4	0.6336(1)	12.2(2)
O11	4c	0.2523(12)	1/4	0.6792(9)	22(1)
O12	8d	0.8576(8)	0.0731(7)	0.5684(7)	17(1)

$$U_{\text{eq}} = \frac{1}{3}[U_{11} + U_{22} + U_{33}] \text{ [17].}$$

Table 5. Selected distances (pm) and angles (degrees) for ErClSeO₃.

Er-O11	219.1(9)	Se1-O11	166.5(8)
Er-O12 (2×)	226.6(5)	Se1-O12 (2×)	172.1(5)
Er-O12 (2×)	236.4(5)		
Er-Cl1	269.5(3)	Er-Cl-Er	143.4(1)
	273.3(5)		

and the structure determination was successful in space group *Pnma* for both compounds. Details of the data collection and the crystallographic data are summarized in Tables 1 - 5.

Results and Discussion

In contrast to α -BiClSeO₃ the chloride selenites NdClSeO₃ and ErClSeO₃ crystallize with the centric space group *Pnma*. In the crystal structure of NdClSeO₃ two crystallographically different neodymium ions, Nd(1)³⁺ and Nd(2)³⁺, are present, both of them located on the special site *4c* of space group *Pnma*. Nd(1)³⁺ is coordinated by eight oxygen atoms and one Cl⁻ ion. The coordination polyhedron can be described as a distorted tricapped trigonal prism. Within the prism the bond lengths Nd(1)-O range from 238 to 250 pm, the distances to the capping oxygen atoms (O12) and the chloride cap (Cl1) are 286 (2×) and 290 pm, respectively (Table 3, Fig. 1a). The [Nd(1)O₈Cl] polyhedra are connected *via* common *cis*-edges (O12-O12') to *zig-zag* chains along [010] (Fig. 2a). Nd(2)³⁺ is surrounded by four oxygen atoms and just as many chloride ions in form of a distorted square antiprism (Fig. 1b). The bond lengths show typical values of 240 (2×) and 243 (2×) pm for Nd-O and 279, 296 and 305 (2×) pm for Nd-Cl (Table 3). Similar to the [Nd(1)O₈Cl] prisms, the [Nd(2)Cl₄O₄] polyhedra are linked to *zig-zag* chains in [010] direction *via* common *cis*-edges (Cl1-Cl1') (Fig. 2b). The different chains are connected by edges of oxygen atoms

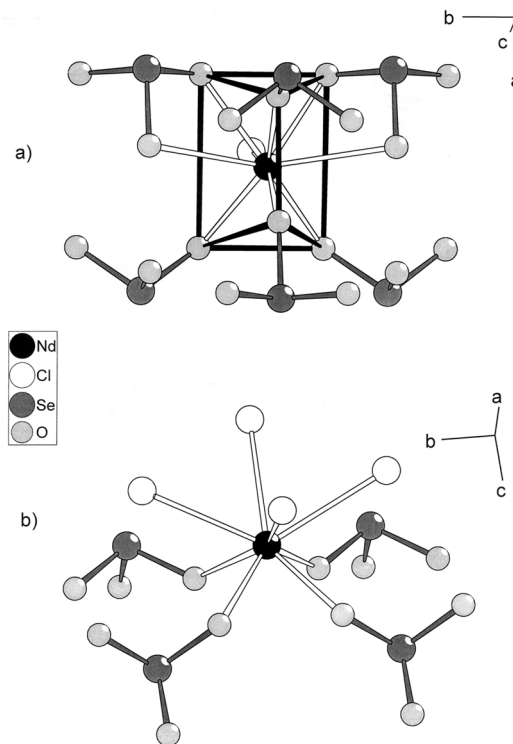


Fig. 1. Coordination of the Nd³⁺ ions in the crystal structure of NdClSeO₃. The trigonal prismatic coordination polyhedron of Nd(1)³⁺ (a) is emphasized with black lines; the three rectangular faces of the prism are capped by two oxygen atoms and a Cl⁻ ion. Nd(2)³⁺ (b) is surrounded by four Cl⁻ and four oxygen ligands in form of a square antiprism.

(O11-O11') in [100] direction as well as by triangular faces (O21-O21'-Cl2) along [001] (Fig. 3). The face linkage leads to a quite short Nd(1)-Nd(2) distance of 381 pm. The eight oxygen atoms of the Nd(1) polyhedron belong to six selenite groups, two of them being attached in a chelating manner whereas the four oxygen atoms of [Nd(2)O₄Cl₄] are donated by four monodentate selenite ions. When viewed along the [010] direction the stereochemical activity of the lone pair of the *pseudo*-tetrahedral SeO₃²⁻ ion is obvious (Fig. 3). The lone pairs are located in channels which are oriented in the same direction. The distances of the selenium atom to the opposite chloride ions are about 330 pm, while the shortest distance Nd-Se is 342 pm.

ErClSeO₃ is also orthorhombic but compared to the neodymium compound it shows a much smaller unit cell, due to the presence of only one Er³⁺, Cl⁻ and SeO₃²⁻ ion in the asymmetric unit. ErClSeO₃

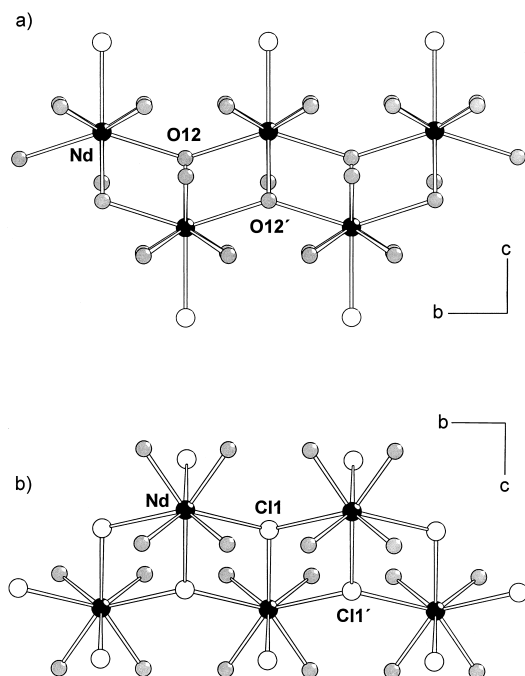


Fig. 2. Linkage of the [Nd(1)O₈Cl] (a) and the [Nd(2)O₄Cl₄] polyhedra (b) to chains along the [010] direction in the crystal structure of NdClSeO₃.

is isotopic with the recently described chloride tellurite HoClTeO₃ [11]. Isotypism of rare earth selenites and tellurites is very rare due to the tendency of Te⁴⁺ to reach higher coordination numbers. For example the selenites M₂Se₃O₉ show discrete SeO₃²⁻ ions corresponding to M₂(SeO₃)₃ [12] while in M₂Te₃O₉ type compounds extended Te-O arrays are found with coordination numbers up to five for Te⁴⁺ [13]. In the crystal structure of ErClSeO₃ the Er³⁺ ion is coordinated by five oxygen atoms with distances Er-O ranging from 219 to 236 pm and two chloride ligands at 270 and 273 pm, respectively (Table 5). The polyhedron [ErO₅Cl₂] is best regarded as a pentagonal bipyramid with the oxygen atom O11 and a chloride ion at the apices (Fig. 4a). The linkage of the polyhedra occurs in [010] direction *via* opposite edges O12-O12' leading to infinite chains (Fig. 4b) which are themselves connected *via* chloride ions to a three-dimensional network (Fig. 5). The oxygen atoms within the [ErO₅Cl₂] polyhedron belong to three monodentate and one chelating SeO₃²⁻ ions. Crystallographically there is only one selenite group so that the monodentate ions are chelating and the

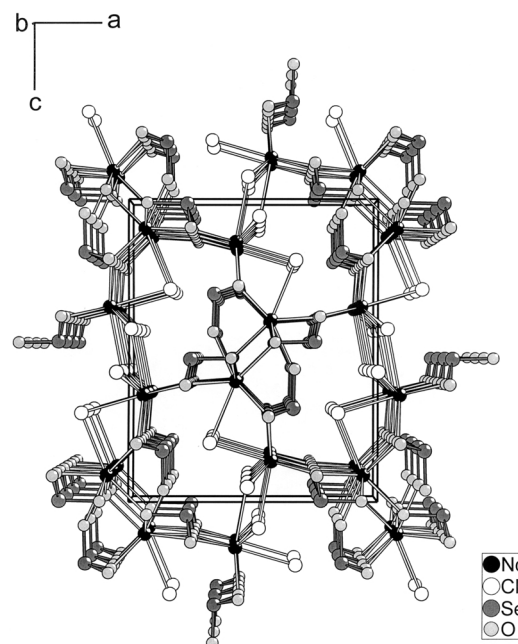


Fig. 3. Perspective view of the crystal structure of NdClSeO₃ in the direction of the chains shown in Fig. 2 ([010]). The empty space near the selenium atoms can be attributed to the stereochemical activity of the lone pairs of electrons.

chelating ones are monodentate to the adjacent polyhedra.

The lower coordination number of Er³⁺ (lanthanide contraction) in ErClSeO₃ compared to Nd³⁺ in NdClSeO₃ leads also to a smaller coordination number of the anions. In NdClSeO₃ the Cl⁻ ions are connected to three and two, the selenite groups to five metal ions. In the erbium compound there is only one two-coordinated chloride ion and the SeO₃²⁻ group is connected to only four Er³⁺ ions.

On the other hand there is a certain similarity between the crystal structures of ErClSeO₃ and α-BiClSeO₃. This is not only reflected by the comparable lattice parameters but also by structural features. Analogous to the erbium compound Bi³⁺ is coordinated by five oxygen and two chloride ligands in form of a pentagonal bipyramid. However, in contrast to the former both Cl⁻ ions are located within the equatorial plane of the polyhedron which features a severe distortion due to the lone electron pair of Bi³⁺.

The main interest of further investigations will focus on the structural characterization of the

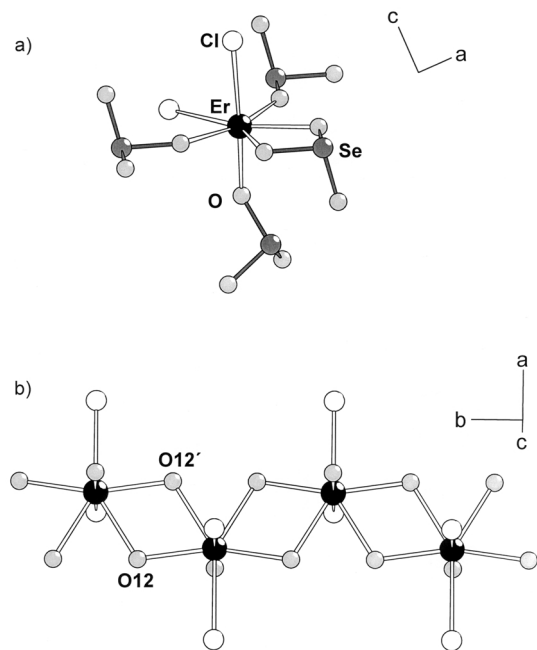


Fig. 4. Coordination of Er³⁺ in the crystal structure of ErClSeO₃ (a). The coordination polyhedron is a pentagonal bipyramid with an oxygen atom and a Cl⁻ ion at the apices; the oxygen atoms belong to three monodentate and one chelating selenite groups; linkage of the polyhedra leads *via* common edges to infinite chains in [010] direction (b).

MClSeO₃ type chloride selenites of the remaining parts of the lanthanide series and on the preparation of single crystals also for the SeO₂ rich species

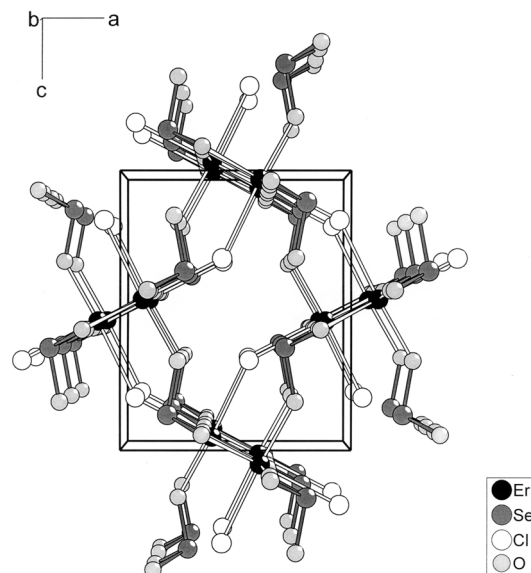


Fig. 5. Perspective view of the crystal structure of ErClSeO₃ along [010]; in this structure the linkage of the chains also provides voids to accommodate the lone pairs of electrons of the selenium atoms.

SmClSe₂O₅ and SmClSe₃O₇ reported by Oppermann.

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