



Crystal structure of $\text{Cs}_2\text{GdNb}_6\text{Cl}_{15}\text{O}_3$ in the structural evolution of niobium oxychlorides with octahedral Nb_6 -cluster units

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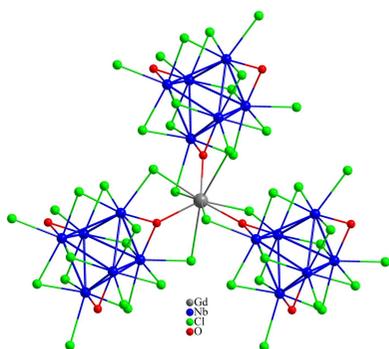
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$\text{Cs}_2\text{GdNb}_6\text{Cl}_{15}\text{O}_3$, dicaesium gadolinium hexaniobium pentadecachloride trioxide, was synthesized by solid-state reactions starting from a stoichiometric mixture of CsCl , Gd_2O_3 , Nb , NbCl_5 , and Nb_2O_5 . The crystal structure is based on octahedral Nb_6 cluster units (point group symmetry 3.2) with composition $[(\text{Nb}_6\text{Cl}_9^i\text{O}_3^a)\text{Cl}_6^a]^{5-}$ where i and a denote inner and outer ligands. $\text{Cs}_2\text{GdNb}_6\text{Cl}_{15}\text{O}_3$ exhibits 14 valence electrons per cluster unit. The cluster units are linked to each other by Cs^I and Gd^{III} atoms, whereby Cs^I (site symmetry 3..) is 12-coordinated by six Cl^i and six Cl^a ligands belonging to six neighboring cluster units and Gd^{III} (site symmetry 3.2) is 9-coordinated by three O^i and six Cl^i ligands belonging to three adjacent cluster units. The arrangement of cluster units corresponds to a stacking of ...AA'A... layers along [001]. $\text{Cs}_2\text{GdNb}_6\text{Cl}_{15}\text{O}_3$ is isotypic with $\text{Cs}_2\text{UNb}_6\text{Cl}_{15}\text{O}_3$.

1. Chemical context

Transition-metal clusters have high potentials and synergetic effects in the fields of biotechnology, catalysis, or sensor applications (Nguyen *et al.*, 2022). The use of these clusters as supramolecular building units is advantageous because of their unique structural, chemical and physical properties (Zhou & Lachgar, 2007). For example, charge-transfer (CT) solids with an anti-perovskite crystal structure have been derived from molybdenum cluster units by electro-crystallization (Hiramatsu *et al.*, 2015), or octahedral cluster units of niobium have been widely used as raw materials for the preparation of novel compounds with interesting structures and magnetic properties (Naumov *et al.*, 2003; Zhang *et al.*, 2011).

A large number of binary, ternary and quaternary niobium compounds with octahedral clusters based on the $[\text{Nb}_6L^i_{12}L^a_6]$ unit (L = halogen or oxygen ligands) have been reported previously (Perrin *et al.*, 2001). In this cluster unit, the edge of the Nb_6 octahedron is bridged by twelve inner ligands (L^i) while the other six outer ligands (L^a) are located at apical positions (Schäfer & von Schnering, 1964). The number of electrons involved in the formation of metal–metal bonds in the cluster is called the valence electron count (VEC). The ideal VEC value per cluster is 16 for chloride compounds and 14 for oxide compounds. In chlorides, the cluster units are interlinked by involving outer ligands (Perrin, 1997), whereas in oxides, the connectivity between the units is achieved through the inner ligands (Köhler *et al.*, 1991).



Mixing of halogen and oxygen as ligands for Nb₆ cluster compounds is a very interesting topic for in-depth studies to enrich our knowledge about new materials and their physical and chemical properties. It has been reported that the structural, magnetic and electronic properties of octahedral clusters of niobium oxychlorides are influenced by oxygen ligands (Fontaine *et al.*, 2011). In this respect, preparation and characterization of new oxychloride compounds with octahedral Nb₆ clusters were reported by Perrin *et al.* with one Oⁱ (Cordier *et al.*, 1996), two Oⁱ (Gulo & Perrin, 2000), three Oⁱ (Cordier *et al.*, 1994, 1997; Gulo & Perrin, 2002), and six Oⁱ (Gulo *et al.*, 2001) ligands per cluster unit. Other oxychloride compounds containing four Oⁱ (Anokhina *et al.*, 1998, 2000) and six Oⁱ (Anokhina *et al.*, 2001) ligands per cluster unit are also known.

The niobium oxychloride compound Cs₂UNb₆Cl₁₅O₃ was synthesized and structurally characterized many years ago (Cordier *et al.*, 1997). We have now prepared a related compound with composition Cs₂GdNb₆Cl₁₅O₃ and have determined its crystal structure where gadolinium occupies the same position as uranium in the previous compound. In the current communication, the crystal structure, interatomic distances, and the role of monovalent and trivalent cations in Cs₂GdNb₆Cl₁₅O₃ are compared with other niobium oxychlorides containing octahedral Nb₆ clusters.

2. Structural commentary

The structure of Cs₂GdNb₆Cl₁₅O₃ is isotypic with Cs₂UNb₆Cl₁₅O₃ and displays the Nb₆ octahedron as the basic cluster motif. The asymmetric unit comprises seven sites: one Cs (site symmetry 3_{..}, multiplicity 4, Wyckoff letter *e*), one Gd (3.2, 2 *c*), one Nb (1, 12 *i*), one O (.2, 6 *h*) and three Cl (Cl1: 6 *h*; Cl2 12 *i*; Cl3: 12 *i*). Six symmetry-equivalent niobium atoms build up the octahedral cluster (centered at a position with site symmetry 3.2, 2 *a*). Each niobium atom is surrounded by one oxygen (O) inner-ligand, three chlorine (Cl1 and Cl2) inner-ligands, and one chlorine (Cl3) outer-ligand. Every edge of the

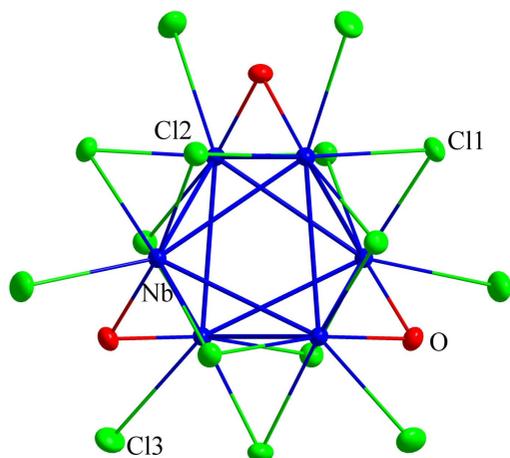


Figure 1
The $[(\text{Nb}_6\text{Cl}_9\text{O}_3)\text{Cl}_6]^{5-}$ unit in the crystal structure of Cs₂GdNb₆Cl₁₅O₃. Displacement ellipsoids are shown at the 60% probability level.

Nb₆ octahedron is bridged by a chlorine or oxygen ligand as inner-ligands, and six other chlorine ligands are attached in apical positions as outer ligands, as shown in Fig. 1. This cluster motif can be written as a developed unit, $[(\text{Nb}_6\text{Cl}_9\text{O}_3)\text{Cl}_6]^{5-}$.

The length of the intracuster Nb–Nb bonds range from 2.7686 (5) to 3.0317 (5) Å corresponding to the edge bridged by the Oⁱ and Clⁱ ligands, respectively; the average bond length is 2.954 Å. Thus, the Nb₆ octahedron undergoes distortions as observed in other niobium oxychloride compounds. The Nb–Nb distances in this compound are significantly shorter than those observed in other compounds containing two or fewer Oⁱ ligands but are significantly longer than those observed in compounds containing four or more Oⁱ ligands (Gulo & Perrin, 2012). In the various oxychloride compounds that have been isolated so far, it seems that an increase in the number of Oⁱ ligands per formula leads to a decrease in the length of intracuster Nb–Nb bonds. This difference is due to a stronger steric effect as observed, for example, in PbLu₃Nb₆Cl₁₅O₆ (Gulo *et al.*, 2001) with six Oⁱ ligands. Cs₂GdNb₆Cl₁₅O₃ has three Oⁱ ligands per cluster. They are localized at *trans*-inner positions relative to the Nb₆ cluster, similar to the arrangement of three Oⁱ ligands in Na_{0.21}Nb₆Cl_{10.5}O₃ where the cluster exhibits point group symmetry 3 (Gulo & Perrin, 2002). In contrast, the three Oⁱ ligands in ScNb₆Cl₁₃O₃ occupy a *cis*-inner position relative to the Nb₆ octahedron to produce a cluster motif with 2 symmetry (Cordier *et al.*, 1994). In the title compound, the Nb₆ clusters are arranged in (001) layers with an ...AA'A... stacking along [001] (Fig. 2).

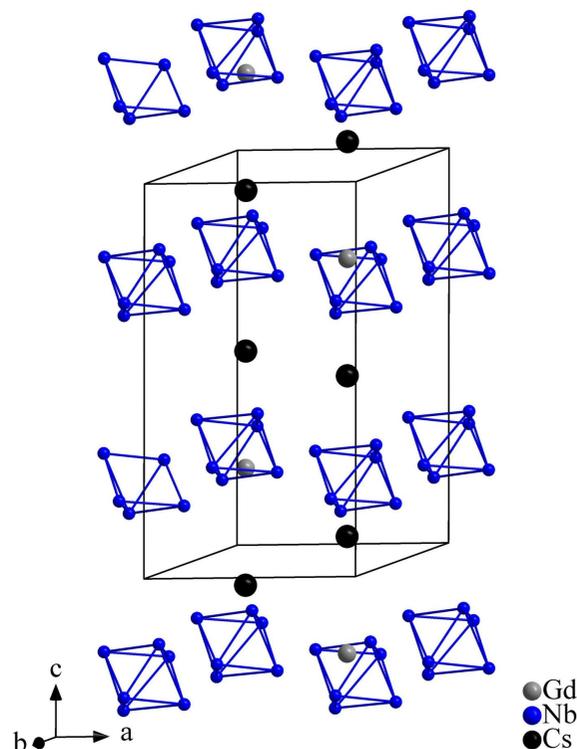


Figure 2
The ...AA'A... stacking of the Nb₆ clusters in the crystal structure of Cs₂GdNb₆Cl₁₅O₃. Cl and O atoms are omitted for clarity

The Nb—Clⁱ distances vary from 2.4543 (7) Å to 2.4802 (7) Å (average 2.468 Å) while the Nb—Cl^a bond is longer, 2.5728 (7) Å. In general, the Nb—L (L = O, Cl) bond lengths in Cs₂GdNb₆Cl₁₅O₃ are not significantly different from that of other niobium oxychloride compounds (Naumov *et al.*, 2003).

In the crystal structure of Cs₂GdNb₆Cl₁₅O₃, the [(Nb₆Clⁱ₉Oⁱ₃)Cl^a₆]⁵⁻ units are interconnected through the Cs^I and Gd^{III} atoms that are located in between the layers of Nb₆ clusters (Fig. 2). The existence of such discrete cluster units or the absence of intercluster connectivity has also been observed in PbLu₃Nb₆Cl₁₅O₆ (Gulo *et al.*, 2001) and Cs₂Ti₄Nb₆Cl₁₈O₆ (Anokhina *et al.*, 2001) where Nb₆-clusters likewise are formed by six symmetry-equivalent Nb atoms in contrast to CsNb₆Cl₁₂O₂ (Gulo & Perrin, 2000) where the Nb₆-octahedron is formed by three different Nb atoms. In the crystal structure of the latter, the cluster units are linked together via bridging O and Cl ligands.

The Gd^{III} atom in Cs₂GdNb₆Cl₁₅O₃ has a coordination number of 9, defined by three Oⁱ and six Cl^a ligands provided by three nearby cluster units (Fig. 3), with bond lengths of Gd—O = 2.322 (3) Å and Gd—Cl = 3.0994 (8) Å. In comparison, in the crystal structure of PbLu₃Nb₆Cl₁₅O₆, the Lu^{III} atom is surrounded by only six ligands, *viz.* two O and four Cl atoms, defining Lu₂Cl₂ entities (Gulo *et al.*, 2001). The Nb₆-clusters in PbLu₃Nb₆Cl₁₅O₆ connect to each other *via* these Lu₂Cl₂ entities whereby each cluster is surrounded by six Lu₂Cl₂ entities, and each of them bridging four adjacent clusters via O and Cl ligands. A related motif is found in Ti₂Nb₆Cl₁₄O₄ where Ti^{III} atoms form zigzag chains of edge-sharing [TiCl₄O₂] octahedra (Anokhina *et al.*, 2000). In other cases, the trivalent ions, such as Sc^{III} in ScNb₆Cl₁₅O₃ (Cordier *et al.*, 1994) or Ti^{III} in Cs₂Ti₃Nb₁₂Cl₂₇O₈ (Anokhina *et al.*, 2000), have a coordination number of five, defined by three O

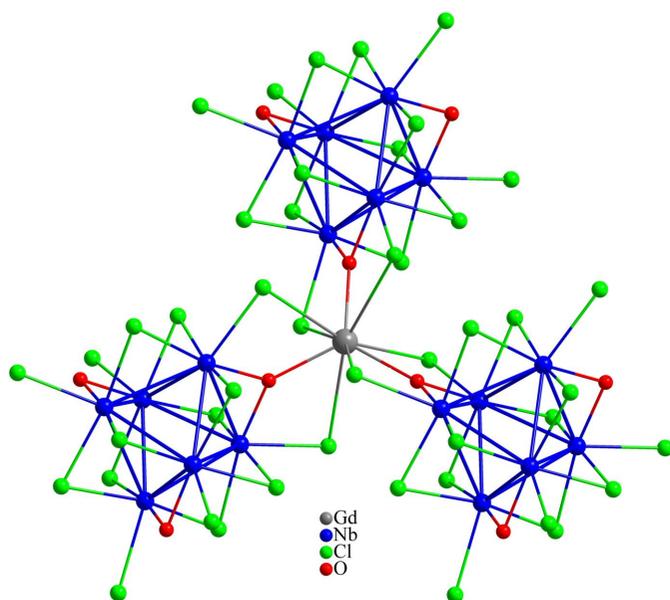


Figure 3
The environment of the Gd^{III} atom in Cs₂GdNb₆Cl₁₅O₃.

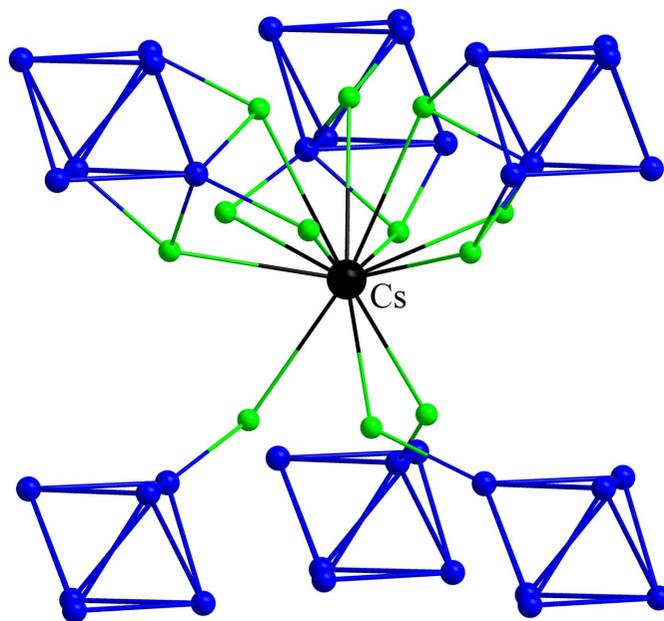


Figure 4
The environment of the Cs^I atom in Cs₂GdNb₆Cl₁₅O₃.

and two Cl ligands. In another case, the Gd^{III} atom in RbGdNb₆Cl₁₈ is octahedrally surrounded by six Cl ligands from six neighboring cluster units (Gulo *et al.*, 2023). In general, in the series of niobium oxychloride compounds containing octahedral Nb₆ clusters, the crystallographic sites associated with trivalent cations are always fully occupied and are surrounded by Cl and O ligands (Gulo & Perrin, 2012). Only in Cs₂GdNb₆Cl₁₅O₃ and the isotypic uranium analogue, the trivalent cation occupy the center of a triangle formed by three adjacent cluster units and are bonded to nine ligands.

In Cs₂GdNb₆Cl₁₅O₃, the monovalent Cs^I atom is surrounded by six Nb₆ clusters and coordinated by twelve Cl ligands (Fig. 4). The lengths of Cs—Cl bonds range from 3.5074 (8) to 3.9770 (6) Å. A similar environment around Cs is found in CsNb₆Cl₁₂O₂ with Cs—Cl distances between 3.330 (5) and 3.862 (4) Å (Gulo & Perrin, 2000). In contrast, the Cs^I atom in Cs₂LuNb₆Cl₁₇O is surrounded by four Nb₆-clusters and is bonded to twelve chlorine ligands with Cs—Cl distances in the range 3.567 (1) to 3.619 (1) Å (Cordier *et al.*, 1996). In RbGdNb₆Cl₁₈ with its smaller monovalent cation Rb^I, the coordination number is likewise 12. Here, the cation is surrounded also by four Nb₆ clusters, and the Rb—Cl bond lengths range from 3.471 (1) Å to 3.557 (2) Å with an average of 3.512 Å (Gulo *et al.*, 2023). The sites of monovalent cations encountered in the crystal structures of oxychlorides with Nb₆ clusters are always surrounded by Cl ligands with the exception of Cs₂LuNb₆Cl₁₇O where an O atom statistically occupies a site among the twelve inner ligands defining the coordination environment of Cs. On the other hand, the sites associated with the (large) monovalent cation often show partial occupancy. For example, in Na_{0.21}Nb₆Cl_{10.5}O₃, the corresponding Na site has an occupancy of only 42.6% (Gulo & Perrin, 2002) and the three Cs sites in Cs₂Ti₄Nb₆Cl₁₈O₆ have occupancies of 38.1%, 57.0% and 6.9% (Anokhina *et al.*, 2001).

Table 1

Experimental details.

Crystal data	
Chemical formula	Cs ₂ GdNb ₆ Cl ₁₅ O ₃
<i>M_r</i>	1560.28
Crystal system, space group	Trigonal, <i>P</i> $\bar{3}$ 1 <i>c</i>
Temperature (K)	293
<i>a</i> , <i>c</i> (Å)	9.1318 (1), 17.1558 (2)
<i>V</i> (Å ³)	1238.95 (3)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	9.83
Crystal size (mm)	0.08 × 0.07 × 0.05
Data collection	
Diffractometer	Nonius KappaCCD
Absorption correction	Multi-scan (<i>DENZO</i> and <i>SCALEPACK</i> ; Otwinowski & Minor, 1997)
<i>T</i> _{min} , <i>T</i> _{max}	0.004, 0.017
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	7607, 2020, 1790
<i>R</i> _{int}	0.026
(sin θ/λ) _{max} (Å ⁻¹)	0.833
Refinement	
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.029, 0.068, 1.15
No. of reflections	2020
No. of parameters	44
Δρ _{max} , Δρ _{min} (e Å ⁻³)	1.38, -1.35

Computer programs: *COLLECT* (Nonius, 1999), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2014), and *pubCIF* (Westrip, 2010).

The VEC in Cs₂GdNb₆Cl₁₅O₃ is 14 per cluster unit, as observed in most oxide (Köhler *et al.*, 1991) and oxychloride compounds (Gulo & Perrin, 2012). The number of Oⁱ ligands per cluster can affect the VEC value. Compounds containing one Oⁱ ligand (Cordier *et al.*, 1996) or two Oⁱ ligands (Gulo & Perrin, 2000) exhibit VEC values of 16 and 15. However, niobium oxychloride compounds containing three or more Oⁱ ligands per cluster unit have always a VEC of 14 per cluster unit.

3. Synthesis and crystallization

Cs₂GdNb₆Cl₁₅O₃ was prepared by solid-state reactions, starting from a stoichiometric mixture of CsCl (Prolabo, purity 99.5%), Gd₂O₃ (Rhône Poulenc), Nb₂O₅ (Merck, Optipur), NbCl₅ (Ventron, purity 99.998%) and niobium powder (Ventron, purity 99.8%). A total of 300 mg of the mixture was mashed and then loaded in a silica tube under argon atmosphere in a glove box. The silica tube sample was then sealed under vacuum condition. The sample was heated in a vertical heating furnace at 973 K for two days, followed by slow cooling to room temperature. Brown single crystals with a block-like form suitable for structural determination were obtained this way.

4. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The remaining maximum and minimum electron density peaks are located 0.19 Å from Nb and 0.54 Å from Cs, respectively.

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Computing details

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *COLLECT* (Nonius, 1999); data reduction: *COLLECT* (Nonius, 1999); program(s) used to solve structure: *SHELXT* (Sheldrick, 2015a); program(s) used to refine structure: *SHELXL* (Sheldrick, 2015b); molecular graphics: *DIAMOND* (Brandenburg, 2014); software used to prepare material for publication: *pubCIF* (Westrip, 2010).

(I)

Crystal data

Cs₂GdNb₆Cl₁₅O₃
M_r = 1560.28
 Trigonal, *P* $\bar{3}$ 1*c*
a = 9.1318 (1) Å
c = 17.1558 (2) Å
V = 1238.95 (3) Å³
Z = 2
F(000) = 1398

D_x = 4.182 Mg m⁻³
 Mo *K*α radiation, λ = 0.71073 Å
 Cell parameters from 25 reflections
 θ = 12–18°
 μ = 9.83 mm⁻¹
T = 293 K
 Block, brown
 0.08 × 0.07 × 0.05 mm

Data collection

Nonius KappaCCD
 diffractometer
 Radiation source: fine-focus sealed tube
 ω scans
 Absorption correction: multi-scan
 (DENZO and SCALEPACK; Otwinowski &
 Minor, 1997)
T_{min} = 0.004, *T_{max}* = 0.017

7607 measured reflections
 2020 independent reflections
 1790 reflections with *I* > 2σ(*I*)
R_{int} = 0.026
 θ_{max} = 36.3°, θ_{min} = 2.4°
h = -15→15
k = -12→12
l = -27→28

Refinement

Refinement on *F*²
 Least-squares matrix: full
R[*F*² > 2σ(*F*²)] = 0.029
wR(*F*²) = 0.068
S = 1.15
 2020 reflections
 44 parameters
 0 restraints
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
w = 1/[σ²(*F_o*²) + (0.0258*P*)² + 3.5848*P*]
 where *P* = (*F_o*² + 2*F_c*²)/3
 (Δ/σ)_{max} = 0.001
 Δρ_{max} = 1.38 e Å⁻³
 Δρ_{min} = -1.35 e Å⁻³
 Extinction correction: SHELXL2018/3
 (Sheldrick, 2015b),
*F_c** = k*F_c*[1 + 0.001*xFc*²λ³/sin(2θ)]^{-1/4}
 Extinction coefficient: 0.00259 (19)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cs	0.333333	0.666667	0.54654 (2)	0.02645 (9)
Gd	0.666667	0.333333	0.750000	0.01649 (8)
Nb	0.19768 (3)	0.01608 (3)	0.68239 (2)	0.01105 (7)
Cl1	0.21283 (6)	-0.21283 (6)	0.750000	0.01643 (17)
Cl2	0.01675 (8)	-0.20367 (8)	0.58643 (4)	0.01569 (12)
Cl3	0.47649 (9)	0.07637 (10)	0.61760 (5)	0.02252 (15)
O	0.3730 (3)	0.18650 (17)	0.750000	0.0142 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cs	0.02466 (12)	0.02466 (12)	0.03002 (19)	0.01233 (6)	0.000	0.000
Gd	0.00919 (9)	0.00919 (9)	0.03108 (19)	0.00460 (5)	0.000	0.000
Nb	0.00836 (10)	0.00944 (10)	0.01540 (12)	0.00448 (7)	0.00090 (7)	0.00034 (7)
Cl1	0.0149 (3)	0.0149 (3)	0.0233 (4)	0.0103 (3)	0.0031 (3)	0.0031 (3)
Cl2	0.0144 (3)	0.0143 (3)	0.0180 (3)	0.0068 (2)	0.0007 (2)	-0.0028 (2)
Cl3	0.0177 (3)	0.0231 (3)	0.0298 (4)	0.0125 (3)	0.0090 (3)	0.0033 (3)
O	0.0092 (10)	0.0139 (9)	0.0179 (13)	0.0046 (5)	0.000	-0.0004 (8)

Geometric parameters (\AA , $^\circ$)

Cs—Cl3 ⁱ	3.5074 (8)	Gd—Cl3	3.0994 (8)
Cs—Cl3 ⁱⁱ	3.5074 (8)	Gd—Cl3 ^{viii}	3.0994 (8)
Cs—Cl3 ⁱⁱⁱ	3.5074 (8)	Gd—Cl3 ^{vii}	3.0994 (8)
Cs—Cl3 ^{iv}	3.5180 (8)	Gd—Cl3 ^{ix}	3.0994 (8)
Cs—Cl3 ^v	3.5180 (8)	Gd—Cl3 ^x	3.0994 (8)
Cs—Cl3 ^{vi}	3.5180 (8)	Gd—Cl3 ⁱⁱⁱ	3.0994 (8)
Cs—Cl2 ⁱ	3.6948 (7)	Nb—O	1.9593 (19)
Cs—Cl2 ⁱⁱⁱ	3.6948 (7)	Nb—Cl1	2.4543 (7)
Cs—Cl2 ⁱⁱ	3.6948 (7)	Nb—Cl2 ⁱⁱ	2.4684 (7)
Cs—Cl1 ⁱⁱⁱ	3.9770 (6)	Nb—Cl2	2.4802 (7)
Cs—Cl1 ⁱⁱ	3.9770 (6)	Nb—Cl3	2.5728 (7)
Cs—Cl1 ⁱ	3.9770 (5)	Nb—Nb ^x	2.7686 (5)
Gd—O	2.322 (3)	Nb—Nb ^{xi}	3.0075 (4)
Gd—O ^{vii}	2.322 (3)	Nb—Nb ⁱⁱ	3.0075 (4)
Gd—O ⁱⁱⁱ	2.322 (3)	Nb—Nb ^{xii}	3.0317 (5)
Cl3 ⁱ —Cs—Cl3 ⁱⁱ	108.589 (15)	O ⁱⁱⁱ —Gd—Cl3 ^{vii}	80.189 (14)
Cl3 ⁱ —Cs—Cl3 ⁱⁱⁱ	108.589 (15)	Cl3—Gd—Cl3 ^{vii}	72.21 (2)

Cl3 ⁱⁱ —Cs—Cl3 ⁱⁱⁱ	108.589 (15)	Cl3 ^{viii} —Gd—Cl3 ^{vii}	98.06 (3)
Cl3 ⁱ —Cs—Cl3 ^{iv}	108.89 (2)	O—Gd—Cl3 ^{ix}	80.189 (13)
Cl3 ⁱⁱ —Cs—Cl3 ^{iv}	76.72 (2)	O ^{vii} —Gd—Cl3 ^{ix}	60.971 (13)
Cl3 ⁱⁱⁱ —Cs—Cl3 ^{iv}	137.786 (19)	O ⁱⁱⁱ —Gd—Cl3 ^{ix}	130.969 (15)
Cl3 ⁱ —Cs—Cl3 ^v	76.72 (2)	Cl3—Gd—Cl3 ^{ix}	98.06 (3)
Cl3 ⁱⁱ —Cs—Cl3 ^v	137.786 (19)	Cl3 ^{viii} —Gd—Cl3 ^{ix}	72.21 (2)
Cl3 ⁱⁱⁱ —Cs—Cl3 ^v	108.89 (2)	Cl3 ^{vii} —Gd—Cl3 ^{ix}	121.94 (2)
Cl3 ^{iv} —Cs—Cl3 ^v	62.55 (2)	O—Gd—Cl3 ^x	60.971 (13)
Cl3 ⁱ —Cs—Cl3 ^{vi}	137.786 (19)	O ^{vii} —Gd—Cl3 ^x	130.969 (14)
Cl3 ⁱⁱ —Cs—Cl3 ^{vi}	108.89 (2)	O ⁱⁱⁱ —Gd—Cl3 ^x	80.189 (14)
Cl3 ⁱⁱⁱ —Cs—Cl3 ^{vi}	76.72 (2)	Cl3—Gd—Cl3 ^x	121.94 (3)
Cl3 ^{iv} —Cs—Cl3 ^{vi}	62.55 (2)	Cl3 ^{viii} —Gd—Cl3 ^x	72.21 (2)
Cl3 ^v —Cs—Cl3 ^{vi}	62.55 (2)	Cl3 ^{vii} —Gd—Cl3 ^x	160.38 (3)
Cl3 ⁱ —Cs—Cl2 ⁱ	61.822 (15)	Cl3 ^{ix} —Gd—Cl3 ^x	72.21 (2)
Cl3 ⁱⁱ —Cs—Cl2 ⁱ	54.828 (15)	O—Gd—Cl3 ⁱⁱⁱ	80.189 (14)
Cl3 ⁱⁱⁱ —Cs—Cl2 ⁱ	148.77 (2)	O ^{vii} —Gd—Cl3 ⁱⁱⁱ	130.969 (14)
Cl3 ^{iv} —Cs—Cl2 ⁱ	69.076 (17)	O ⁱⁱⁱ —Gd—Cl3 ⁱⁱⁱ	60.971 (13)
Cl3 ^v —Cs—Cl2 ⁱ	97.986 (17)	Cl3—Gd—Cl3 ⁱⁱⁱ	72.20 (2)
Cl3 ^{vi} —Cs—Cl2 ⁱ	131.531 (19)	Cl3 ^{viii} —Gd—Cl3 ⁱⁱⁱ	121.94 (3)
Cl3 ⁱ —Cs—Cl2 ⁱⁱⁱ	54.828 (15)	Cl3 ^{vii} —Gd—Cl3 ⁱⁱⁱ	72.21 (2)
Cl3 ⁱⁱ —Cs—Cl2 ⁱⁱⁱ	148.77 (2)	Cl3 ^{ix} —Gd—Cl3 ⁱⁱⁱ	160.38 (3)
Cl3 ⁱⁱⁱ —Cs—Cl2 ⁱⁱⁱ	61.822 (15)	Cl3 ^x —Gd—Cl3 ⁱⁱⁱ	98.06 (3)
Cl3 ^{iv} —Cs—Cl2 ⁱⁱⁱ	131.531 (19)	O—Nb—Cl1	91.438 (10)
Cl3 ^v —Cs—Cl2 ⁱⁱⁱ	69.076 (18)	O—Nb—Cl2 ⁱⁱ	95.39 (2)
Cl3 ^{vi} —Cs—Cl2 ⁱⁱⁱ	97.986 (17)	Cl1—Nb—Cl2 ⁱⁱ	165.85 (2)
Cl2 ⁱ —Cs—Cl2 ⁱⁱⁱ	116.649 (8)	O—Nb—Cl2	169.99 (6)
Cl3 ⁱ —Cs—Cl2 ⁱⁱ	148.77 (2)	Cl1—Nb—Cl2	85.583 (18)
Cl3 ⁱⁱ —Cs—Cl2 ⁱⁱ	61.822 (15)	Cl2 ⁱⁱ —Nb—Cl2	85.58 (3)
Cl3 ⁱⁱⁱ —Cs—Cl2 ⁱⁱ	54.828 (15)	O—Nb—Cl3	75.97 (6)
Cl3 ^{iv} —Cs—Cl2 ⁱⁱ	97.986 (17)	Cl1—Nb—Cl3	85.14 (2)
Cl3 ^v —Cs—Cl2 ⁱⁱ	131.531 (19)	Cl2 ⁱⁱ —Nb—Cl3	84.52 (2)
Cl3 ^{vi} —Cs—Cl2 ⁱⁱ	69.076 (17)	Cl2—Nb—Cl3	94.24 (3)
Cl2 ⁱ —Cs—Cl2 ⁱⁱ	116.649 (8)	O—Nb—Nb ^x	45.05 (6)
Cl2 ⁱⁱⁱ —Cs—Cl2 ⁱⁱ	116.649 (8)	Cl1—Nb—Nb ^x	94.843 (15)
Cl3 ⁱ —Cs—Cl1 ⁱⁱⁱ	62.628 (14)	Cl2 ⁱⁱ —Nb—Nb ^x	98.75 (2)
Cl3 ⁱⁱ —Cs—Cl1 ⁱⁱⁱ	97.912 (19)	Cl2—Nb—Nb ^x	144.687 (16)
Cl3 ⁱⁱⁱ —Cs—Cl1 ⁱⁱⁱ	53.624 (14)	Cl3—Nb—Nb ^x	121.017 (19)
Cl3 ^{iv} —Cs—Cl1 ⁱⁱⁱ	168.335 (15)	O—Nb—Nb ^{xi}	137.22 (6)
Cl3 ^v —Cs—Cl1 ⁱⁱⁱ	119.844 (17)	Cl1—Nb—Nb ^{xi}	89.097 (14)
Cl3 ^{vi} —Cs—Cl1 ⁱⁱⁱ	129.093 (15)	Cl2 ⁱⁱ —Nb—Nb ^{xi}	94.227 (16)
Cl2 ⁱ —Cs—Cl1 ⁱⁱⁱ	99.332 (16)	Cl2—Nb—Nb ^{xi}	52.396 (17)
Cl2 ⁱⁱⁱ —Cs—Cl1 ⁱⁱⁱ	51.659 (16)	Cl3—Nb—Nb ^{xi}	146.53 (2)
Cl2 ⁱⁱ —Cs—Cl1 ⁱⁱⁱ	88.306 (13)	Nb ^x —Nb—Nb ^{xi}	92.291 (4)
Cl3 ⁱ —Cs—Cl1 ⁱⁱ	97.912 (19)	O—Nb—Nb ⁱⁱ	94.52 (4)
Cl3 ⁱⁱ —Cs—Cl1 ⁱⁱ	53.623 (14)	Cl1—Nb—Nb ⁱⁱ	139.044 (15)
Cl3 ⁱⁱⁱ —Cs—Cl1 ⁱⁱ	62.629 (14)	Cl2 ⁱⁱ —Nb—Nb ⁱⁱ	52.752 (17)
Cl3 ^{iv} —Cs—Cl1 ⁱⁱ	129.092 (15)	Cl2—Nb—Nb ⁱⁱ	93.982 (16)
Cl3 ^v —Cs—Cl1 ⁱⁱ	168.336 (16)	Cl3—Nb—Nb ⁱⁱ	135.56 (2)

Cl3 ^{vi} —Cs—Cl1 ⁱⁱ	119.844 (17)	Nb ^x —Nb—Nb ⁱⁱ	63.159 (10)
Cl2 ⁱ —Cs—Cl1 ⁱⁱ	88.305 (13)	Nb ^{xi} —Nb—Nb ⁱⁱ	60.0
Cl2 ⁱⁱⁱ —Cs—Cl1 ⁱⁱ	99.332 (16)	O—Nb—Nb ^{xii}	93.78 (4)
Cl2 ⁱⁱ —Cs—Cl1 ⁱⁱ	51.660 (16)	Cl1—Nb—Nb ^{xii}	51.856 (14)
Cl1 ⁱⁱⁱ —Cs—Cl1 ⁱⁱ	49.043 (19)	Cl2 ⁱⁱ —Nb—Nb ^{xii}	139.534 (16)
Cl3 ⁱ —Cs—Cl1 ⁱ	53.623 (14)	Cl2—Nb—Nb ^{xii}	91.888 (19)
Cl3 ⁱⁱ —Cs—Cl1 ⁱ	62.629 (15)	Cl3—Nb—Nb ^{xii}	135.895 (19)
Cl3 ⁱⁱⁱ —Cs—Cl1 ⁱ	97.912 (19)	Nb ^x —Nb—Nb ^{xii}	62.269 (11)
Cl3 ^{iv} —Cs—Cl1 ⁱ	119.843 (17)	Nb ^{xi} —Nb—Nb ^{xii}	54.570 (9)
Cl3 ^v —Cs—Cl1 ⁱ	129.092 (15)	Nb ⁱⁱ —Nb—Nb ^{xii}	87.296 (5)
Cl3 ^{vi} —Cs—Cl1 ⁱ	168.336 (16)	Nb ^{xii} —Cl1—Nb	76.29 (3)
Cl2 ⁱ —Cs—Cl1 ⁱ	51.659 (16)	Nb ^{xii} —Cl1—Cs ^{xiii}	142.343 (15)
Cl2 ⁱⁱⁱ —Cs—Cl1 ⁱ	88.305 (13)	Nb—Cl1—Cs ^{xiii}	87.830 (6)
Cl2 ⁱⁱ —Cs—Cl1 ⁱ	99.333 (16)	Nb ^{xii} —Cl1—Cs ^{xiv}	87.831 (6)
Cl1 ⁱⁱⁱ —Cs—Cl1 ⁱ	49.043 (19)	Nb—Cl1—Cs ^{xiv}	142.343 (15)
Cl1 ⁱⁱ —Cs—Cl1 ⁱ	49.043 (19)	Cs ^{xiii} —Cl1—Cs ^{xiv}	122.73 (2)
O—Gd—O ^{vii}	120.0	Nb ^{xi} —Cl2—Nb	74.85 (2)
O—Gd—O ⁱⁱⁱ	120.0	Nb ^{xi} —Cl2—Cs ^{xiii}	146.20 (3)
O ^{vii} —Gd—O ⁱⁱⁱ	120.000 (1)	Nb—Cl2—Cs ^{xiii}	94.06 (2)
O—Gd—Cl3	60.971 (13)	Nb—Cl3—Gd	88.01 (2)
O ^{vii} —Gd—Cl3	80.190 (14)	Nb—Cl3—Cs ^{xiii}	96.94 (2)
O ⁱⁱⁱ —Gd—Cl3	130.969 (14)	Gd—Cl3—Cs ^{xiii}	146.22 (3)
O—Gd—Cl3 ^{viii}	130.969 (14)	Nb—Cl3—Cs ^v	126.46 (3)
O ^{vii} —Gd—Cl3 ^{viii}	80.189 (14)	Gd—Cl3—Cs ^v	100.30 (2)
O ⁱⁱⁱ —Gd—Cl3 ^{viii}	60.971 (13)	Cs ^{xiii} —Cl3—Cs ^v	103.28 (2)
Cl3—Gd—Cl3 ^{viii}	160.38 (3)	Nb ^x —O—Nb	89.91 (11)
O—Gd—Cl3 ^{vii}	130.969 (15)	Nb ^x —O—Gd	135.05 (6)
O ^{vii} —Gd—Cl3 ^{vii}	60.971 (13)	Nb—O—Gd	135.05 (6)

Symmetry codes: (i) $x, y+1, z$; (ii) $-y, x-y, z$; (iii) $-x+y+1, -x+1, z$; (iv) $y, -x+y+1, -z+1$; (v) $-x+1, -y+1, -z+1$; (vi) $x-y, x, -z+1$; (vii) $-y+1, x-y, z$; (viii) $-y+1, -x+1, -z+3/2$; (ix) $-x+y+1, y, -z+3/2$; (x) $x, x-y, -z+3/2$; (xi) $-x+y, -x, z$; (xii) $-y, -x, -z+3/2$; (xiii) $x, y-1, z$; (xiv) $-y+1, -x, -z+3/2$.