

A NOVEL OCTAHEDRAL NIOBIUM OXYCHLORIDE CLUSTER BUILT FROM INTERCONNECTED $\text{Nb}_6\text{Cl}_{12}\text{O}_4$ UNITS: $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$

Fakhili Gulo

*Department of Chemical Education, FKIP Universitas Sriwijaya
Jalan Palembang-Prabumulih Km 32 Indralaya, OI 30662*

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ABSTRACT

A novel octahedral niobium cluster oxychloride compound, $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ was synthesized by solid-state route techniques from stoichiometric mixture of CsCl , Sc_2O_3 , Nb , NbCl_5 , and Nb_2O_5 , heated at 700 °C for two days. The crystal structure was determined by single crystal X-ray diffraction method. It crystallizes in orthorhombic system with space group of $Pnma$, $a = 17.5206(1)$ Å, $b = 29.6899(3)$ Å, $c = 9.2114(1)$ Å, and $V = 4791.63(8)$ Å³. The structure is based on $(\text{Nb}_6\text{Cl}_8\text{O}_4)\text{Cl}_{3/2}\text{Cl}_3^a$ unit in which four oxygen ligands selectively occupy inner positions arranged in sets of three and one on opposite side of the Nb_6 octahedron. Each cluster shares three apical-chlorine ligands with three adjacent clusters to form layers with topology similar to that of graphite. The cluster units are also connected to each other by both cesium and scandium atoms to form a three-dimensional framework. This compound exhibits 14 valence electrons per cluster.

Keywords: cluster compound, crystal structure, valence electron

INTRODUCTION

The early transition elements favor the formation of metal-metal bonds in their compounds with low oxidation states and display a propensity for forming hexanuclear clusters based on an octahedral arrangement of metal atoms [1]. A cluster can be defined as an aggregate of metallic atoms with finite dimension and high symmetry, in which the metallic atoms are linked together by metal-metal bonds [2]. In the cluster core, the distances between metallic atoms are close to those in the metal bulk. The most common structural units in these compounds are octahedral unit of $(\text{M}_6\text{L}_8^i)\text{L}_6^a$ and $(\text{M}_6\text{L}_{12}^i)\text{L}_6^a$ in which the inner ligands (L^i) cap the faces or bridge the edges of the metal octahedron, respectively, and the apical ligands (L^a) are located in the terminal positions.

The increasing interest in transition metal cluster compounds encountered this last decade is due to their fascinating basic aspects of structures, remarkable physical properties as superconductivity, ionic conductivity, catalytic activity, and various applications [3]. Indeed, some of these compounds are now well known for their unusual physical properties in $\text{A}_x\text{Mo}_6\text{L}_8$ ($\text{A} = \text{Pb}, \text{Sn}, \text{Cu}, \text{Li}, \text{La}, \text{Eu}, \text{etc.}; \text{L} = \text{S}, \text{Se}, \text{Te}$) that turned out to be a superconductor at 14 K [4-5]. The ultimate condensation of the $(\text{Nb}_6\text{O}_{12})\text{O}_6^a$ units, observed in the $\text{NbO}(\text{Nb}_{6/2}\text{O}_{12/4})$ binary compound, induces transport properties with a superconducting transition at low temperature [6]. These cluster compound types could be

used as precursors for the synthesis of organomineral hybrids [7] and inorganic polymeric cluster materials of different dimensionality [8-9] via soft chemistry.

The octahedral clusters of niobium tend to adopt structures with edge-bridged octahedral geometry, Nb_6L_{18} cluster unit in which an octahedron of niobium atoms surrounded by twelve inner ligands (L^i) and six apical ligands (L^a). A large number of binary, ternary, and quaternary compounds based on the Nb_6L_{18} ($\text{L} = \text{Cl}, \text{Br}$ or O) cluster units have been reported [9-10]. Each compound, in which discrete or interconnected units are encountered, possesses its own electronic and structural features in relation with the nature of ligands bonded to Nb_6 cluster.

Frameworks of reduced niobium oxides and halides are based on the same cluster type. Discrete cluster units usually characterize the halides as found in $\text{Cs}_2\text{PbNb}_6\text{Cl}_{18}$ [11], while the oxides have dense frameworks as found in $\text{KNb}_8\text{O}_{14}$ [12]. However, important differences between halide and oxide compounds exist in their composition and structural characteristics, in relation with the difference between both sizes and formal charges of oxygen and halogen ligands. In the Nb_6 halide compounds, the interunit connections are most frequently built by apical ligands shared between adjacent units as in $\text{NaNb}_6\text{Cl}_{15}$ [13]. This arrangement gives long intercluster distances. In contrast to halides, the linkages between the units in the Nb_6 oxides, involve preferentially inner ligands like in $\text{LaNb}_7\text{O}_{12}$ [14], which result in the short intercluster distances.

* Corresponding author.
Email address : fgulo@unsri.ac.id

Table 1. Crystal data and structure refinement for $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$

Empirical formula	$\text{Cs}_{1.97}\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$
Formula weight	2596.12
Temperature	298(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	<i>Pnma</i>
Unit cell dimensions	a = 17.5206(1) Å b = 29.6899(3) Å c = 9.2114(1) Å
Volume	4791.63(8) Å ³
Z	4
Density (calculated)	3.599 g.m ⁻³
Absorption coefficient	6.148 mm ⁻¹
F(000)	4744
Crystal size	0.15 x 0.08 x 0.05 mm ³
Theta range for data collection	3.02 to 33.94 °
Index ranges	-26 ≤ h ≤ 26; -46 ≤ k ≤ 46; -14 ≤ l ≤ 14
Reflections collected	17398
Independent reflections	9332 [$R_{\text{int}} = 0.0271$]
Reflections observed (>2σ)	7063
Data Completeness	0.944
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9332 / 0 / 259
Goodness-of-fit on F^2	1.052
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0368$, $wR_2 = 0.0769$
R indices (all data)	$R_1 = 0.0609$, $wR_2 = 0.0850$

The discovery of the first Nb_6 oxychloride, $\text{ScNb}_6\text{Cl}_{13}\text{O}_3$ [15] opened the field of a new class of octahedral niobium cluster compounds by using a combination of ligands. Modification of the cluster units by introduction of both halogen and oxygen as ligands can lead to changes in electronic configuration, charge, and symmetry, and is, therefore, conducive to formation of new structural types.

Herein, we report the structure of a novel octahedral niobium cluster oxychloride compound, $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ with mixed-ligands of oxygen and chlorine. This new compound contains four oxygen inner ligands and exhibits valence electron counts of 14 per cluster.

EXPERIMENTAL SECTION

Materials

In this experiment, we used the following materials: Nb powders (Ventron, m2N8), CsCl, Sc_2O_3 (Alfa, 99.5%), NbCl_5 (Alfa, 99.9%), Nb_2O_5 (Alfa, 99.5%),

Nitrogen liquid, oxygen gas, hydrogen gas, and silica tube.

Instrumentation

The used instrumentations in this experiment are glove box, analytical balance, tube furnace, scanning electron microscope (SEM), and Nonius KappaCCD X-ray diffractometer.

Procedure

Synthesis

The compound, $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ was synthesized at high-temperature reaction of stoichiometric amounts of Nb powders (Ventron, m2N8), CsCl, Sc_2O_3 (Alfa, 99.5%), NbCl_5 (Alfa, 99.9%), and Nb_2O_5 (Alfa, 99.5%). The mixture was prepared in glove box under argon atmosphere, sealed under vacuum in silica tube, and heated at 700 °C for two days. The $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ phases were obtained as black crystals. The elemental composition of the products was derived from single crystal X-ray diffraction analysis and confirmed by energy-dispersive X-ray analysis performed on single crystals.

Crystal X-ray Data Collection

A suitable single crystal of $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ was selected and used for structural determination by X-ray diffraction. Intensity data were collected at room temperature by a Nonius KappaCCD diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073$ Å). A crystal-to-detector distance of 25 mm was applied and data collection strategy was performed by using the COLLECT program of KappaCCD software package to measure all the Bragg reflections inside the full sphere until $\theta = 33.94^\circ$. A total of 17,398 reflections were collected with $\Delta\Phi = 2^\circ$ rotation scans and $\Delta\omega = 2^\circ$ rotation scans to fill the asymmetric unit cell (exposition time = 30 sec/deg). Finally, 9,332 reflections were indexed, Lorentz-polarization corrected, and then integrated in the orthorhombic symmetry by the DENZO program of the KappaCCD software package.

Structural Determination

The extinction conditions indicated *Pnma* as a unique choice of the space group. Initial atomic positions of all atoms were determined by using direct methods with Shelxs Program [16]. The refinement was carried out with full-matrix least squares methods and Fourier syntheses on F^2 with Shelxl Program [17]. All the atoms were refined with anisotropic displacement factors. The short distance between the three symmetry-equivalent positions of cesium (0.569, 1.165, and 2.20 Å) indicated a partial occupancy of these sites.

Table 2. Atomic coordinates and equivalent isotropic displacement parameters (\AA^2) for $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$

Atom	x	Y	z	U(eq)
Nb1	0.2219(1)	0.0711(1)	0.5967(1)	0.012(1)
Nb2	0.3700(1)	0.0900(1)	0.6893(1)	0.013(1)
Nb3	0.2804(1)	0.1673(1)	0.5688(1)	0.013(1)
Nb4	0.3435(1)	0.0421(1)	0.4086(1)	0.013(1)
Nb5	0.4072(1)	0.1356(1)	0.4135(1)	0.013(1)
Nb6	0.2510(1)	0.1116(1)	0.3073(1)	0.014(1)
Sc1	0.4349(1)	1/4	0.4120(1)	0.012(1)
Sc2	0.2832(1)	0.0515(1)	0.0013(1)	0.015(1)
Cl1	0.4925(1)	0.1244(1)	0.6218(1)	0.021(1)
Cl2	0.2411(1)	1/4	0.6542(1)	0.022(1)
Cl3	0.4195(1)	0.0161(1)	0.6183(1)	0.020(1)
Cl4	0.1299(1)	0.0794(1)	0.3929(1)	0.021(1)
Cl5	0.1612(1)	0.1425(1)	0.6912(1)	0.019(1)
Cl6	0.3532(1)	0.1476(1)	0.1717(1)	0.020(1)
Cl7	0.3420(1)	0.1635(1)	0.8073(1)	0.020(1)
Cl8	0.1198(1)	0.0304(1)	0.7582(1)	0.022(1)
Cl9	0.5204(1)	0.1861(1)	0.3179(1)	0.023(1)
Cl10	0.3735(1)	1/4	0.1723(2)	0.030(1)
Cl11	0.1857(1)	0.1106(1)	0.0528(1)	0.024(1)
Cl12	0.4198(1)	0.0644(1)	0.9447(1)	0.023(1)
Cl13	0.5099(1)	1/4	0.6351(2)	0.037(1)
Cl14	0.4664(1)	0.0688(1)	0.3045(1)	0.018(1)
Cl15	0.2004(1)	0.1882(1)	0.3574(1)	0.020(1)
O1	0.2477(1)	-0.0116(1)	0.0045(3)	0.015(1)
O2	0.2781(1)	0.0638(1)	0.7815(2)	0.015(1)
O3	0.2892(1)	0.0544(1)	0.2247(3)	0.016(1)
O4	0.3709(1)	0.1965(1)	0.4794(3)	0.016(1)
Cs1	0.1915(1)	0.2404(1)	0.0131(1)	0.051(1)
Cs2	0.5401(1)	1/4	0.9837(2)	0.067(1)
Cs3	0.5209(3)	0.2129(4)	0.9635(3)	0.124(4)

U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

The final refinement cycles converged to $R_1=0.0368$, $wR_2=0.0769$ for $I>2\sigma(I)$ and $R_1=0.0609$, $wR_2=0.0850$ for all data with highest peak of 3.49 at 0.72 Å from Sc1 site and Goodness-of-fit on F^2 of 1.052. Details of data collection and structure refinement are summarized in Table 1. Atomic positions and equivalent isotropic displacement parameters are reported in Table 2. Selected interatomic distances are listed in Table 3. Anisotropic thermal factors and observed and calculated structure factors are available from the authors upon request.

RESULT AND DISCUSSION

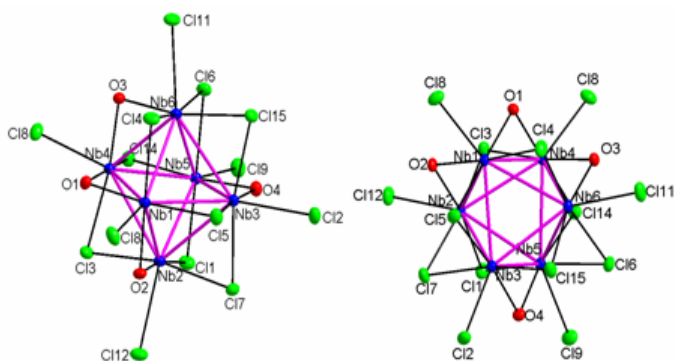
In this paper, we describe and discuss the novel cluster oxychloride compound, $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$. This compound crystallizes in an original structure type of orthorhombic system with space group of $Pnma$. The Nb_6 cluster is built from six crystallographically independent niobium atoms lying in a pyramidal site of ligands. One Nb atom has coordination spheres of two inner-chlorines (Cl^i), two inner-oxygens (O^i), and one apical-chlorine (Cl^a) ligands and five Nb atoms are surrounded by two Cl^i , two O^i , and one Cl^a ligands. Each

octahedral Nb_6 cluster of this compound contains four oxygen and eight chlorine ligands at inner position and six chlorine ligands at terminal position. The main building block of the compound is an octahedral cluster unit of $(\text{Nb}_6\text{Cl}_8\text{O}_4)\text{Cl}_6^a$. In this cluster unit, four oxygen ligands selectively occupy inner positions arranged in sets of three 'triad' and one on opposite side of the Nb_6 octahedron (Fig. 1).

The octahedral niobium cluster oxychlorides with four oxygen ligands were also encountered in the structure of $[\text{Ti}_5(\text{Ti}_2\text{Cl}_9)][(\text{Nb}_6\text{Cl}_{12}\text{O}_4)_3(\text{Ti}_3\text{Cl}_4)_2]$ [18], $\text{Ti}_2\text{Nb}_6\text{Cl}_{14}\text{O}_4$ [19], and $\text{CsNb}_6\text{Cl}_{12}\text{O}_2$ [20]. However in contrast to $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$, the O^i ligands in $\text{CsNb}_6\text{Cl}_{12}\text{O}_2$ are arranged centrosymmetrically in two sets of 'two', leading to a different isomer. The oxygen ligands are located in two inner positions on opposite sides of the Nb_6 octahedron and in two outer positions that are *trans* to each other. This ligand distribution results in an anisotropic cluster unit with symmetry close to C_{2h} . A cluster unit in which the oxygen ligands are arranged in a 'triad' similar to that in $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$, was found in the previously reported oxychloride, $\text{ScNb}_6\text{Cl}_{13}\text{O}_3$ [15] that has three inner-oxygen ligands per cluster.

Table 3. Selected interatomic distances [Å] for Cs₂Sc₃Nb₁₂Cl₂₇O₈

Nb₆ cluster			
Nb1-Nb2	2.7884(4)	Nb2-Nb5	2.9506(4)
Nb1-Nb3	3.0447(5)	Nb3-Nb5	2.8062(4)
Nb1-Nb4	2.8773(4)	Nb3-Nb6	2.9680(4)
Nb1-Nb6	2.9672(4)	Nb4-Nb5	2.9901(5)
Nb2-Nb3	2.9952(5)	Nb4-Nb6	2.7835(5)
Nb2-Nb4	2.9864(4)	Nb5-Nb6	2.9937(4)
Nb₆ cluster environment			
Nb1-Cl4	2.4868(9)	Nb4-Cl3	2.4704(9)
Nb1-Cl5	2.5264(10)	Nb4-Cl8	2.6407(10)
Nb1-Cl8	2.6226(9)	Nb4-Cl14	2.4858(9)
Nb1-O1	2.032(3)	Nb4-O1	2.038(2)
Nb1-O2	1.978(2)	Nb4-O3	1.977(2)
Nb2-Cl1	2.4570(10)	Nb5-Cl1	2.4536(9)
Nb2-Cl3	2.4467(10)	Nb5-Cl14	2.4521(9)
Nb2-Cl7	2.4868(10)	Nb5-Cl6	2.4460(9)
Nb2-Cl12	2.6217(9)	Nb5-Cl9	2.6374(10)
Nb2-O2	1.979(2)	Nb5-O4	2.011(3)
Nb3-Cl2	2.6676(6)	Nb6-Cl4	2.4554(10)
Nb3-Cl5	2.4854(9)	Nb6-Cl6	2.4315(10)
Nb3-Cl7	2.4502(9)	Nb6-Cl11	2.6084(9)
Nb3-Cl15	2.4783(9)	Nb6-Cl15	2.4840(10)
Nb3-O4	1.985(2)	Nb6-O3	1.977(3)
Scandium environment			
Sc1-Cl9	2.5689(11) x2	Sc2-Cl11	2.4943(12)
Sc1-Cl10	2.4560(17)	Sc2-Cl12	2.4778(12)
Sc1-Cl13	2.4395(18)	Sc2-O1	1.976(3)
Sc1-O4	2.042(3) x2	Sc2-O2	2.060(2)
		Sc2-O3	2.062(2)
Cesium environment			
Cs1-Cl2	3.4304(14)	Cs2-Cl9	3.6324(18)
Cs1-Cl7	3.9712(14)	Cs2-Cl9	3.6324(18)
Cs1-Cl9	3.7436(13)	Cs2-Cl15	3.6606(19)
Cs1-Cl9	4.0215(14)	Cs3-Cl5	3.527(5)
Cs2-Cl10	3.396(2)	Cs3-Cl6	4.010(8)
Cs1-Cl13	3.4730(19)	Cs3-Cl9	3.360(3)
Cs1-Cl15	3.8183(13)	Cs3-Cl10	3.402(3)
Cs2-Cl2	3.745(2)	Cs3-Cl15	3.626(3)
Interatomic shortest			
Cs1-Cs1	0.569(3)		
Cs2-Cs3	1.165(12)		
Cs3-Cs3	2.20(2)		

**Fig 1.** The octahedral cluster unit $(\text{Nb}_6\text{Cl}_8\text{O}_4)\text{Cl}_6^a$ in $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$

In $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$, the Nb_6 octahedron is significantly distorted due to the steric effect of the mixed-ligands. The Nb–Nb distances for oxygen-bridged edges are 2.7835(5) Å to 2.8773(4) Å, and those for chlorine-bridged edges range from 2.9672(4) Å to 3.0447(5) Å (Table 3). These bond lengths are similar to those found in the other niobium cluster oxychloride compounds and are also consistent with the presence of 14 valence electrons per cluster [9].

Linkage between the cluster units is made by sharing the apical-chlorine ligands between two adjacent units. Each cluster shares three of its six apical-chlorine ligands with three adjacent clusters with connectivity formula of $(\text{Nb}_6\text{Cl}_8\text{O}_4)\text{Cl}_{3/2}^a\text{Cl}_3^a$ (Fig. 2). These

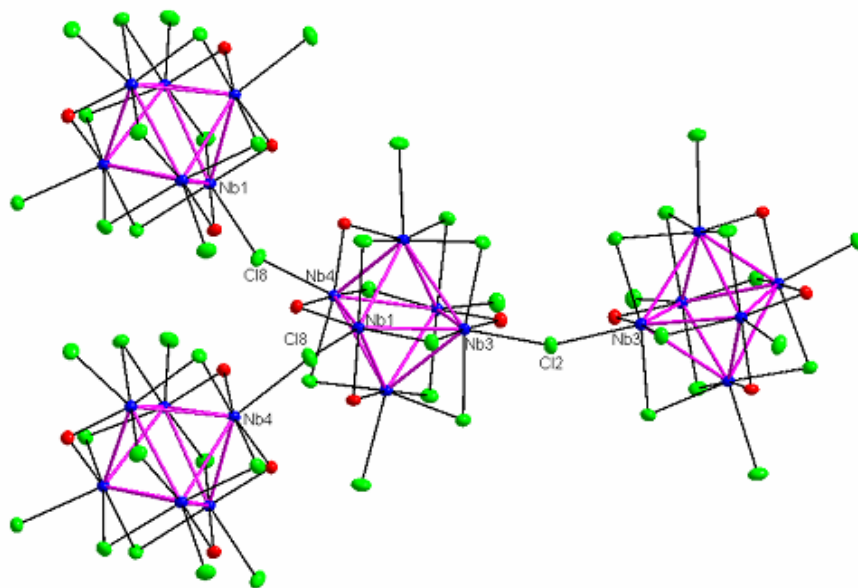


Fig 2. Connection of Nb₆ cluster with three adjacent clusters with connectivity formula, $(\text{Nb}_6\text{Cl}_8^i\text{O}_4^j)\text{Cl}_{3/2}^{i-a}\text{Cl}_3^j$

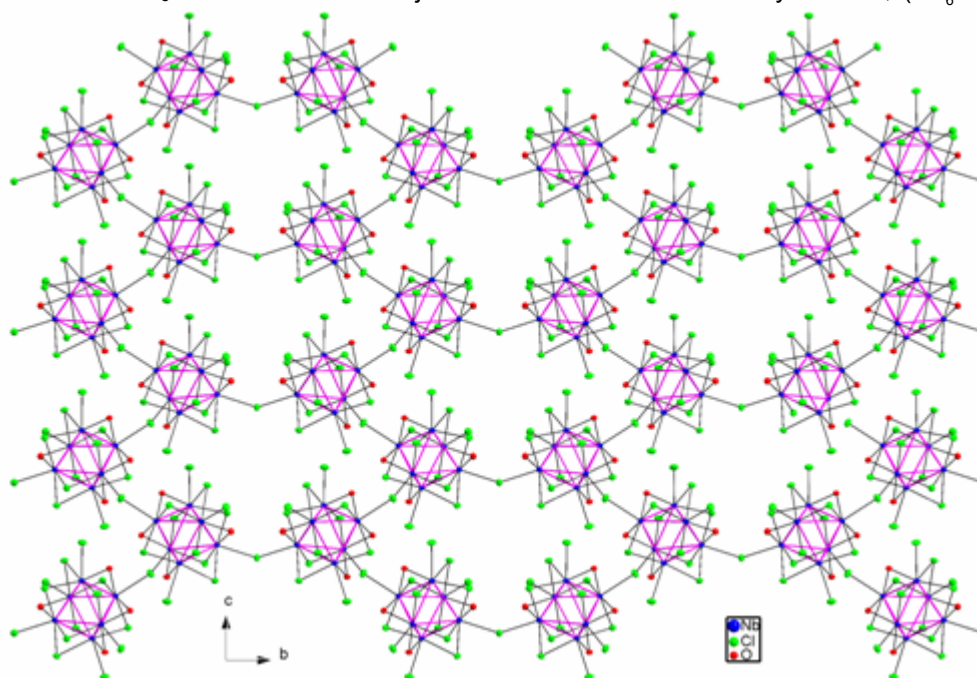


Fig 3. A view of cluster layers with graphite-topology in *bc*-plane for Cs₂Sc₃Nb₁₂Cl₂₇O₈

linkages lead to form layers with topology similar to that of graphite as found in the structure of Na_{0.21}Nb₆Cl_{10.5}O₃ [21] with connectivity formula of $(\text{Nb}_6\text{Cl}_9^i\text{O}_{3/2}^{i-a})\text{O}_{3/2}^{a-i}\text{Cl}_{3/2}^{i-a}$. In Na_{0.21}Nb₆Cl_{10.5}O₃, the six-member cluster rings are constructed by inner-apical oxygen ligands while in Cs₂Sc₃Nb₁₂Cl₂₇O₈, those are built by apical-apical chlorine ligands. In the *bc* plane, adjacent clusters are bridged through outer chlorine ligands. The cluster linkages in the *a*-direction are constructed by cesium and scandium atoms.

The arrangement of ligands in the cluster unit of Cs₂Sc₃Nb₁₂Cl₂₇O₈ favors the formation of zig-zag chains (Fig. 4) in which the clusters are linked through the scandium atoms and apical-chlorine ligands. The first scandium atom, Sc1 links to two cluster units via inner-oxygen and apical-chlorine ligands. This scandium atom coordinates to two inner-oxygens (Oⁱ) and two apical-chlorine (Cl^a) ligands, arranged in a distorted square-planar geometry (Fig. 5). Its environment is completed by two additional chlorines to a distorted octahedral or square-pyramidal geometry. The

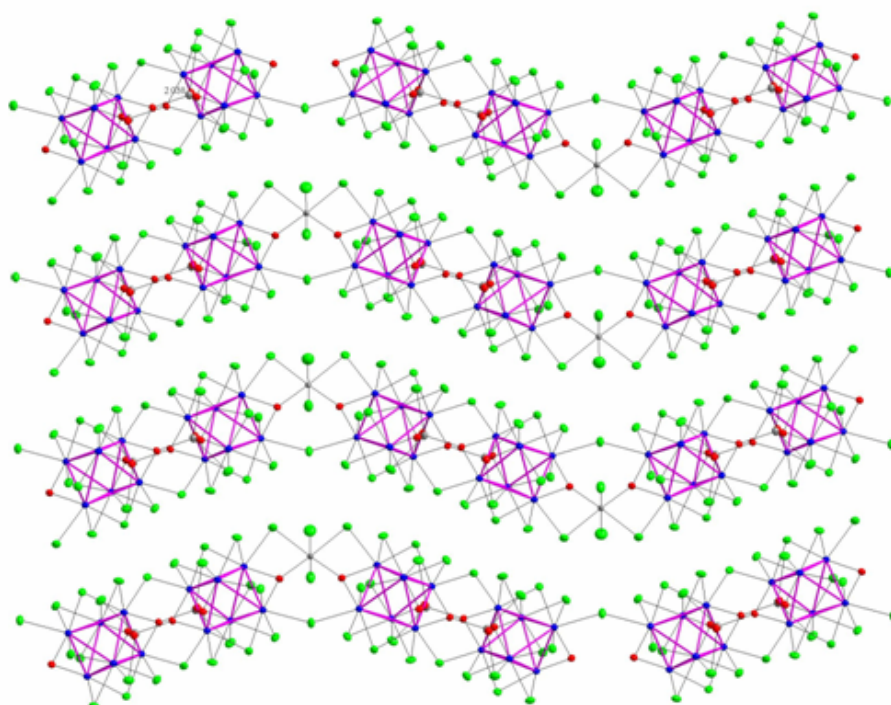


Fig 4. A view of the crystal structure of $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ in the [001] direction with zig-zag chains

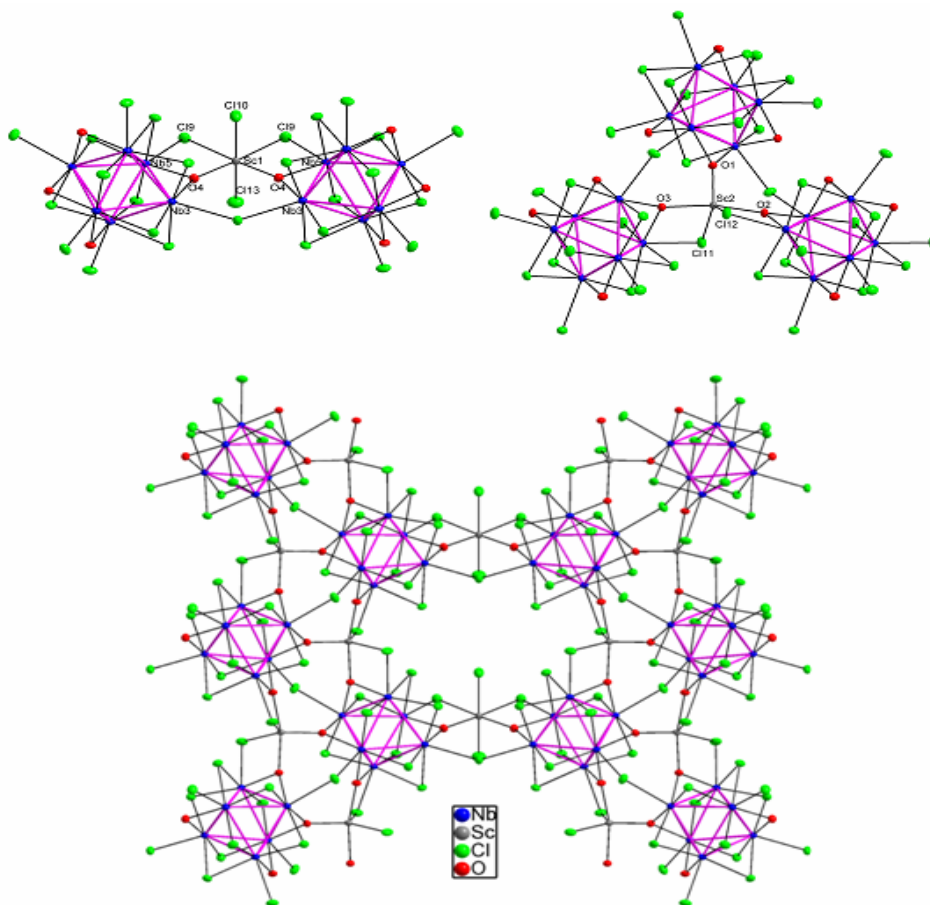


Fig 5. Scandium environment in $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$

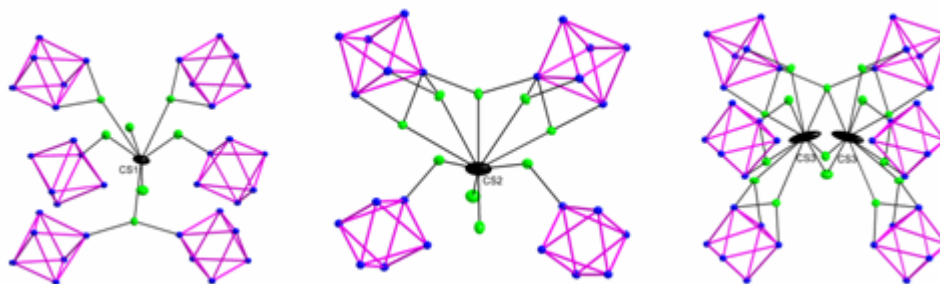


Fig 6. Cesium environment in $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$

second scandium atom, Sc2 links three clusters and has environment of unusual trigonal-bipyramidal geometry formed by three inner-oxygen ligands and two apical-chlorine ligands. The same environment of counter cations was also encountered in the structure of $\text{ScNb}_6\text{Cl}_{13}\text{O}_3$ [15] that contain three inner-oxygen ligands.

Adjacent layers in $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ are related by a plane perpendicular to *c*-direction and interact through cesium atoms. The cesium atoms are distributed over three independent sites (Cs1, Cs2, Cs3). The site Cs1 is a half occupied and coordinated by 9 chlorines within 4.2 Å. The Cs2 and Cs3 sites, separated by 1.165 Å, are located in the channels running between the layers in the *b*-direction. These two sites are partially occupied (Cs2: 50%, Cs3: 23%), and also coordinated by 9 chlorines within 4.2 Å. The number of cesium atoms per cluster was refined to 0.99(2) which agrees with the oxidation states assigned to the transition metals.

The structural properties of the novel niobium cluster oxychloride, $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ demonstrate the effectiveness of using mixed-ligands to prepare low-dimensional materials. The ordered oxygen and chlorine ligands distribution leads to great distortions of the cluster and to various electronic counts. The physical properties of the cluster compounds are related to the strength of interaction between cluster units and the number of electrons available for metal-metal bonding, the so-called valence electron count (VEC).

From the structural data, the VEC per cluster calculated for $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ is 14. This VEC value is confirmed by the average Nb-Nb intracluster distance that is shorter for $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ than those for $\text{CsNb}_6\text{Cl}_{12}\text{O}_2$ (VEC = 15) [20] and $\text{Cs}_2\text{LuNb}_6\text{Cl}_{17}\text{O}$ (VEC = 16) [23]. Indeed, if we consider only the size effect of O^i on the cluster, we should expect a smaller average Nb-Nb bond length for $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ with four O^i per unit than for $\text{ScNb}_6\text{Cl}_{13}\text{O}_3$ with three O^i per unit, for $\text{CsNb}_6\text{Cl}_{12}\text{O}_2$ with two O^i per unit and for $\text{Cs}_2\text{LuNb}_6\text{Cl}_{17}\text{O}$ with only one O^i per unit, but in fact it is the opposite. This feature is easily explained by the predominant effect of the VEC value of 15 in the case of $\text{ANb}_6\text{Cl}_{12}\text{O}_2$ (A = Cs, Rb) [20-22], instead of 16 for $\text{Cs}_2\text{LuNb}_6\text{Cl}_{17}\text{O}$. Indeed, this lower VEC value corresponds to a

weakening of the Nb-Nb intracluster bonds because one electron is removed from Nb-Nb bonding states, and thus to an increasing of the corresponding bond lengths.

The partial population of the ' a_{2u} ' state in $\text{ANb}_6\text{Cl}_{12}\text{O}_2$ is consistent with the trend that the number of valence electrons decreases as the chlorine ligands in $\text{Nb}_6\text{Cl}_{18}$ clusters are progressively substituted by oxygen [23]. The most stable electronic configuration in these clusters is determined by the balance between Nb-Nb bonding and Nb-Lⁱ antibonding contributions to the ' a_{2u} ' state. The identity of the apical ligands does not affect the character of the ' a_{2u} ' level, because they do not contribute to this state. In niobium chlorides, the ' a_{2u} ' state is generally fully occupied, leading to 16 valence electrons per cluster. In the oxides, the stronger Nb-Oⁱ interaction results in an overall antibonding character of the ' a_{2u} ' level and a typical VEC of 14.

Most oxychloride cluster compounds with three to six inner oxygen ligands have VEC of 14 [9], indicating the dominating influence of the oxygen ligands. In contrast, the compound $\text{Cs}_2\text{LuNb}_6\text{Cl}_{17}\text{O}$ with one oxygen ligand per cluster has VEC of 16 as in most chloride clusters. The cluster unit with two inner oxygen ligands, such as that in $\text{CsNb}_6\text{Cl}_{12}\text{O}_2$, represents, probably, an intermediate case in which the addition of electrons to the ' a_{2u} ' state neither decreases nor increases the stability of the cluster. This could account for the observed variations in the composition of the title series. Thus, from the electronic point of view, the cluster framework can be expected to be stable with VEC of 14, i.e. without the presence of Cs^+ cations. However, we did not succeed in preparing the ternary $\text{Nb}_6\text{Cl}_{12}\text{O}_2$ by high-temperature techniques, which may imply that the Cs^+ cations are required for the formation of the framework and act as templates.

In conclusion, a novel octahedral niobium cluster oxychloride compound, $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ was obtained by solid-state reaction. Its crystal structure is based on $(\text{Nb}_6\text{Cl}_8\text{O}_4^i)\text{Cl}_{3/2}^a\text{Cl}_3^a$ in which four oxygen ligands selectively occupy inner positions arranged in sets of three and one on opposite side of the Nb_6

octahedron. Each cluster shares three of its six apical-chlorine ligands with three adjacent clusters to form layers with topology similar to that of graphite. The arrangement of ligands favors the formation of zig-zag chains in which the clusters are linked through the scandium atoms and apical-chlorine ligands. This compound exhibits valence electron counts of 14 per cluster.

CONCLUSION

A novel octahedral niobium cluster oxychloride compound, $\text{Cs}_2\text{Sc}_3\text{Nb}_{12}\text{Cl}_{27}\text{O}_8$ was obtained by solid-state reaction. Its crystal structure is based on $(\text{Nb}_6\text{Cl}_8\text{O}_4)\text{Cl}_{3/2}\text{Cl}_3^a$ in which four oxygen ligands selectively occupy inner positions arranged in sets of three and one on opposite side of the Nb_6 octahedron. Each cluster shares three of its six apical-chlorine ligands with three adjacent clusters to form layers with topology similar to that of graphite. The arrangement of ligands favors the formation of zig-zag chains in which the clusters are linked through the scandium atoms and apical-chlorine ligands. This compound exhibits valence electron counts of 14 per cluster.

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