A New Niobium Cluster Oxychloride Built from Interconnected $Nb_6Cl_{12}O_6$ Units: $Na_{0.21}Nb_6Cl_{10.5}O_3$

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The new $Na_{0.21}Nb_6Cl_{10.5}O_3$ oxychloride was synthesized by a solid state route, from NaCl, Nb_2O_5, $NbCl_5$, and Nb, heated at 680°C for 2 weeks. The structure was determined by single-crystal X-ray diffraction. It crystallizes in the trigonal system ($R\bar{3}c$ space group, $a = 11.5048(1)$ Å, $c = 44.9446(7)$ Å, $V = 5151.88(10)$ Å^3, $Z = 12$). The structure is built from $[(Nb_6Cl_9^iO_3^i)O_3^aCl_3^a]$ units, which share their inner and apical oxygens forming pseudolayers with short Nb–Nb intercluster distances (3.399 Å). Along the c axis, these layers are interconnected by apical–apical chlorines. The sodium atoms are randomly distributed in the voids arranged between two adjacent layers, in a deformed chlorine prismatic coordination. The developed formula $Na_{0.21}[(Nb_6Cl_9^iO_{3/2}^{i-a})O_{3/2}^{a-i}Cl_{3/2}^{a-a}]$ leads to a number of valence electrons per cluster close to 14. This oxychloride will be compared to $CsNb_6Cl_{12}O_2$ which we have previously isolated and which was the first example of a Nb_6 oxyhalide involving O^{i-a}, O^{a-i} interunit connections.   © 2002 Elsevier Science

Key Words: solid state synthesis; single-crystal X-ray diffraction; Nb_6 cluster; niobium oxychloride.

INTRODUCTION

The increasing interest in transition metal cluster compounds encountered these last years is due not only to their original basic aspects related to the various possibilities for arrangements of such metallic nanoparticles in the solid state, but also to their potential applications. Indeed, some of these compounds are now well known for their unusual physical properties like superconductivity at high magnetic field or the coexistence of magnetism and superconductivity in $M_xMo_6S_8$ Chevrel phases (1) as well as for their various applications like catalysis (2) or redox intercalation–desintercalation (3), and their use as precursors for the synthesis of organomineral hybrids by solution chemistry (4).

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Nb_6 halide and Nb_6 oxide chemistries are now well developed. All these compounds are built from the edge-capped $Nb_6L_{12}^iL_6^a$ units (L^i = inner ligand bridging the edge of the Nb_6 octahedron, L^a = apical ligand on a terminal position) (5–7). However, important differences between these two classes of compounds exist in their composition and structural characteristics, in relation with the difference between both sizes and formal charges of oxygen and halogen ligands. Indeed, usually in the halide compounds, niobium forms only Nb_6 clusters, while in the oxide ones, isolated niobium and triangular Nb_3 clusters are frequently encountered besides the Nb_6 clusters. In the Nb_6 halides, the interunit connections are most frequently built by apical ligands shared between adjacent units as in $NaNb_6Cl_{15}$ (8). This arrangement gives long intercluster distances and, consequently, a strong molecular character remains in these halides leading to insulating behavior. Oppositely, in the Nb_6 oxides the connections between the units involve preferentially inner ligands like in KNb_8O_{14} (9) or $LaNb_7O_{12}$ (10), which give short intercluster distances. In the latter case, the molecular character decreases and a semiconducting behavior is frequently encountered. Between these two classes of compounds, it was interesting to try to obtain Nb_6 oxyhalides with various distributions of chlorine and oxygen ligands around the cluster in order to favor anisotropic materials. For this purpose we have started the investigation of Nb_6 oxyhalides and obtained several original series of compounds with various arrangements of one, three, four, and six oxygen ligands per unit as in $Cs_2LuNb_6Cl_{17}O$ (11), $ScNb_6Cl_{13}O_3$ (12) or $Cs_2UNb_6Cl_{15}O_3$ (13), $CsNb_6Cl_{12}O_2$ (14), and $PbLu_3Nb_6Cl_{15}O_6$ (15), respectively. Several years after the beginning of our investigation, other Nb_6 oxychlorides containing four oxygens per unit in two different arrangements with titanium as countercation have also been reported (16, 17).

In this paper we present the crystal structure of $Na_{0.21}Nb_6Cl_{10.5}O_3$, a new Nb_6 oxychloride that exhibits six oxygens per unit organized in a novel arrangement around the cluster. This oxychloride constitutes the second known

example of a compound containing interunit connections by O^{i-a}, O^{a-i} ligands in Nb_6 oxychloride chemistry, the first example being the $MNb_6Cl_{12}O_2$ (M = Na, K, Rb, Cs) series that we recently isolated (14, 18).

EXPERIMENTAL SECTION

A single crystal of the title compound was initially obtained from a solid state reaction performed to synthesize new Nb_6 oxychlorides in the Na/Nb/Cl/O system, with a small amount of NaF added to the starting mixture in order to favor the crystallization. The composition of the crystal was determined by energy-dispersive X-ray spectrometry (EDS), which indicated the presence of sodium, niobium, and chlorine in a ratio close to 0.3/6/10. Oxygen has been clearly detected, but no quantification was attempted due to limited accuracy in the presence of heavy elements. No traces of fluorine have been detected. The stoichiometry has been confirmed by structural determination performed by single-crystal X-ray diffraction. Subsequently, this compound was prepared from a stoichiometric mixture of NaCl (Prolabo), Nb_2O_5 (Merck, Optipur), $NbCl_5$ (Alfa, 99.9%), and Nb powder (Ventron, m2N8), handled under an inert atmosphere and heated in a sealed silica tube at 680°C for 2 days. It is stable in ambient atmosphere. The X-ray pattern of the final product evidences the presence of several secondary phases formed simultaneously with the title compound, such as $Na_4Nb_6Cl_{18}$ (19), NbO_2 (20), $NbOCl_2$ (21), and Nb_3Cl_8 (22), as well as another unidentified niobium oxyhalide. Our attempts to prepare $Na_{0.21}Nb_6Cl_{10.5}O_3$ in a pure form have not been successful despite various modifications in the synthesis conditions: changes of temperature, stoichiometry, and reaction time, and subsequent annealings. No range of homogeneity around the sodium stoichiometry found by structural determination could have been clearly evidenced, despite various sodium compositions that we have used in the starting mixtures.

STRUCTURAL DETERMINATION

$Na_{0.21}Nb_6Cl_{10.5}O_3$ single-crystal data collection was carried out at room temperature with a Nonius KappaCCD diffractometer (Centre de Diffractométrie, Université de Rennes 1, France) with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). A crystal-to-detector distance of 25 mm has been used and data collection has been performed with the help of the COLLECT program (23) to measure all the Bragg reflections inside the full sphere corresponding to $2.24° < \theta < 37.03°$. A total of 373 frames were recorded using $\Delta\Phi = 1.7°$ and $\Delta\omega = 1.7°$ rotation scans to fill the asymmetric unit cell (exposition time = 15 s/deg). Finally, 57,972 reflections have been indexed, Lorentz-polarization corrected, and then integrated in the hexagonal symmetry ($R3$ point group) by the DENZO program of the KappaCCD software package.

TABLE 1
Crystal Data and Structure Refinement for $Na_{0.21}Nb_6Cl_{10.5}O_3$

Empirical formula	$Na_{0.21}Nb_6Cl_{10.5}O_3$
Formula weight	982.59 g.mol^{-1}
Crystal system	Trigonal
Space group	$R\bar{3}c$ (No. 167), hexagonal setting
Unit cell dimensions	$a = 11.5048(1)$ Å
	$c = 44.9446(7)$ Å
Volume	5151.88(10) Å^3
Z	12
Density (calculated)	3.800 g.cm^{-3}
Absorption coefficient	5.502 mm^{-1}
Crystal size	$0.12 \times 0.10 \times 0.07$ mm^3
θ range for data collection	2.24 to 37.03°
Index ranges	$0 \le h \le 19$; $-16 \le k \le 0$;
	$-75 \le l \le 76$
Reflections collected	5518
Independent reflections	2929 ($R_{int} = 0.0211$)
Reflections observed ($> 2\sigma$)	2416
Refinement method	Full-matrix least-squares on F^2
Parameters	63
Goodness-of-fit on F^2 (S)	1.050
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0416$; w$R_2 = 0.0940$
R indices (all data)	$R_1 = 0.0527$; w$R_2 = 0.0997$
Largest Fourier diff. peak and hole	1.892 and -2.360 e.Å^{-3}

Frames scaling and merging of the equivalent, redundant, and Friedel reflections were performed using the SCALE-PACK program (24). No absorption corrections were applied. Finally, 2929 independent reflections ($R_{int} = 0.0211$) have been used to solve the structure by direct methods (25) in the $R\bar{3}c$ space group that is in good agreement with the observed conditions limiting the possible reflections. The refinement was carried out by full-matrix least-squares methods and Fourier syntheses on F^2 (26). All the atoms have been refined with anisotropic displacement factors. All of them fully occupy their crystallographic sites, excepted the sodium atom which is randomly distributed in its site

TABLE 2
Fractional Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Na_{0.21}Nb_6Cl_{10.5}O_3$

Atom	Wickoff position	sof[a]	τ[b]	x	y	z	U(eq)[c]
Nb1	36f	1	1	0.4930(1)	0.6877(1)	0.0485(1)	0.010(1)
Nb2	36f	1	1	0.3785(1)	0.5420(1)	$-0.0032(1)$	0.011(1)
Cl1	36f	1	1	0.5209(1)	0.7133(1)	$-0.0402(1)$	0.016(1)
Cl2	36f	1	1	0.4920(1)	0.8489(1)	0.0836(1)	0.018(1)
Cl3	36f	1	1	0.6680(1)	0.8841(1)	0.0211(1)	0.016(1)
Cl4	18e	$\frac{1}{2}$	1	$\frac{2}{3}$	0.6822(1)	$\frac{1}{2}$	0.019(1)
O	36f	1	1	0.5292(2)	0.5707(2)	0.0229(1)	0.012(1)
Na	6a	0.071(3)	0.426	$\frac{1}{3}$	$\frac{2}{3}$	$-\frac{1}{12}$	0.035(4)

[a] sof = site occupancy factor.

[b] τ = atomic occupancy of the site.

[c] U(eq) is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3
Selected Interatomic Distances (Å) and Angles (°) for
$Na_{0.21}Nb_6Cl_{10.5}O_3$

|			
	Nb_6 Cluster		
Nb1–Nb1	2.9939(5) 3x	Nb1–Nb1–Nb2	63.172(10)
Nb1–Nb2	2.7825(4) 3x	Nb1–Nb1–Nb2	55.008(9)
Nb1–Nb2	3.0308(4) 3x	Nb1–Nb2–Nb1	61.820(12)
Nb2–Nb2	3.0364(5) 3x	Nb1–Nb2–Nb2	62.602(9)
Nb1–Nb2	4.1795(4) 3x	Nb2–Nb1–Nb2	62.803(12)
		Nb1–Nb2–Nb2	54.595(9)
	$[(Nb_6Cl_9^iO_3^i)O_3^aCl_3^a]$ unit		
Nb1O^i	1.967(2)	Cl4–Nb1–O^i	84.57(7)
Nb1–Cl2	2.4403(9)	Cl4–Nb1–Cl2	85.62(3)
Nb1–Cl2	2.4450(9)	Cl4–Nb1–Cl2	76.25(2)
Nb1–Cl3	2.4748(9)	Cl4–Nb1–Cl3	92.17(2)
Nb1–Cl4	2.5640(6)		
Nb2–O^i	1.982(2)	O^a–Nb2–O^i	72.58(10)
Nb2–O^a	2.228(2)	O^a–Nb2–Cl1	82.99(7)
Nb2–Cl1	2.4703(9)	O^a–Nb2–Cl1	98.91(6)
Nb2–Cl1	2.5132(9)	O^a–Nb2–Cl3	87.39(7)
Nb2–Cl3	2.4511(8)		
	Sodium environments^a		
Na–Cl1	2.7470(9) 6x	Cl1–Cl1–Cl1	60
Cl1–Na–Cl1	75.68(3)	Cl1–Na–Cl1	93.07(3)
	Other Shortest Distances and Angles		
Nb2–Nb2 intercluster	3.3966(6)	Nb2–O–Nb2	107.42(10)
Nb1–Nb2 intercluster	4.1490(4)	Nb1–O–Nb2	162.91(13)
Nb1–Nb1 intercluster	4.6674(6)	Nb1–Cl4–Nb1	131.06(5)
Na–Nb2	4.0044(3)	Na–Cl1–Nb2	100.13(3)

^{a} These values correspond to the average ones between empty and full sites.

with an occupancy factor that converged to 0.071(3), giving 0.21(1) Na per formula. The largest residual difference Fourier peak and hole are close to the Nb2 atom position (1.89 e.Å^{-3} at 0.10 Å and -2.36 e.Å^{-3} at 0.57 Å). Crystal data, experimental conditions for intensity data collection, and structure refinement are given in Table 1. Atomic positions, site occupancy, and isotropic equivalent displacement factors are reported in Table 2. Relevant interatomic distances and angles are summarized in Table 3. Anisotropic thermal factors and observed and calculated structure factors are available from the authors upon request.

RESULTS

This new oxychloride crystallizes in an original structure type represented in Fig. 1, built from $[(Nb_6Cl_9^iO_3^i)O_3^aCl_3^a]$ units (Fig. 2) centered on a three-fold axis. All oxygen and chlorine ligands are ordered on inner and apical positions. The three O^a ligands are arranged on one side of the Nb_6 octahedron while the three Cl^a ligands are located on the opposite side, which gives an important asymmetry to the unit.

The Nb_6 cluster is built from two crystallographically independent niobium atoms, each of them lying in a pyr-
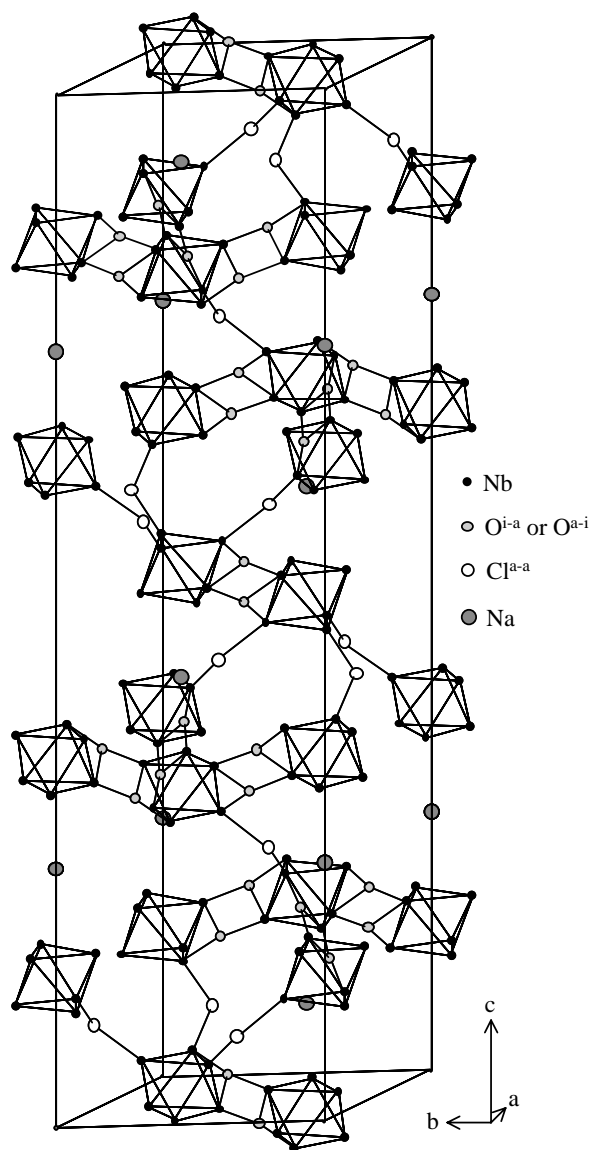
FIG. 1. Unit cell of $Na_{0.21}Nb_6Cl_{10.5}O_3$. For the sake of clarity, the inner chlorines are not represented.

amidal site of ligands with the respective coordination spheres: Nb1, three Cl^i, one O^i, and one Cl^a; Nb2, three Cl^i, one O^i, and one O^a. The Nb_6 cluster is significantly distorted since the Nb–Nb distances range from 2.7825(4) Å to 2.9939(5)–3.0364(5) Å for the O-capped and Cl-capped bonds, respectively, owing to the steric effect of the ligands as usually found for other Nb_6 oxychlorides (27). As expected, the average niobium–ligand distances depend on the type of linkage (Nb–O^i = 1.974 Å, Nb–O^a = 2.228 Å, Nb–Cl^i = 2.466 Å, and Nb–Cl^a = 2.564 Å) and are in the range of typical values usually observed in Nb_6 cluster compounds (5–7). Indeed, the ligands forming the basis of the pyramidal site occupied by the niobium atom repel the
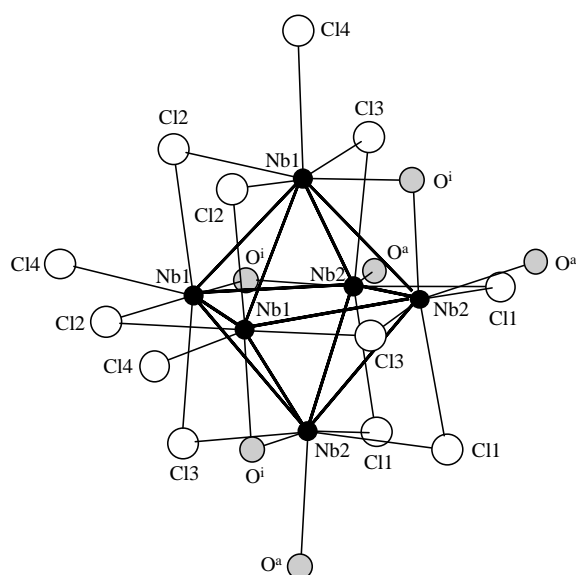
FIG. 2. The $[(Nb_6Cl_9^iO_3^i)O_3^aCl_3^a]$ unit with atoms labeled.

apical ligand by electrostatic and steric effects, which leads to a longer $Nb–L^a$ distance compared to the $Nb–L^i$ ones.

The connection between the units is achieved by sharing all the apical ligands (three O^{a-i} and three Cl^{a-a}) and three inner ligands (three O^{i-a}) between two adjacent units. Each unit is linked to six neighboring ones by three Cl^{a-a} connections that develop on one side of the Nb_6 cluster and by three O^{i-a} or O^{a-i} ones, which develop on the opposite side (Fig. 3). In the latter type of interconnection by inner-apical ligands, the Nb2 atom shares both its inner and apical oxygens with the Nb2 atom of an adjacent cluster giving
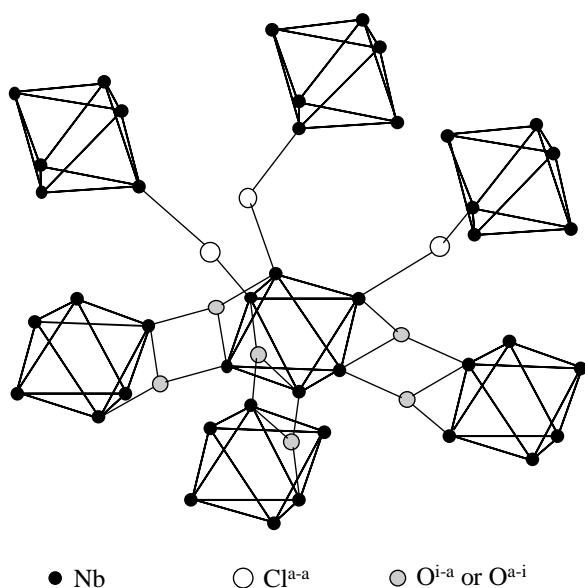
FIG. 3. Connection of the Nb_6 cluster with the six adjacent clusters, by O^{i-a}, O^{a-i} and Cl^{a-a} ligands.

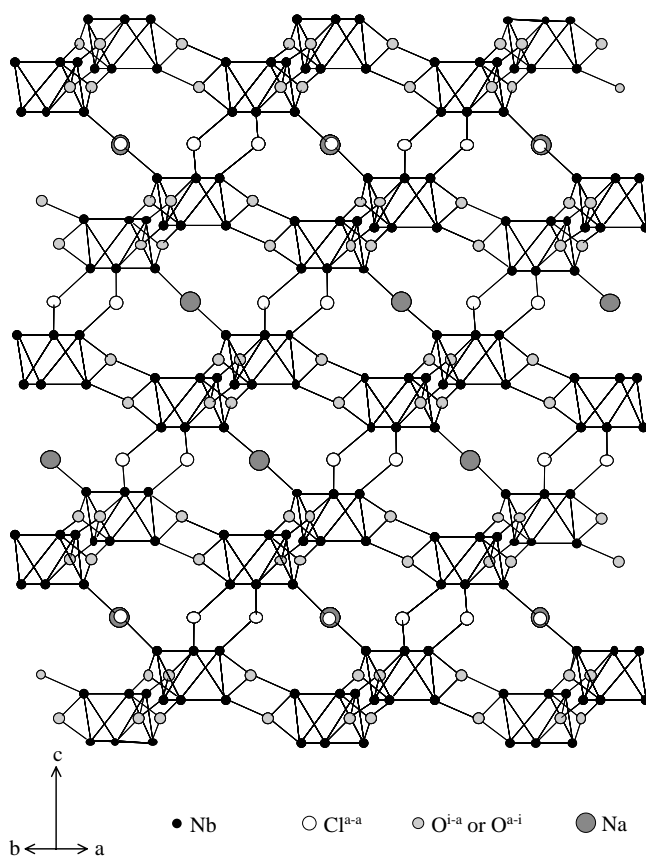● Nb   ○ Cl^{a-a} ◔ O^{i-a} or O^{a-i} ● Na

FIG. 4. Projection of the structure along the [110] direction. Inner chlorines are not represented.

a short Nb2–Nb2 intercluster distance (3.3966(6) Å). The unit network represented in Fig. 4 can be written according to the developed formula: $[(Nb_6Cl_9^iO_{3/2}^{i-a})O_{3/2}^{a-i}Cl_{3/2}^{a-a}]$. It is formed by successive pseudolayers of units linked together by Cl^{a-a} ligands.

The sodium atom occupies partially a void formed by inner ligands. If this site were fully occupied by sodium, the resulting stoichiometry would be $Na_{0.5}Nb_6Cl_{10.5}O_3$. In fact, this site is only 42.6% occupied giving 0.21 Na per formula. Locally, the sodium atom is coordinated to a pseudoprism formed by six inner chlorines belonging to two neighboring clusters of two adjacent layers, with Na–Cl distance of 2.7470(9) Å (Fig. 5). This distance, which corresponds to the average distances between full and empty sites, is close to the sum of Na$^+$ (1.02 Å) and Cl$^-$ (1.81 Å) ionic radii. It means that the volumes of the empty and full Cl_6 sites are quite similar and the presence of the sodium in this site does not locally greatly distort the network.

DISCUSSION

The $[(Nb_6Cl_9^iO_3^i)O_3^aCl_3^a]$ unit observed in $Na_{0.21}Nb_6Cl_{10.5}O_3$ constitutes the second example of a Nb_6L_{18} unit
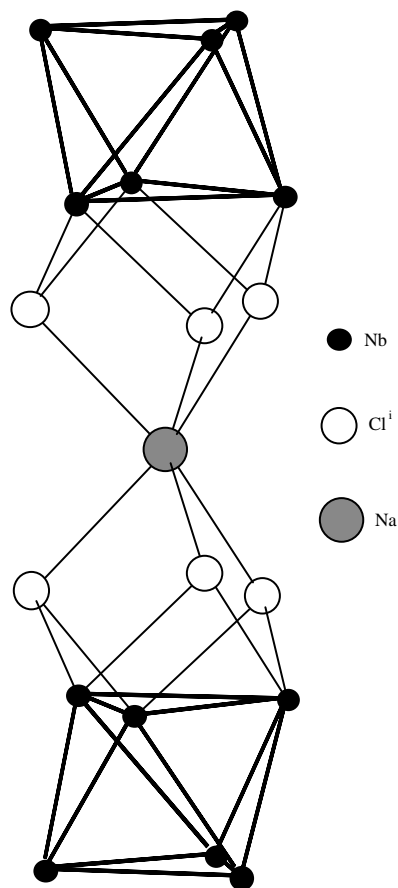
FIG. 5. The sodium environment.

The intercluster connections by inner-apical oxygens are similar to those observed in the $MNb_6Cl_{12}O_2$ (M = Na, K, Rb, Cs) series (14, 18) in which this type of bridge was found for the first time in Nb_6 oxyhalides. However, in the title compound the O^{i-a}, O^{a-i} interconnections built pseudolayers of units represented in Fig. 7a with short Nb–Nb intercluster distances (dNb2–Nb2 = 3.3966(6) Å and Nb2–O–Nb2 = 107.4(1)°) while in $CsNb_6Cl_{12}O_2$, the O^{i-a}, O^{a-i} connections run along one direction forming infinite chains of units (Fig. 7b) with Nb–Nb intercluster distances of 3.345(2) Å and Nb–O–Nb = 106.2(3)°. A first simplistic approach to describe the topology of the materials regardless of the Cl^{a-a} ligands should be to compare the cluster network in $Na_{0.21}Nb_6Cl_{10.5}O_3$ to a graphite framework with successive ABC layers of $(Nb_6Cl_9^iO_{3/2}^{i-a})O_{3/2}^{a-i}$ units, but of course this cannot describe the electronic structure. In the title compound and $CsNb_6Cl_{12}O_2$, the pseudolayers and the chains of units are linked by Cl^{a-a} ligands in one and two directions, respectively. The Nb–Nb intercluster distances and angles involved in these Cl^{a-a} connections are very close in the two structures: dNb1–Nb1 = 4.6674(6) Å, Nb1–Cl^{a-a}–Nb1 = 131.06(5)° and dNb–Nb = 4.858(3) Å, Nb–Cl^{a-a}–Nb = 137.1(1)°, respectively. This type of interunit linkage by inner-apical ligands in the two latter oxychlorides is similar to that observed in the three directions for $Ti_2Nb_6O_{12}$ (29) and $(Z)Zr_6I_{12}$ (30). It was found a long time ago in the well-known superconducting Chevrel phases,
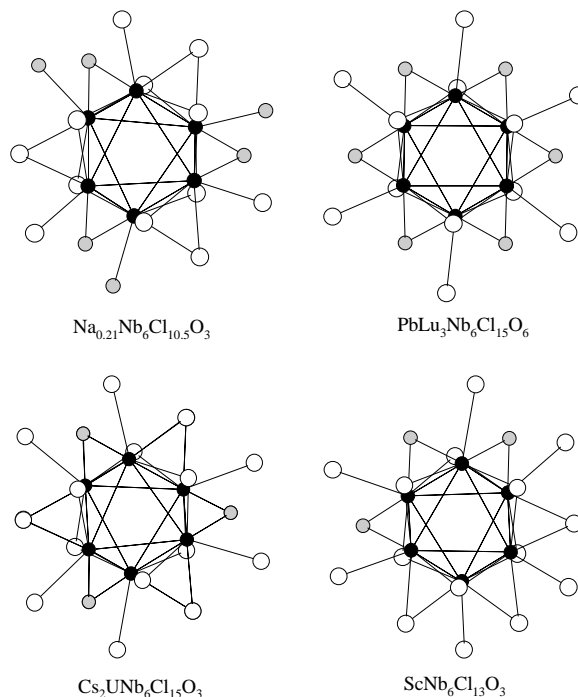
involving 6 oxygen and 12 chlorine ligands. Indeed, six oxygen ligands per unit were also encountered for the first time in $PbLu_3Nb_6Cl_{15}O_6$ (15); however, in contrast to the title compound, all the oxygen ligands in the latter oxychloride are ordered on inner positions and bridge the six edges between two triangular faces forming the Nb_6 cluster (Fig. 6), while in $Na_{0.21}Nb_6Cl_{10.5}O_3$ these six edges are alternatively occupied by O and Cl, which results in a *trans* arrangement of the three oxygens around the Nb_6 cluster. The latter arrangement of the three inner oxygens is the same as in $Cs_2UNb_6Cl_{15}O_3$ (13), but different from the *cis* arrangement encountered for the isomeric unit in $ScNb_6Cl_{13}O_3$ (12) (Fig. 6). This great diversity of oxygen and chlorine distribution around the Nb_6 cluster lets us envisage a number of other possibilities not yet found, with obvious steric limitations because the cluster cannot be too distorted. We have to mention that very recently three W_6 oxyhalides based on W_6L_{18} units have been reported (28). Two of them exhibit six oxygens per unit; in the first one, they are arranged exactly like in $PbLu_3Nb_6Cl_{15}O_6$ and in the second one, the oxygen inner ligand positions are occupied by chlorine and vice versa.

$Na_{0.21}Nb_6Cl_{10.5}O_3$

$PbLu_3Nb_6Cl_{15}O_6$

$Cs_2UNb_6Cl_{15}O_3$

$ScNb_6Cl_{13}O_3$

FIG. 6. Representation of the Nb_6L_{18} unit in $Na_{0.21}Nb_6Cl_{10.5}O_3$ and $PbLu_3Nb_6Cl_{15}O_6$ with six oxygens per unit, and $Cs_2UNb_6Cl_{15}O_3$ and $ScNb_6Cl_{13}O_3$ with three oxygens per unit.
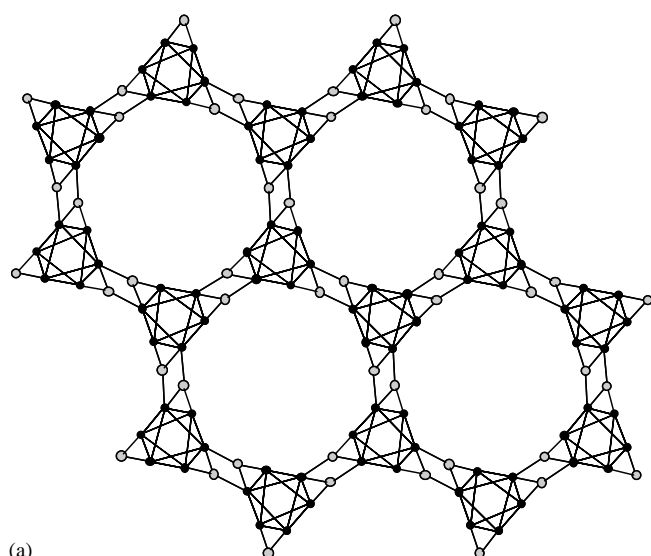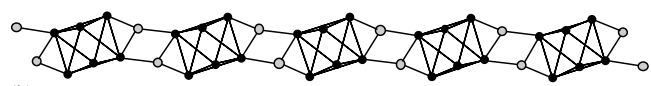
FIG. 7. (a) $Na_{0.21}Nb_6Cl_{10.5}O_3$: projection of a pseudolayer formed by O^{i-a}, O^{a-i} interconnections, along the [001] direction. (b) $CsNb_6Cl_{12}O_2$: chains formed by O^{i-a}, O^{a-i} interconnections running parallel to the a axis.

$M_xMo_6S_8$, built from the face-capped Mo_6L_{14} units, which gives also short Mo–Mo intercluster distances (Mo–Mo = 3.267 Å in $PbMo_6S_8$) (1). We have also encountered for the first time in a Nb_3 cluster oxychloride, interunit connections through O^{i-a}, O^{a-i} ligands in $Nb_3O_2Cl_5$, but the arrangement of the adjacent clusters is different, which gives slightly longer Nb–Nb intercluster distances (dNb–Nb = 3.506(1) Å) (31).

From the stoichiometry determined by structural data, $Na_{0.21}Nb_6Cl_{10.5}O_3$ has a number of valence electrons per cluster (VEC) close to 14. A VEC value of 14 is expected for this Nb_6 oxychloride with three inner oxygens per unit. Indeed, the antibonding Nb–L^i contribution at the Nb–Nb bonding state a_{2u} that is weak for the halides becomes preponderant for the cluster with three O^i per unit or more (32). In the latter cases, this level that is the HOMO for the halides is destabilized and becomes the LUMO as in the oxides for which the preferred VEC is 14 (33) instead of 16 for halides. The VEC value of 13.71 found for $Na_{0.21}Nb_6Cl_{10.5}O_3$ means that in this compound, some clusters exhibit a VEC = 13 instead of 14 as for the other ones, in relation with the statistical occupancy of the sodium sites. A VEC value of 13 is not very usual, but has been already found in some Nb_6 and Ta_6 compounds, for in-

stance, $SrNb_8O_{14}$ (34), $Cs_2BaTa_6Br_{15}O_3$ (35), and $A_2Ta_{15}O_{32}$ (A = K, Rb) (36). This value of 13.71 is confirmed by the average Nb–Nb intracluster distance (2.961 Å) in $Na_{0.21}Nb_6Cl_{10.5}O_3$ that is slightly larger than the value found for $Cs_2UNb_6Cl_{15}O_3$ (2.947 Å) or $ScNb_6Cl_{13}O_3$ (2.943 Å), two other oxyhalides with three inner oxygens and the VEC value of 14. Indeed, a lower VEC value corresponds to a weakening of the Nb–Nb intracluster bonds and consequently larger Nb–Nb distances, since fewer valence electrons are available in the Nb–Nb bonding states.

The insufficient purity of the powdered sample of $Na_{0.21}Nb_6Cl_{10.5}O_3$ and the difficulty to obtain crystals of sufficient size for physical measurements have prevented us from performing such studies. However, it is well known that in Nb_6 cluster compounds with VEC = 14, all the valence electrons are paired and no magnetic behavior due to the cluster is expected. The situation is different for compounds with 15 electrons per cluster, in which the cluster is magnetic due to the presence of one unpaired electron. This feature has been observed only for one series of Nb_6 oxychlorides, $MNb_6Cl_{12}O_2$, that exhibits a VEC of 15. In the latter case, a Curie–Weiss paramagnetism is observed (μ_{eff} = 1.42 μ_B for $CsNb_6Cl_{12}O_2$) with antiferromagnetic interactions between magnetic clusters and an unusual behavior below 50 K (18).

In conclusion, the $Na_{0.21}Nb_6Cl_{10.5}O_3$ oxyhalide reported in this paper is a new example of a mixed-ligand cluster compound with anisotropic interunit connections due to the inhomogeneous repartition of oxygen and chlorine ligands around the Nb_6 cluster. This oxychloride in which the adjacent units share the greatest number of oxygens observed up to now in this type of chemistry opens the way to other compounds with closer Nb_6–Nb_6 contacts, sharing an increasing number of oxygen ligands between the units, perhaps through both O^{i-a} and O^{i-i} ligands as in Nb_6 oxides. Our research on Nb_6 oxychloride chemistry is now in progress in this way.

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