The crystal structure of $CsNb_6Cl_{12}O_2$, a novel niobium cluster oxychloride with interconnected $Nb_6Cl_{14}O_4$ units

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New $MNb_6Cl_{12}O_2$ (M = Rb, Cs) oxychlorides have been synthesized from MCl, Nb_2O_5, $NbCl_5$ and Nb, heated at 650 °C. The structure of $CsNb_6Cl_{12}O_2$ has been determined by single-crystal X-ray diffraction. It crystallizes in the monoclinic system ($a = 6.807(3)$ Å, $b = 11.714(2)$ Å, $c = 12.665(5)$ Å, $\beta = 101.60(2)°$, $V = 989.2(6)$ Å^3 and $Z = 2$) with the $P2_1/c$ space group. The structure is built from $[(Nb_6Cl^i_{10}O^i_2)O^a_2Cl^a_4]$ units interconnected by O^{i-a}, O^{a-i} ligands in one dimension, giving chains of units with short Nb–Nb intercluster distances (3.345(2) Å). These chains are linked together along the two other dimensions by Cl^{a-a} ligands, which build voids in which the caesium atoms are randomly distributed. Thus, the developed formula of the compounds can be written: $M[(Nb_6Cl^i_{10}O^{i-a}_{2/2})O^{a-i}_{2/2}Cl^{a-a}_{4/2}]$. These new oxychlorides exhibit 15 valence electrons per Nb_6 cluster.

Introduction

The chemistry of Nb_6 chlorides consists of a great number of compounds built from discrete or interconnected $Nb_6Cl^i_{12}Cl^a_6$ units in which the Nb_6 octahedral cluster is edge-capped by twelve inner chlorines, while six apical ones are bonded to its apices.[1,2] Paramagnetism due to one unpaired electron per Nb_6 cluster appears when the valence electron concentration per cluster (VEC) is 15, while electrical insulating behaviour is usually encountered. Indeed, the distances between Nb_6 clusters remain large, which does not favour significant intercluster interactions. The latter could be enhanced by reducing the size of the ligands, for instance by replacing chlorine with the smaller oxygen ligand. For this purpose, these last years we have started to prospect the unexplored field of Nb_6 oxychloride chemistry and obtained the three first series represented by the following structure types: $Cs_2LuNb_6Cl_{17}O$,[3] $Cs_2UNb_6Cl_{15}O_3$,[4] $ScNb_6Cl_{13}O_3$.[5] The first compound has a VEC value of 16, while it is 14 for the two others. These series have been completed by $Ti_2Nb_6Cl_{14}O_4$ (VEC = 14)[6] and more recently by $KLu_3Nb_6Cl_{15}O_6$.[7] In all these compounds, the oxygen, which is always located on the inner positions, is either randomly distributed in $Cs_2LuNb_6Cl_{17}O$ or ordered in the other oxychlorides. In some of these compounds, the cluster separation is significantly reduced, but their even VEC value leads to non-magnetic behaviour of the cluster.

We report here the synthesis of a new Nb_6 oxychloride series obtained for the first time without a trivalent cation, $MNb_6Cl_{12}O_2$ (M = Rb, Cs), and we describe the crystal structure of $CsNb_6Cl_{12}O_2$, the formula of which can be written: $M[(Nb_6Cl^i_{10}O^{i-a}_{2/2})O^{a-i}_{2/2}Cl^{a-a}_{4/2}]$. This compound exhibits connections between the clusters *via* O^{i-a}, O^{a-i} ligands in one dimension giving chains of units, and a VEC value of 15, two features being original in Nb_6 oxychloride chemistry.

Experimental

Synthesis

$CsNb_6Cl_{12}O_2$ was synthesized from a stoichiometric amount of CsCl (Prolabo, purity 99.5%), Nb_2O_5 (Merck, Optipur), $NbCl_5$

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(Ventron, purity 99.998%) and Nb (Ventron, purity 99.8%). The mixture was heated at 650 °C for 7 days in a silica tube sealed under vacuum. After reaction, the compound was obtained as a microcrystalline powder of dark brown colour, stable in ambient atmosphere. The X-ray powder pattern, recorded with a INEL CPS 120 diffractometer using CuKα1 radiation, corresponded to the theoretical one computed from the structural data, without significant additional peaks. The unit cell constants refined by least square calculations from powder data were: $a = 6.817(2)$ Å, $b = 11.728(3)$ Å, $c = 12.660(2)$ Å, $\beta = 101.56(2)°$ and $V = 991.60$ Å^3.

$RbNb_6Cl_{12}O_2$ was also isolated as a stable dark brown microcrystalline powder. The X-ray diffraction powder pattern suggested a structure isotypical with $CsNb_6Cl_{12}O_2$. The unit-cell constants for the Rb compound, refined from least square calculations, were the following: $a = 6.800(3)$ Å, $b = 11.656(4)$ Å, $c = 12.607(6)$ Å, $\beta = 101.38(1)°$, $V = 979.60$ Å^3. Some attempts to obtain a similar phase with potassium or sodium have not yet been successful.

Crystal structure determination

A platelet crystal of $CsNb_6Cl_{12}O_2$ ($0.07 \times 0.06 \times 0.03$ mm^3) obtained during a reaction time of two weeks was used for structural determination performed by X-ray diffraction using an Enraf-NONIUS CAD-4 four circle diffractometer. The crystal data and experimental conditions for intensity data collection and structural determination are given in Table 1.

Intensity data treatment and refinement calculations were performed with MOLEN programs from Enraf-Nonius.[8] The structure was solved by direct method with use of MULTAN 11/82. The refinement of the fractional atomic coordinates and anisotropic displacement parameters of all atoms was carried out using full-matrix least-square techniques.[9] All the positions were fully occupied except the caesium one. In the latter case, attempts to position Cs on the 2d site (1/2 0 0) with full occupancy led to a very large displacement parameter and to a significant residual electron density peak close to this position. Therefore, we shifted this atom towards a general 4e position close to the 2d one and we refined its site occupancy. Such a refinement gave a reasonable displacement parameter and a site occupancy very close to 0.5. All these structural results agree with the $CsNb_6Cl_{12}O_2$ formula. The atomic positions and equivalent anisotropic displacement parameters are reported in

Table 1 Crystal data and structure refinement for $CsNb_6Cl_{12}O_2$

|	
Chemical formula	$CsNb_6Cl_{12}O_2$
Formula weight/g mol^{-1}	1147.78
Crystal system	Monoclinic
Unit cell dimensions:	
a/Å	6.807(3)
b/Å	11.714(2)
c/Å	12.665(5)
β/°	101.60(2)
Volume/Å^3	989.2(6)
Absorption coefficient, μ/cm^{-1}	66.54
Crystal size/mm^3	$0.07 \times 0.06 \times 0.03$
Temperature of data collection/K	295
Space group	$P2_1/c$, No. 14 (choice 2)
Z	2
Reflections collected	3251
Independent reflections	2886 [R(int) = 0.022]
Final R indices [$I > 3\sigma(I)$]	$R = 0.045$, $R_w = 0.055$
Goodness-of-fit on F	1.015
Largest diff. peak and hole/e$^-$ Å^{-3}	1.3(3) and $-0.8(3)$

Table 2. The main interatomic distances and angles are given in Table 3.

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Results

The structure of $CsNb_6Cl_{12}O_2$ is based on [$(Nb_6Cl^i_{10}O^i_2)O^a_2$-$Cl^a_4$] units represented in Fig. 1. It is the first time that oxygen ligands have been found located both in inner and apical positions in an Nb_6 oxychloride. The units are centred on -1 symmetry sites, in the 1/2 0 1/2 and 0 1/2 0 positions of the unit cell. The Nb_6 cluster is built from three crystallographically independent niobium atoms in pyramidal sites of ligands with the respective coordination spheres: Nb(1): three Cl^i, one O^i and one Cl^a, Nb(2): four Cl^i and one Cl^a, Nb(3): three Cl^i, one O^i and one O^a. The Nb–Nb intracluster distances range from 2.804(1) Å to 3.037(1) Å (average Nb–Nb = 2.933 Å), the smallest ones corresponding to the O-capped Nb–Nb bonds as usually observed for other Nb_6 oxychlorides.[7] All the intraunit distances are in the range of typical values observed for oxychlorides.

The interconnection of the clusters is made by the oxygen atoms and by the apical chlorines, both ligands shared between adjacent units. Thus, the unit of the compound can be written according to the formula: $Nb_6Cl^i_{10}O^{i-a}_{2/2}O^{a-i}_{2/2}Cl^{a-a}_{4/2}$. The Nb(3) atom shares both its inner and apical oxygens with the Nb(3) atom of the adjacent cluster giving short Nb–Nb intercluster distance (3.345(2) Å). This type of linkage via O^{i-a} and O^{a-i} ligands develops along one direction of space, parallel to the a axis, giving chains of units (Fig. 2). These chains are connected together in the two dimensions by the apical–apical Cl(1) atoms, with a Nb(1)–Cl(1)–Nb(2) angle of 137.1(1)° (Fig. 3).
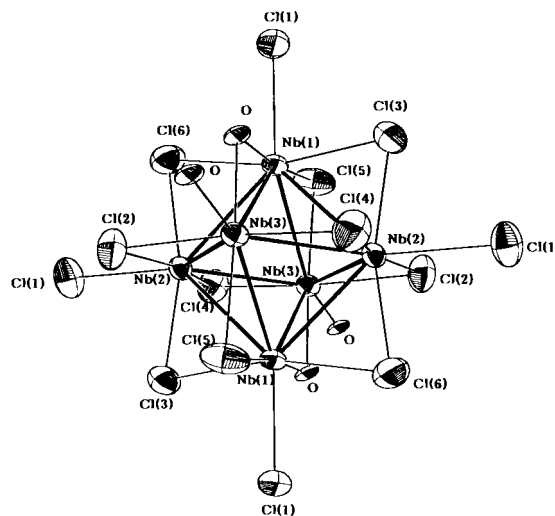
Fig. 1 The $Nb_6Cl^i_{10}O^i_2O^a_2Cl^a_4$ unit with atom labels (perspective view).

The caesium atom is located in the voids arranged between the chains of units (Fig. 3), in a complex site represented in Fig. 4. It is shifted from the 2d position (1/2 0 0) towards a general 4e position. Thus, each caesium position is coupled with another one at a distance of 0.796 Å with a site occupancy very close to 0.5 (see Table 2). The latter half-occupancy is in good agreement with the fact that the caesium atom cannot be coupled to another one due to the too short Cs–Cs distance which would result. The Cs–Cl distances given in Table 3 cannot be discussed rigorously due to this random distribution. Indeed, the short Cs–Cl(1) distance of 3.330(5) Å reported in Table 3 corresponds to the average value of Cs–Cl(1) and vacancy–Cl(1) distances. In fact, we can reasonably suppose that locally the actual Cs–Cl distance is significantly larger when the caesium atom is present on the corresponding site. The large anisotropy of the displacement factor found for Cs appears in good agreement with the geometry of its Cl environment (see Fig. 4 and Table 3).

Discussion

For the first time in any Nb_6 oxychloride, the structure of $CsNb_6Cl_{12}O_2$ exhibits, in one dimension, the same interunit linkage by inner–apical ligands as the one observed in three dimensions for the well-known Chevrel phases based on interconnected Mo_6S_{14} units.[10] Such a connection was also found in one or two dimensions in other M_6L_{14} chalcohalides or chalcogenides resulting in all cases in short metal–metal intercluster distances; some relevant examples are $Mo_6Br_6S_3$,[11] and $Re_6Se_8Cl_2$,[12] both of which have 24 e$^-$/M_6. More recently, such a type of connection was reported in three dimensions for

Table 2 Positional parameters and their estimated standard deviations for $CsNb_6Cl_{12}O_2{}^a$

Atom	Position	x	y	z	B/Å^2
Nb(1)	4e	0.3367(1)	0.13679(8)	0.42331(7)	0.50(1)
Nb(2)	4e	0.5544(1)	0.09043(8)	0.64513(7)	0.56(1)
Nb(3)	4e	0.7694(1)	0.05576(8)	0.46900(7)	0.52(1)
Cl(1)	4e	0.6152(4)	0.1961(2)	0.8310(2)	1.12(4)
Cl(2)	4e	0.2602(4)	0.0238(2)	0.7129(2)	1.11(4)
Cl(3)	4e	0.2473(4)	0.0555(2)	0.2419(2)	1.15(4)
Cl(4)	4e	0.8644(4)	0.1847(2)	0.6228(2)	1.10(4)
Cl(5)	4e	0.6300(4)	0.2353(2)	0.3706(2)	1.11(4)
Cl(6)	4e	0.8743(4)	0.2330(2)	0.0793(2)	1.18(4)
O	4e	0.082(1)	0.0783(6)	0.4564(5)	0.7(1)
Cs^b	4e	0.4561(4)	0.0212(2)	0.0034(2)	4.39(5)

^{a}The isotropic equivalent displacement parameter is defined as: $(4/3)[a^2B(1,1)+b^2B(2,2)+c^2B(3,3)+ab(\cos\gamma)B(1,2)+ac(\cos\beta)B(1,3)+bc(\cos\alpha)B(2,3)]$. ^{b}For Cs, the refined multiplicity is 0.496(2), instead of 1 corresponding to the full occupancy of this position.
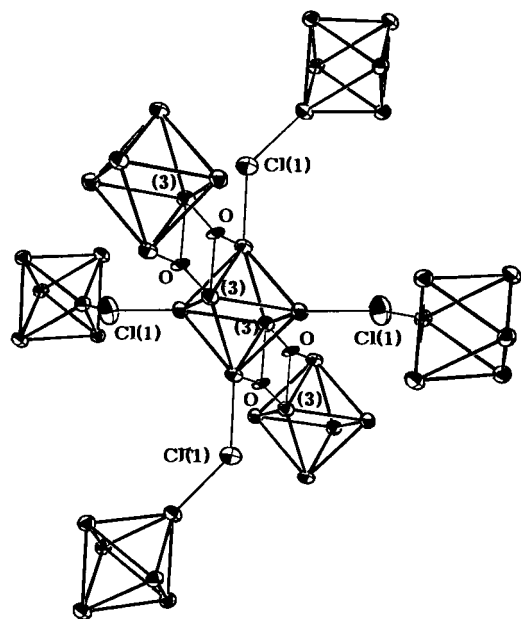
Fig. 2 Connection of the Nb_6 cluster with the six adjacent clusters, by O^{i-a}, O^{a-i} and Cl^{a-a} ligands.

M_6L_{18} cluster compounds, for instance in $(Z)Zr_6I_{12}$[13] and in $Ti_2Nb_6O_{12}$,[14] which can be described as a Chevrel phase framework in which the Mo_6S_{14} units are replaced by M_6L_{18} ones. While in the iodide, the size effect of the iodine does not allow short M–M intercluster distances, in contrast the latter can appear in $Ti_2Nb_6O_{12}$ and they are close to the Mo–Mo intercluster distances reported for $M_xMo_6S_8$. However, in contrast to Chevrel phases, the latter oxide is not conducting since it exhibits 14 e^-/Nb_6 leading to semiconducting behaviour. In $CsNb_6Cl_{12}O_2$, the $Nb–O^{i-a}$, $Nb–O^{a-i}$, and intercluster Nb(3)–Nb(3) distances are close to the corresponding ones in $Ti_2Nb_6O_{12}$ (2.113 Å, 2.212 Å and 3.315 Å respectively). We can point out that the Nb_6Cl_{14} chloride[15] has the same formula as $CsNb_6Cl_{12}O_2$, $Nb_6Cl^i_{10}Cl^{i-a}_{2/2}$-$Cl^{a-i}_{2/2}Cl^{a-a}_{4/2}$. However in this binary Nb_6Cl_{14} chloride, the connection by Cl^{i-a}, Cl^{a-i} ligands is differently arranged and does not allow short metal–metal distances between adjacent clusters.
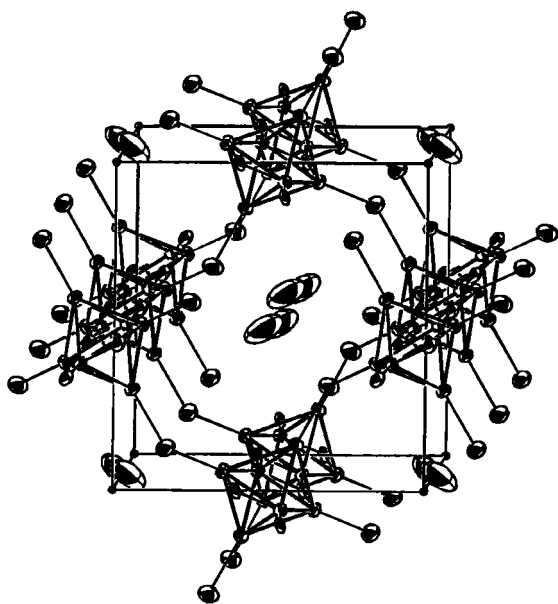

Fig. 3 Representation of the chains of units and their connections by Cl^{a-a} ligands. One of the two split positions is statistically occupied by Cs.

Table 3 Selected interatomic distances (Å) and angles (°) in $CsNb_6Cl_{12}O_2$

| Nb₆ cluster			
Nb(1)–Nb(2)	2.940(1)	Nb(1)–Nb(1)	4.153(2)
Nb(1)–Nb(2)	2.951(1)	Nb(2)–Nb(2)	4.178(2)
Nb(1)–Nb(3)	2.804(1)	Nb(3)–Nb(3)	4.114(3)
Nb(1)–Nb(3)	3.037(1)		
Nb(2)–Nb(3)	2.932(1)		
Nb(2)–Nb(3)	2.932(1)		
Nb₆Cl$^i_{10}$O$^i_2$O$^a_2$Cl$^a_4$ unit			
Nb(1)–O	1.988(7)		
Nb(1)–Cl(3)	2.448(3)	Nb(3)–O	2.000(7)
Nb(1)–Cl(5)	2.510(3)	Nb(3)–O	2.179(7)
Nb(1)–Cl(6)	2.469(3)	Nb(3)–Cl(2)	2.455(3)
Nb(1)–Cl(1)	2.600(3)	Nb(3)–Cl(4)	2.446(3)
Nb(2)–Cl(2)	2.459(3)	Nb(3)–Cl(5)	2.530(3)
Nb(2)–Cl(3)	2.452(3)		
Nb(2)–Cl(4)	2.448(3)	Nb(1)–Cl(1)–Nb(2)	137.1(1)
Nb(2)–Cl(6)	2.463(3)	Nb(1)–O–Nb(3)	164.4(4)
Nb(2)–Cl(1)	2.618(3)		
Caesium environment			
Cs–Cl(1)	3.330(5)	Cs–Cl(2)	3.759(5)
Cs–Cl(1)	3.395(5)	Cs–Cl(5)	3.792(4)
Cs–Cl(3)	3.609(5)	Cs–Cl(4)	3.862(4)
Cs–Cl(2)	3.653(5)	Cs–Cl(3)	4.131(4)
Cs–Cl(6)	3.752(5)	Cs–Cl(5)	4.460(4)
Cs–Cl(6)	3.752(5)	Cs–Cl(4)	4.514(4)
Other shortest distances and angles			
Nb(3)–Nb(3) intercluster	3.345(2)	Nb(3)–O–Nb(3)	106.2(3)
Cs–Nb(2)	4.654(4)		
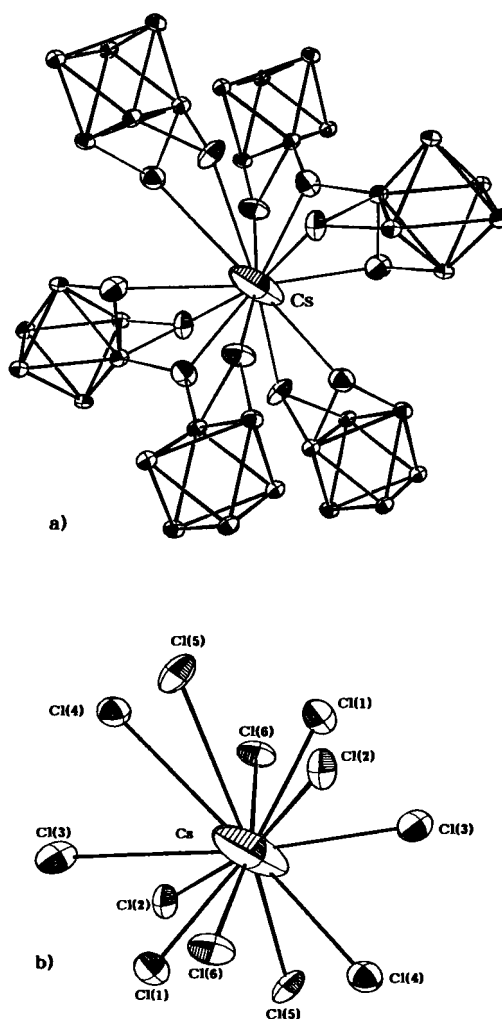
Fig. 4 The local caesium environment: a) connection with the adjacent clusters, b) labelled chlorines forming the coordination sphere.

From the structural data reported in this paper, the valence electron concentration per cluster calculated for $CsNb_6Cl_{12}O_2$ is 15. This VEC value is confirmed by the average Nb–Nb intracluster distance that is larger for $CsNb_6Cl_{12}O_2$ (2.933 Å) than for $Cs_2LuNb_6Cl_{17}O$ (2.916 Å, VEC = 16). 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 $CsNb_6Cl_{12}O_2$ with two O^i per unit than for $Cs_2LuNb_6Cl_{17}O$ with only one O^i per unit, but in fact the opposite is found. This feature is easily explained by the predominant effect of the VEC value of 15 in the case of $CsNb_6Cl_{12}O_2$, instead of 16 for $Cs_2LuNb_6Cl_{17}O$. Indeed, this lower VEC value corresponds to a weakening of the Nb–Nb intracluster bonds since one electron is removed from Nb–Nb bonding states, and thus to an increasing of the corresponding bond lengths.[16] This VEC value of 15 calculated for $CsNb_6Cl_{12}O_2$ is also confirmed by its ESR spectrum recorded at room temperature, showing a single resonance with $g = 1.951$ and $\Delta H = 100$ G. Indeed, it is similar to the spectrum usually observed for compounds based on Nb_6L_{18} units with 15 e$^-$/Nb_6, for instance $(Et_4N)_3Nb_6Cl_{18}$.[17] Magnetic susceptibility measurements at low temperature are planned to determine if the short Nb–Nb intercluster distances lead to magnetic interactions between magnetic clusters like in $LuNb_6Cl_{18}$.[18]

It is the first time that such a VEC value of 15 is found for Nb_6 oxychlorides. Increasing the number of inner oxygens to three or more per unit leads to a VEC value of 14 like in $Cs_2UNb_6Cl_{15}O_3$, $ScNb_6Cl_{13}O_3$ or $Ti_2Nb_6Cl_{14}O_4$. Theoretical calculations performed on Nb_6L_{18} units[16] have shown that the HOMO level of a_{2u} symmetry which is Nb–Nb bonding has a Nb–L^i antibonding contribution, while the apical ligands have no contribution at this level. The antibonding contribution due to the inner ligands is not important for the Nb_6 halides that are stabilized for VEC = 16 or 15 (corresponding to the HOMO level filled or half-filled respectively), but it becomes significant when oxygen replaces inner chlorine.[16] It is preponderant for three or more inner oxygens per unit, and in these cases the HOMO level is destabilized leading to a preferential VEC value of 14 for the corresponding oxyhalides as well as for the Nb_6 oxides.[19] For $CsNb_6Cl_{12}O_2$ built from $Nb_6Cl_{14}O_4$ units, there are four oxygens per unit, but in fact only two of them lie on inner positions while the other two are on apical ones. Thus, the antibonding Nb–O^i contribution due to only two O^i is not sufficient to destabilize the HOMO level and the molecular orbital diagram remains similar to the one of the Nb_6 halides or the $Cs_2LuNb_6Cl_{17}O$ oxychloride. This feature can explain why the VEC obtained for this compound with four oxygens per unit (two O^i and two O^a) is 15 and not 14 like in the other oxyhalides with four O^i per unit.

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