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# The crystal structure of $PbLu_3Nb_6Cl_{15}O_6$, a new oxychloride based on discrete $Nb_6Cl_{12}O_6$ units

**Fakhili Gulo,† Thierry Roisnel and Christiane Perrin***

*Laboratoire de Chimie du Solide et Inorganique Moléculaire, UMR 6511 CNRS-Université de Rennes1, Institut de Chimie de Rennes, Avenue du Général Leclerc, 35042 Rennes Cedex, France. E-mail: christiane.perrin@univ-rennes1.fr*

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A new $Nb_6$ oxychloride, $PbLu_3Nb_6Cl_{15}O_6$, has been synthesized from stoichiometric amounts of PbO, $Lu_2O_3$, $Nb_2O_5$, $NbCl_5$ and Nb, heated at 680 °C. The crystal structure has been determined by single crystal X-ray diffraction (cubic, $Pn\bar{3}$, $a = 13.8327(4)$ Å, $V = 2646.8(1)$ Å$^3$, $Z = 4$). The structure consists of a f.c.c. stacking of discrete edge-capped $Nb_6Cl^i{}_6O^i{}_6Cl^a{}_6$ units in which six oxygen and six chlorine atoms are ordered on the twelve inner positions, while the six apical ones are occupied by six chlorines. Additional chlorines, which do not belong to the former units, are bonded to the lutetium atoms to form $Lu_2Cl_2$ entities that occupy 3/4 of the tetrahedral cavities of the stacking units, while the lead ions are randomly distributed in the 1/4 remaining tetrahedral and in the octahedral cavities. The $Nb_6Cl_{12}O_6$ units are connected to each other by both the $Lu_2Cl_2$ entities and the lead ions to form a three-dimensional framework. This compound exhibits 14 valence electrons per cluster.

## Introduction

For several decades, transition metal cluster chemistry has attracted the attention of many groups in the world not only because of the fascinating basic aspects of such nanoparticles of high symmetry, perfectly self-organized in the solid state, but also owing to their potential applications. Indeed, many of these compounds are now well known in the materials community for their remarkable physical properties like superconductivity at high critical magnetic fields in $M_xMo_6S_8$ Chevrel phases[1] or dielectric relaxations,[2] as well as for their applications in various areas like catalysis[3] or redox intercalation–deintercalation processes,[4] and their use as precursors for reactions in solution chemistry.[5]

The chemistry of $Nb_6$ cluster halides and oxides is now well documented and a large number of binary, ternary and quaternary compounds based on the $Nb_6L^i{}_{12}L^a{}_6$ (L = Cl, Br or O) units have been reported.[6–8] In these units, the $Nb_6$ cluster is edge-capped by twelve inner ligands ($L^i$), while six additional apical ligands ($L^a$) are located on terminal positions. Each of these two classes of materials, in which discrete or interconnected units are encountered, possesses its own electronic and structural features in relation to the nature of the ligands bonded to the $Nb_6$ cluster. In fact, the replacement of halogen by oxygen that is $2^-$ charged, smaller and more electronegative leads for the oxides to changes in the VEC (Valence Electron Count) per $Nb_6$ cluster, the interunit connection and the charge of the units. The ideal electron count per cluster decreases from 16 or 15 for the $Nb_6$ halides[9] to 14 for the $Nb_6$ oxides.[10] Moreover, the connection between the units involving mainly apical ligands in the halides[7] is most frequently built up by inner ligands in the oxides, a feature allowed by the small size of oxygen.[11,12] These two different types of interunit connections lead to large intercluster distances in the halides, while the clusters are close to each other in the oxides for which band structures are usually encountered.[8,10]

Between these two classes of $Nb_6$ halides and oxides, it was interesting to explore the synthesis of new $Nb_6$ oxyhalides with various halogen/oxygen arrangements around the cluster, in order to favour anisotropic interconnection between the units and thus the specific properties that are related to it. For this purpose we have started the investigation of these new compounds, which begin now to form an important class of intermediate materials. Indeed, after the discovery of the three first series of $Nb_6$ oxychlorides, $A_2RENb_6Cl_{17}O$,[13] $A_2RENb_6Cl_{15}O_3$,[14] and $RENb_6Cl_{13}O_3$ (A = monovalent cation, RE = rare earth),[15] other examples like $Ti_2Nb_6Cl_{14}O_4$,[16] and more recently $[Tl_5(Ti_2Cl_9)][(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$,[17] $Cs_2Ti_3(Nb_6Cl_{12.5}O_4)_2Cl_2$,[18] and $CsNb_6Cl_{12}O_2$,[19] have been isolated. In these compounds, the $Nb_6L_{18}$ units exhibit one, two, three or four oxygen ligands on inner positions, while the apical ones are always occupied by halogens with the exception of $CsNb_6Cl_{12}O_2$ that exhibits two inner and two apical oxygens shared between adjacent units. Up to now, the number of oxygen ligands bonded to the $Nb_6$ cluster is low, and from a structural point of view the $Nb_6$ oxyhalides remain similar to the halides. We began to increase the number of oxygen ligands around the $Nb_6$ cluster in order to approach the electronic and structural features of $Nb_6$ oxides.

In this paper, we present the crystal structure of the first $Nb_6$ oxychloride exhibiting six oxygens on the inner positions, $PbLu_3Nb_6Cl_{15}O_6$. It crystallizes in an original structure type based on discrete $Nb_6Cl_{12}O_6$ units. Additional chlorines form $Lu_2Cl_2$ entities that bridge the clusters to build the three-dimensional network.

## Experimental

### Synthesis

$PbLu_3Nb_6Cl_{15}O_6$ was prepared from stoichiometric mixtures of PbO (Prolabo, purity 99.5%), $Lu_2O_3$ (Rhône Poulenc),

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†Permanent address: FKIP Universitas Sriwijaya, Kampus-Inderalaya, Palembang, Indonesia

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**Table 1** Crystal data and structure refinement for $PbLu_3Nb_6Cl_{15}O_6$

| | |
|---|---|
| Chemical formula | $PbLu_3Nb_6Cl_{15}O_6$ |
| Formula weight/g mol$^{-1}$ | 1917.31 |
| Temperature of data collection/K | 295 |
| Wavelength/Å | 0.71073 |
| Crystal size/mm$^3$ | 0.05 × 0.05 × 0.05 |
| Crystal system | Cubic |
| Space group | $Pn\bar{3}$ (No. 201) |
| Unit cell dimensions: $a$/Å | 13.8327(4) |
| Volume/Å$^3$ | 2646.80(13) |
| $Z$ | 4 |
| Absorption coefficient, $\mu$/mm$^{-1}$ | 21.436 |
| $\theta$ range for data collection/° | 2.55 to 27.08 |
| Integrated reflections | 25958 |
| Independent reflections used in the refinement | 980 |
| Refined parameters | 56 |
| Final $R$ indices $[I > 2\sigma(I)]$ | $R_1 = 0.0316$, $wR_2 = 0.0699$ |
| Goodness-of-fit on $F$ | 1.097 |
| Largest diff. peak and hole/e Å$^{-3}$ | 1.881 and −1.316 |

$Nb_2O_5$ (Merck, Optipur), $NbCl_5$ (Ventron, purity 99.998%) and Nb (Ventron, purity 99.8%), heated in an evacuated sealed silica tube at 680 °C. After one week of reaction the compound was obtained as a microcrystalline powder stable in ambient atmosphere. Some single crystals suitable for structural determination were obtained during the synthesis. They grew in the form of black truncated octahedra but a brown powder was obtained when they were ground. Energy-dispersive X-ray spectrometry (EDS) on the heavy elements indicated the presence of lead, lutetium, niobium and chlorine atoms in all the crystals analysed. The compound exhibited an X-ray powder pattern attributed to an original phase, and which corresponds to the theoretical one calculated after structural determination.

### Crystal data collection and structural determination

$PbLu_3Nb_6Cl_{15}O_6$ 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 30 mm was used and data collection strategy was performed with the help of the COLLECT program[20] to measure all the Bragg reflections inside the full sphere until $\theta = 27.08°$. A total of 183 frames were recorded using $\Delta\omega = 1.5°$ rotation scans to fill the asymmetric unit cell (exposition time = 60 s deg$^{-1}$). Finally, 25958 reflections were indexed, Lorentz-polarization corrected and then integrated in the cubic symmetry (23 point group) by the DENZO program of the KappaCCD software package. Frames scaling and merging of the equivalent, redundant and Friedel reflections in the $P23$ point group were performed using the SCALEPACK program,[21] leading to 1111 independent reflections with an internal agreement factor $R_{int} = 0.056$. No absorption corrections were applied.

The structure was solved using direct methods,[22] in the $Pn\bar{3}$ centrosymmetric 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 $F^2$.[23] All the atoms were refined with anisotropic displacement factors. All of them fully occupy their crystallographic sites, except for the lead atoms, which are randomly distributed on three crystallographic sites giving a stoichiometry of 0.96(1) Pb per formula unit. For the sake of clarity, in the following we round the formula to $PbLu_3Nb_6Cl_{15}O_6$. The largest residual difference Fourier peak and hole are close to the lutetium atom position: 1.881 e Å$^{-3}$ at 0.06 Å and −1.316 e Å$^{-3}$ at 0.67 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.

CCDC reference number 158628. See http://www.rsc.org/suppdata/jm/b0/b008609f/ for crystallographic data in CIF or other electronic format.

## Results

$PbLu_3Nb_6Cl_{15}O_6$ crystallizes in an original structure type built up from discrete $Nb_6Cl^i_6O^i_6Cl^a_6$ units arranged according to a face-centred cubic packing, in which lead and lutetium atoms occupy the octahedral and tetrahedral voids between the units (Fig. 1). This compound represents the first example of $Nb_6$ oxychloride in which the twelve inner ligands coordinated to the cluster consist of six oxygen and six chlorine atoms.

The unit represented in Fig. 2 is centred on a −3 inversion axis: six O and six Cl(3) are ordered on the twelve inner positions while the six apical ones are occupied by Cl(2). The six niobium atoms of the cluster are equivalent, located in a pyramidal site, the basis of which is formed by two *cis*-oxygen and two *cis*-chlorine atoms. The $Nb_6$ cluster is significantly distorted ($d\{Nb–Nb\} = 2.7900(8)$ Å and 3.0173(9) Å for the O-capped and Cl-capped Nb–Nb bonds respectively) due to the size effect of oxygen, as usually observed in other $Nb_6$ oxychlorides.[24] All the Nb–Nb, Nb–Cl and Nb–O distances are consistent with the ones previously found for other $Nb_6$ oxyhalides, in $Cs_2UNb_6Cl_{15}O_3$[14] or $ScNb_6Cl_{13}O_3$,[15] for example.

An extra chlorine, Cl(1), which does not belong to the $Nb_6Cl_{12}O_6$ unit, is found in the structure. Indeed, two Cl(1) atoms bridge two lutetium atoms with Lu–Cl(1) = 2.718(1) Å, Lu–Cl(1)–Lu = 108.01(8)° and Lu–Lu = 4.3978(8) Å, to form a $Lu_2Cl_2$ entity that is characteristic of this compound (Fig. 3). These entities are centred on 1/4, 1/4, 3/4 positions and thus occupy 3/4 of the tetrahedral cavities arranged in the f.c.c. packing of $Nb_6Cl_{12}O_6$ units. These entities are relatively close to each other because the lutetium atom is located at 3.120(2) Å

**Table 2** Atomic coordinates and equivalent isotropic displacement parameters (Å$^2$) for $PbLu_3Nb_6Cl_{15}O_6$

| Atom | Wyckoff position | sof$^a$ | $\tau^b$ | $x$ | $y$ | $z$ | $U$(eq)$^c$ |
|---|---|---|---|---|---|---|---|
| Lu | 12g | ½ | 1 | 0.5910(1) | ¾ | ¼ | 0.019(1) |
| Nb | 24h | 1 | 1 | 0.5185(1) | 0.6449(1) | 0.4730(1) | 0.014(1) |
| Cl(1) | 12g | ½ | 1 | ¾ | 0.8655(2) | ¼ | 0.024(1) |
| Cl(2) | 24h | 1 | 1 | 0.5508(1) | 0.8217(1) | 0.4211(1) | 0.022(1) |
| Cl(3) | 24h | 1 | 1 | 0.5039(1) | 0.6996(1) | 0.6441(1) | 0.021(1) |
| O | 24h | 1 | 1 | 0.5437(3) | 0.6227(3) | 0.3329(3) | 0.018(1) |
| Pb(1) | 8e | 0.1381(8) | 0.4143 | 0.6353(1) | 0.8647 | 0.6353 | 0.035(1) |
| Pb(2) | 2a | 0.0130(5) | 0.1560 | ¾ | ¾ | ¾ | 0.048(3) |
| Pb(3) | 4b | 0.0084(5) | 0.0504 | ½ | 0 | ½ | 0.020(4) |

$^a$sof = site occupancy factor. $^b\tau$ = 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 $PbLu_3Nb_6Cl_{15}O_6$

| | | | |
|---|---|---|---|
| **$Nb_6$ cluster** | | | |
| Nb–Nb | 2.7900(8) 6 × | Nb–Nb–Nb | 65.47(2) |
| Nb–Nb | 3.0173(9) 6 × | Nb–Nb–Nb | 57.27(1) |
| Nb–Nb | 4.1096(10) 3 × | | |
| **$[Nb_6Cl_6O_6]Cl_6$ unit** | | | |
| Nb–O | 1.990(4) | O–Nb–Cl(2) | 81.14(13) |
| Nb–O | 1.993(4) | O–Nb–Cl(2) | 89.51(13) |
| Nb–Cl(3) | 2.493(1) | Cl(2)–Nb–Cl(3) | 83.14(5) |
| Nb–Cl(3) | 2.541(1) | Cl(2)–Nb–Cl(3) | 89.45(5) |
| Nb–Cl(2) | 2.588(2) | | |
| **Lutetium environment** | | | |
| Lu–O | 2.202(4) 2 × | Cl(1)–Lu–Cl(1) | 71.99(8) |
| Lu–Cl(2) | 2.626(1) 2 × | Lu–Cl(1)–Lu | 108.01(8) |
| Lu–Cl(1) | 2.718(1) 2 × | Lu–Cl(2)–Nb | 85.96(5) |
| Lu–Cl(1) | 3.120(2) | Lu–O–Nb | 115.8(2) |
| Lu–Nb | 3.5548(5) | | |
| Lu–Lu | 4.3978(8) | | |
| **Lead environments (<4.0 Å)**[a] | | | |
| Pb1–Cl(3) | 2.921(1) 3 × | Pb(1)–Pb(2) | 2.7473(14) |
| Pb1–Cl(2) | 3.240(2) 3 × | Pb(1)–Pb(3) | 3.2425(14) |
| Pb1–Cl(3) | 3.661(2) 3 × | | |
| Pb2–Cl(3) | 3.771(2) 12 × | | |
| Pb3–Cl(2) | 2.787(1) 6 × | | |

[a] These values correspond to the average distances between empty and full sites.

from the Cl(1) atom of an adjacent entity. It means that a weak interaction may occur between them.

The clusters connect to each other *via* these $Lu_2Cl_2$ entities to form a three-dimensional network. Each cluster is surrounded by six $Lu_2Cl_2$ entities, each of them bridging four adjacent clusters *via* O and Cl(2) ligands with Lu–O = 2.202(4) Å, Lu–Cl(2) = 2.626(1) Å, and Lu–Nb = 3.5548(5) Å. Finally, the coordination sphere of $Lu^{3+}$ is formed by 2 $O^i$, 2 $Cl^a$ and 2 extra Cl atoms.

The three lead atoms, Pb(2), Pb(1) and Pb(3), are respectively randomly distributed in the 1/4 remaining tetrahedral cavities or shifted from the latter position, and in the octahedral cavities arranged by the packing of $Nb_6Cl_{12}O_6$ units. These three sites are partially occupied (Pb(1): 41.43%, Pb(2): 15.60%, Pb(3): 5.04%) and coordinated by 9, 12 and 6 chlorines within 4 Å, respectively. No oxygen participates in these coordination spheres (Fig. 4). The Pb(1) site is separated by 2.746(1) Å from the Pb(2) site and by 3.243(1) Å from the Pb(3) site. These short distances, when compared to the $Pb^{2+}$ radius, imply that the two neighbouring sites cannot be occupied simultaneously, in good agreement with the partial occupancies observed. The values of the isotropic equivalent displacement factors of these three lead atoms correlate to the sizes of their sites: the largest $U_{eq}$ value corresponds to the largest Pb–Cl distances. However, these distances cannot be discussed rigorously, because they result from the average distances between empty and full sites and thus it is not possible to determine the actual local Pb–Cl distances.

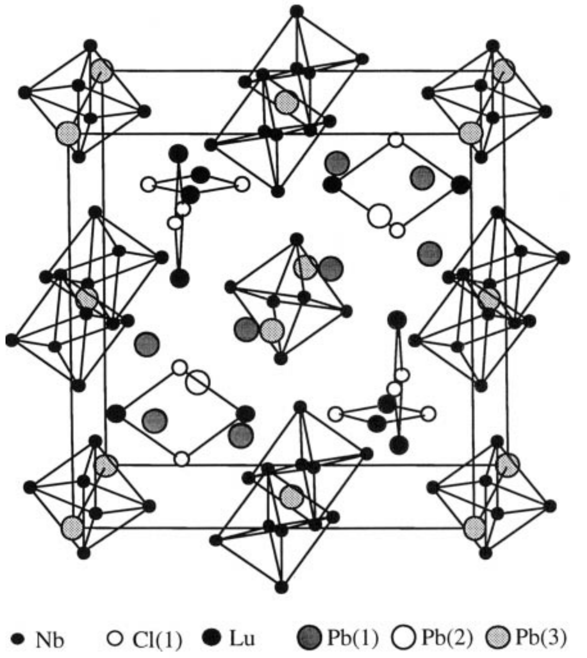

**Fig. 1** Unit cell of $PbLu_3Nb_6Cl_{15}O_6$. For sake of clarity, Nb atoms, $Lu_2Cl_2$ entities and Pb atoms are only represented (one Pb per formula is statistically distributed over three crystallographic sites).

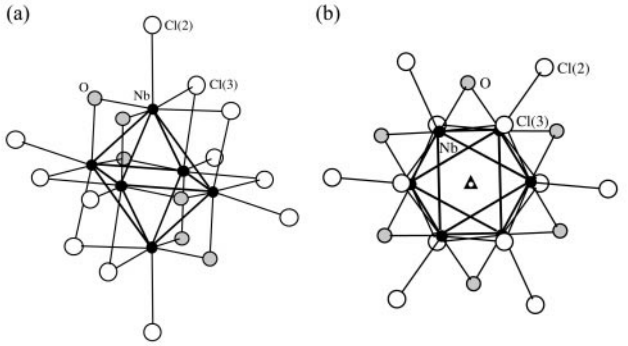

**Fig. 2** (a) A view of the $Nb_6Cl^i{}_6O^i{}_6Cl^a{}_6$ unit with the atoms labeled, (b) projection of the unit along the threefold axis.

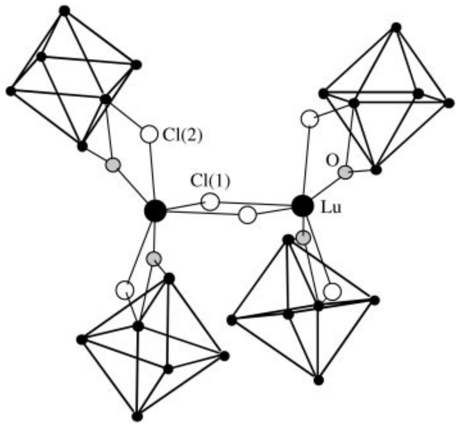

**Fig. 3** The $Lu_2Cl_2$ entity with the coordination sphere of lutetium.

## Discussion

In $PbLu_3Nb_6Cl_{15}O_6$, the $Lu_2Cl_2$ entities formed by extra chlorines can be formally considered as complex cations. Then, the formula of the compound can be written as $Pb(Lu_2Cl_2)_{1.5}[Nb_6Cl_{12}O_6]$ in which the unit exhibits the highest anionic charge ($8^-$) observed up to now in the $Nb_6$ oxyhalides. Such extra chlorines have been also encountered in $Ti_2Nb_6Cl_{14}O_4$,[16] but in this case, they are bonded to titanium cations to form infinite –Cl–Ti–Cl–Ti– chains and not to give discrete polycations as in $PbLu_3Nb_6Cl_{15}O_6$. Other examples of extra halogens can be mentioned, for instance in $[Na_2NbF_6–(Nb_6Cl_8F_7)]$,[25] where they form an octahedral $NbF_6$ entity, or in the zirconium cluster compounds like $(A_4Br)Zr_6(Z)Br_{18}$ (A = Na–Cs, Z = Be, B, H, Mn),[26] in which the extra Br is coordinated by four cations A to form $[A_4Br]^{3+}$ complex cations connecting four nearest clusters.

The new $PbLu_3Nb_6Cl_{15}O_6$ exhibits the largest O/Cl ratio

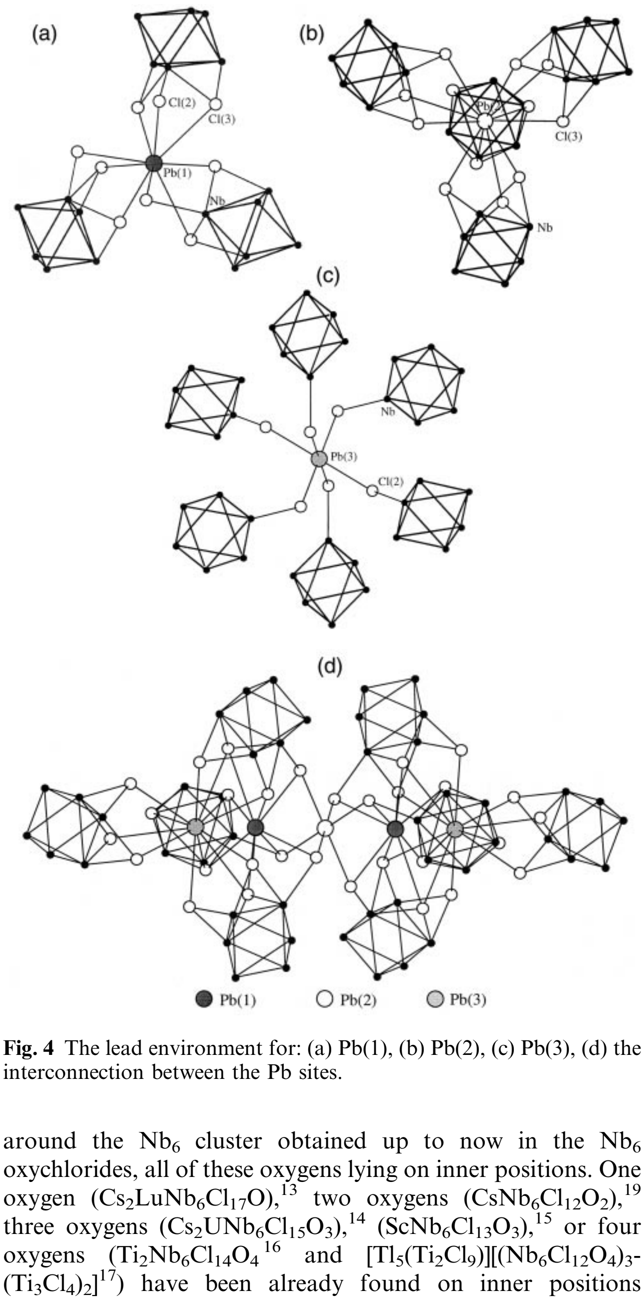

**Fig. 4** The lead environment for: (a) Pb(1), (b) Pb(2), (c) Pb(3), (d) the interconnection between the Pb sites.

around the $Nb_6$ cluster obtained up to now in the $Nb_6$ oxychlorides, all of these oxygens lying on inner positions. One oxygen ($Cs_2LuNb_6Cl_{17}O$),[13] two oxygens ($CsNb_6Cl_{12}O_2$),[19] three oxygens ($Cs_2UNb_6Cl_{15}O_3$),[14] ($ScNb_6Cl_{13}O_3$),[15] or four oxygens ($Ti_2Nb_6Cl_{14}O_4$[16] and $[Tl_5(Ti_2Cl_9)][(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$[17]) have been already found on inner positions around the $Nb_6$ cluster. Such high inner oxygen content favours the VEC value of 14 calculated from the stoichiometry determined by the structural data. Indeed, we have found by theoretical calculations,[9] and confirmed during our study of $CsNb_6Cl_{12}O_2$, that for one or two $O^i$ per formula unit, the antibonding Nb–$L^i$ contribution at the $a_{2u}$ HOMO level is not sufficient to destabilize this level. Thus, the electronic properties of the corresponding oxyhalides remain similar to those of the halides, favouring VEC values of 16 or 15. In contrast, for three or more $O^i$ per unit, the M–$L^i$ antibonding contribution becomes preponderant like in the $Nb_6$ oxides and the corresponding oxyhalides exhibit a VEC value of 14 like in the $Nb_6$ oxides. It is not possible to confirm accurately this VEC value of 14 in $PbLu_3Nb_6Cl_{15}O_6$ from a comparison of the Nb–Nb intracluster distances with the corresponding ones in other $Nb_6$ oxyhalides, because the matrix effect of oxygen due to various O/Cl ratios, the different VEC values and the different anionic charges of the units observed in all these compounds have differing effects on these Nb–Nb intracluster distances and prevent their comparison.

Another oxychloride, isostructural with $PbLu_3Nb_6Cl_{15}O_6$, has been obtained by the replacement of the lead atom with potassium.[27] In the latter compound, a potassium stoichiometry close to 1 per $Nb_6$ results in a VEC of 13 per cluster, an unusual value for this class of compound. This result needs to be confirmed by additional physical studies, which are now in progress. Notice that a VEC of 13 was previously reported for $KNb_8O_{14}$,[11] and more recently in $Ta_6$ cluster oxides, $M_2Ta_{15}O_{32}$ (M = K, Rb).[28]

In conclusion, the new $PbLu_3Nb_6Cl_{15}O_6$ oxychloride exhibits, for the first time, six inner oxygen ligands coordinated to the cluster and also additional chlorines not bonded to the cluster. It opens the way to the synthesis of other original $Nb_6$ cluster oxychlorides with large O/Cl ratios and new structure types. In such compounds, two different subnetworks, formed by both $Nb_6L_{18}$ (L = O, Cl) units and other chlorine-based entities, could be associated in the same material and may interact, leading to original physical properties. Moreover, the presence of two different ligands, namely oxygen and chlorine, bonded to the $Nb_6$ cluster in various conformations, could give access to selective substitutions by organic ligands in solution chemistry, which could control the catalytic activity of this family of $Nb_6$ oxychlorides.

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