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The novel $Cs_4Nb_6F^i_{8.5}I^i_{3.5}I^a_6$ octahedral niobium cluster fluoro-iodide: a step towards the $Nb_6F^i_{12}$ cluster core excision

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Abstract

The solid state synthesis of $Cs_4Nb_6F^i_{8.5}I^i_{3.5}I^a_6$ starting from Nb_6F_{15} binary fluoride, as well as its crystal structure determined by X-ray single crystal diffraction, are presented in this work. This novel cluster compound is based on a $Nb_6I^i_3F^i_6L^i_3I^a_6$ ($L = F$, I) discrete unit and crystallizes in the monoclinic system (space group $C2/m$; $Z = 4$; $a = 10.4363(4)$ Å, $b = 18.1227(7)$ Å, $c = 19.5102(9)$ Å $\beta = 101.223(1)°$, $V = 3619.5(3)$ Å^3, $R_1 = 0.057$; w$R_2 = 0.159$). This halide is the first octahedral niobium cluster compound containing unshared terminal I^a ligands together with ordered μ_2-I^i and μ_2-F^i ligands on nine inner positions whilst the three last ones (L^i) are slightly affected by a I/F random occupancy. The structural findings are discussed and compared with those of Nb_6F_{15}, Nb_6I_{11}, $CsNb_6I_{11}$ and the fluorochlorides and fluorobromides recently reported.
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1. Introduction

Halides of niobium and tantalum elements in their low oxidation state are well-known to form metallic clusters characterized by *M*–*M* bond lengths close to those found in the metals themselves. Tantalum octahedral clusters exhibit 12 edge-bridging ligands whatever the halogen (except fluorine for which no tantalum cluster compound has been obtained up to now) whilst niobium octahedral clusters are found to be edge bridged for F, Cl and Br ligands but are face capped by μ_3-I^i iodine with the two corresponding unit formulas $Nb_6X^i_{12}X^a_6$ ($X = $ F, Cl, Br) and $Nb_6I^i_8I^a_6$ respectively ($L^i = $ inner ligand and $L^a = $ apical ligand [1]).

In the halides synthesized via solid state route, the $Nb_6X^i_{12}X^a_6$ units can be either discrete for instance in $M_4Nb_6X_{18}$ ($M = $ alkali cation) [2–4] or $M^IM^{III}Nb_6X_{18}$ halides ($M^I = $ alkali cations, $M^{III} = $ rare earth) [5] built from the $[(Nb_6X^i_{12})X^a_6]^{4-}$ ($X = $ Cl, Br) anionic units, or interconnected by shared apical ligands leading to structures with various dimensionalities ($NaNb_6Cl^i_{12}Cl^{a-a}_{6/2}$ [6], $Nb_6F^i_{12}F^{a-a}_{6/2}$ [7]: three-dimensional network (3D); $Li_2Nb_6Cl^i_{12}Cl^a_2Cl^{a-a}_{4/2}$ [8]: two-dimensional network (2D); $Cs_2Nb_6Br^i_5F^i_7F^a_4F^{a-a}_{2/2}$ [9]: one-dimensional framework (1D)). On the other hand, no niobium octahedral cluster iodide has been found hitherto with unshared apical ligands. Indeed, the two reported niobium iodides synthesized via solid state route namely Nb_6I_{11} [10] and $CsNb_6I_{11}$ [11] exhibit a 3D character with $Nb_6I^i_8I^a_6$ units interconnected via six I^{a-a} bridges ($Nb_6I^i_8I^{a-a}_{6/2}$). Similar interunit connections are also observed in the $Nb_6Cl_{12-x}I_{2+x}$ mixed halide system ($x < 2$) [12] but between three units instead of two in pure iodides.

For a long time Nb_6F_{15} [7] was the only known cluster compound containing edge-bridging fluorine. The combined use of fluorine and chlorine or bromine has allowed isolating new cluster compounds leading to a better understanding of the fluorine specificity in cluster chemistry [9,13–15]. In particular, a random distribution of fluorine and chlorine on the inner ligand sites has been evidenced systematically and to a less extent with bromine. The large discrepancy between the ionic radii of iodine and fluorine as well as the difference between their electronic affinities should lead to cluster compounds in which an iodine/fluorine ordering would appear. Indeed, recently the $(Nb_3IF_7L$-$(NbL_2)_{0.25}$

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(L = O, F) oxyhalide containing Nb_3 triangular cluster with ordered face capping μ_3-I^i iodine and μ_2-F^i has been isolated and characterized [16].

In the present paper we report the synthesis and the characterization of $Cs_4Nb_6F_{8.5}^iI_{3.5}^iI_6^a$ obtained by the reaction between CsI, I_2 and Nb_6F_{15} (4:2.75:1) at high temperature in niobium container. This novel cluster halide is based on a $Nb_6I_3^iF_6^iL_3^iI_6^a$ unit (L = I, F) containing for the first time unshared terminal I^a ligands together with ordered μ_2-I^i and μ_2-F^i ligands on nine inner positions whilst the three last ones (L^i) are slightly affected by a F/I random distribution. The structural findings will be discussed and compared with those of Nb_6F_{15}, Nb_6I_{11}, $CsNb_6I_{11}$ and the Nb_6 mixed halides recently reported.

2. Experimental

2.1. Synthesis and characterization

2.1.1. Synthesis and characterization of Nb_6F_{15}

A stoichiometric mixture of niobium (0.5 g, Ventron m2N8) and NbF_5 (1.0 g, 99%, Assay) was weighted, ground, formed as a pellet under inert atmosphere and introduced in a niobium container (Plansee). After welding, the tube was encapsulated in an evacuated silica ampoule subsequently placed in a furnace and brought up to 800°C. After 48 h of reaction, the furnace was switched off and the sample was taken off after complete cooling. The X-ray powder pattern of the resulting light-brown product did not reveal the presence of any impurity. Let us point out that owing to the high vapor pressure of niobium pentafluoride, an inhomogeneous niobium welding could lead to an explosion of the niobium container during the reaction.

2.1.2. Synthesis and characterization of $Cs_4Nb_6F_{8.5}^iI_{3.5}^iI_6^a$

$Cs_4Nb_6F_{8.5}^iI_{3.5}^iI_6^a$ was firstly obtained from a 6:1 CsI/Nb_6F_{15} mixture prepared according to the above-described procedure and heated at 570°C for 2 days. EDS (Energy Dispersive Spectrometry) analyses performed on crystal batches of several preparations showed that they all contain the expected elements with a homogeneous composition. The X-ray single crystal diffraction results performed on single crystals from different preparations lead to the same refined stoichiometry within the s.u.'s. The X-ray powder diffraction patterns revealed supplementary lines attributed to the presence of small amount of unidentified impurity. Their relative proportions depends on the initial CsI:Nb_6F_{15} ratio. Low CsI:Nb_6F_{15} ratio (1:1–4:1) leads to incomplete reaction of Nb_6F_{15} whilst high CsI:Nb_6F_{15} ratio (up to 8:1) favors the disproportionation of Nb_6F_{15} and consequently the formation of compounds with niobium in high oxidation state as already found during the

investigation of the Cs/Nb/Br/F system [9]. Further experiments starting from stoichiometric mixtures of CsI, I_2 and Nb_6F_{15} (4:2.75:1) allowed to obtain purer samples. However in any case, the lines corresponding to the title compound were not shifted from a preparation to another corroborating the fact that the phase breath of $Cs_4Nb_6F_{8.5}I_{9.5}$ is not significant.

2.2. Single-crystal analysis and structural determination

A suitable single crystal of the title compound was mounted on a Nonius KappaCCD X-ray area-detector diffractometer with $MoK\alpha$ radiation ($\lambda = 0.71073$ Å). Once the data processing was performed by the KappaCCD analysis software [17], the cell parameters were refined as follows: $a = 10.4363(4)$ Å, $b = 18.1227(7)$ Å, $c = 19.5102(9)$ Å, $\beta = 101.223(1)°$, $V = 3619.5(3)$ Å^3. A multiscan absorption correction was performed [18]. The lattice, according to the observed systematic extinctions, is C-centered. The structure has been solved in the $C2/m$ space group by direct methods (SIR97 program [19]). Structural refinements against F^2 by least-square techniques, combined to Fourier difference syntheses, were performed using SHELXL-97 program [20].

Once atomic positions of the cluster units and cesium cations are refined, it turned out that the positions of Cs1 and Cs3 were not fully occupied and that residual electronic peaks remained close to F7 and F8. Indeed, I7 and I8 were positioned on these remaining residues. The sum of the occupancies of I7 and F7 as well as I8 and F8 were restricted to the values corresponding to full occupied positions. All the atoms were successfully refined anisotropically. Details on structural refinement parameters are reported in Table 1. The final atomic parameters and selected geometrical parameters are reported in Tables 2 and 3 respectively. The final refinement led to the $Cs_{4.03(1)}Nb_6F_{8.58(2)}^iI_{3.42(2)}^iI_6^a$ formula that will be round to $Cs_4Nb_6F_{8.5}^iI_{3.5}^iI_6^a$ in the following. Further details of the crystal structure investigation can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: (49) 7247-808-666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD_413213."

3. Results

The structure of the title compound is built from discrete anionic $[(Nb_6I_3^iF_6^iL_3^iI_6^a]^{4-}$ (L = F, I) units in which the octahedral cluster is edge bridged by 12 fluorine and iodine inner ligands and additionally bonded to six apical iodine atoms (Figs. 1 and 2). The Nb_6 cluster that exhibits a mirror plane as symmetry element is constituted by four independent niobium atoms. Two of them, Nb1 and Nb4, lie in general 8j

positions and the other two Nb2 and Nb3, are located on the symmetry plan of the unit on $4i$ positions. Nine over the 12 inner ligand positions are fully occupied by six fluorine and three iodine ligands while last three are randomly occupied by iodine and fluorine with the following ratios: I7/F7 (located on $8j$ Wyckoff positions) $= 0.15/0.85$ and I8/F8 (located on $4i$ Wyckoff position) $= 0.12/0.88$. Considering the unit as a succession of halogen and niobium triangles along the pseudo-

threefold axis of the unit lying through Nb2–Nb4–Nb4 and Nb3–Nb1–Nb1 triangles, the inner ligand arrangement can be described as a I_3^i, F_3^i, F_3^i ($F_{2.58}^i I_{0.42}^i$) sequence (see Fig. 1). Indeed, according to the structural refinement, one of these triangles is affected by a F/I random distribution (0.42 iodine and 2.58 fluorine) leading to the developed formula: $Nb_6F_{8.58(2)}^i I_{3.42(2)}^i I_6^a$. The fact that less than one iodine randomly occupies three possible inner positions leaves open the question about the local ordering of iodine and fluorine ligands within the structure. The separation of $Nb_6F_6^i I_6^i (SCN)_6^a$ units starting from $Cs_4Nb_6F_{8.5}^i I_{3.5}^i I_6^a$ is in agreement with coexistence of ordered $Nb_6F_9^i I_3^i I_6^a$ and $Nb_6F_6^i I_6^i I_6^a$ units with a 5:1 ratio [21]. The presence of these two units within the same compound does not create a super-structure but the correlation between the occupation of $L7$ and $L8$ by iodine and the vacancies on Cs1 and Cs3 sites (see below) evidences some local ordering of the $Nb_6F_9^i I_3^i I_6^a$ and $Nb_6F_6^i I_6^i I_6^a$ units. Such an iodine random distribution on the inner ligand positions was previously encountered in $Nb_6Cl_{10.8}I_{3.2}$ (the single composition in the $Nb_6Cl_{12-x}I_{2+x}$ system ($x<2$) for which the crystal structure was determined, the only reported Nb_6 compound edge bridged by iodine [12]. The random distribution of Cl and I has been observed on two inner ligand triangles leading to the following inner ligand sequence along the pseudo-three fold axis of the unit $(Cl_{2.38}^i I_{0.62}^i)$ Cl_3^i, Cl_3^i, $(Cl_{2.38}^i I_{0.62}^i)$.

The Nb–F^i bond lengths (2.053(8)–2.123(8) Å) are similar to the corresponding ones in Nb_6F_{15} (2.049 Å) and in mixed F/Cl or F/Br niobium cluster compounds [7,9,13–15]. The Nb–I^a interatomic distances (2.913(2)–2.952(2) Å) are longer than the Nb–I^i ones as always

Table 1
Crystal data and conditions of data collection for $Cs_4Nb_6F_{8.5}I_{9.5}$

Refined formula	$Cs_{4.03(1)}Nb_6F_{8.58(2)}I_{9.42(2)}$
Temperature (K)	298
Formula weight (g/mol)	2460.90
Crystal size (mm^3)	$0.012 \times 0.03 \times 0.054$
Crystal system	Monoclinic
Space group	$C\,2/m$ (No. 12)
a (Å)	10.4363(4)
b (Å)	18.1227(7)
c (Å)	19.5102(9)
β (deg)	101.223(1)
V (Å^3)	3619.5(3)
Z	4
d_{calc} (g/cm^3)	4.516
μ (mm^{-1})	13.945
Transmission range	0.595–0.715
Number of reflections collected	18260
Number of independent reflections	4120 [$R_{int} = 0.103$]
Data/restraints/parameters	4120/0/161
$R_1(I>2\sigma(I))$,	0.057
wR_2 (all data)	0.159
Goodness of fit on F^2	1.035
$(\Delta\rho)$ max, min ($e/Å^3$)	1.804, −1.751

$R_1 = \sum_{hkl}|F_o - F_c|/\sum_{hkl}|F_o|$; $wR_2 = [\sum_{hkl}[w(F_o^2 - F_c^2)^2]/\sum_{hkl}[w(F_o^2)^2]]^{1/2}$.

Table 2
Atomic coordinates, site occupancies and isotropic equivalent displacement parameters for $Cs_4Nb_6F_{8.5}I_{9.5}$

Atom	Site	Site occ.	x	y	z	U_{eq}
Nb1	$8j$	1	−0.01473(12)	0.08088(6)	0.18619(7)	0.0271(3)
Nb2	$4i$	1	−0.04830(17)	0	0.30428(10)	0.0308(4)
Nb3	$4i$	1	0.22788(16)	0	0.18711(10)	0.0270(4)
Nb4	$8j$	1	0.18566(12)	0.07739(7)	0.30569(7)	0.0317(3)
I1	$4i$	1	−0.18533(13)	0	0.08576(8)	0.0391(4)
I2	$8j$	1	0.13939(10)	0.10809(6)	0.08719(6)	0.0401(3)
I3	$4i$	1	0.46753(15)	0	0.12789(10)	0.0521(4)
I4	$8j$	1	−0.16554(11)	0.21078(6)	0.12578(7)	0.0515(3)
I5	$4i$	1	−0.2481(2)	0	0.39061(12)	0.0716(6)
I6	$8j$	1	0.33121(17)	0.19052(9)	0.39442(9)	0.0862(6)
I7	$8j$	0.151	0.4563(8)	0.3937(5)	0.5924(5)	0.046(3)
F7	$8j$	0.849	0.0471(11)	0.0816(6)	0.3714(8)	0.042(3)
F8	$4i$	0.884	0.7909(17)	1/2	0.3704(11)	0.049(4)
I8	$4i$	0.116	0.8511(17)	1/2	0.4084(11)	0.052(7)
F1	$8j$	1	0.3389(8)	0.0798(5)	0.2530(4)	0.038(2)
F2	$8j$	1	0.0870(8)	0.1639(4)	0.2514(5)	0.037(2)
F3	$8j$	1	−0.1572(8)	0.0839(5)	0.2504(5)	0.037(2)
Cs1	$4h$	0.673	1/2	0.34802(13)	1/2	0.058(1)
Cs2	$4g$	1	0	0.33438(11)	0	0.0659(5)
Cs3	$2d$	0.714	0	1/2	1/2	0.071(2)
Cs4	$8j$	1	0.09326(11)	0.33234(6)	0.26426(8)	0.0571(4)

Table 3
Interatomic distances (Å) and angles (deg) in $Cs_4Nb_6F_{8.5}I_{9.5}$

Intraunit distances:

Nb_6 cluster

Nb1–Nb1	2.932(2)		Nb2–Nb4	2.811(2)	×2
Nb1–Nb2	2.810(2)	×2	Nb3–Nb4	2.813(2)	×2
Nb1–Nb3	2.923(2)	×2	Nb4–Nb4	2.805(3)	
Nb1–Nb4	2.813(2)	×2			

Average Nb–Nb: 2.840 Å

$Nb–L^i$ distances

Nb1–F2	2.117(8)	×2	Nb3–F1	2.122(8)	×2
Nb1–F3	2.123(8)	×2	Nb3–I2	2.791(2)	×2
Nb1–I1	2.793(2)	×2	Nb4–F1	2.063(9)	×2
Nb1–I2	2.787(2)	×2	Nb4–F2	2.053(8)	×2
Nb2–F3	2.060(8)	×2	Nb4–I7	2.750(9)	×2
Nb2–I7	2.818(10)	×2	Nb4–F7	2.112(14)	×2
Nb2–F7	2.093(14)	×2	Nb4–I8	2.759(18)	×2
			Nb4–F8	2.056(15)	×2

$Nb–L^a$ distances

Nb1–I4	2.947(2)	×2	Nb4–I6	2.913(2)	×2
Nb3–I3	2.952(2)		Nb2–I5	2.925(3)	

Cesium environments[a]

Cs1–I7	2.114(10)	×2	Cs3–I8	2.129(21)	×2
Cs1–F7	2.941(16)	×2	Cs3–F8	3.001(20)	×2
Cs1–I6	3.752(2)	×2	Cs3–I5	3.694(2)	×2
Cs1–I5	4.086(2)	×2	Cs3–I6	4.225(2)	×4
Cs1–I6	4.410(2)	×2			
Cs2–I4	3.942(1)	×2	Cs4–F2	3.063(8)	
Cs2–I4	3.959(2)	×2	Cs4–F1	3.067(8)	
Cs2–I3	3.960(2)	×2	Cs4–F3	3.072(8)	
Cs2–I1	4.523(2)	×2	Cs4–I5	4.057(2)	
Cs2–I2	4.543(2)	×2	Cs4–I4	4.075(2)	
Cs2–I2	4.568(2)	×2	Cs4–I3	4.083(2)	
			Cs4–I6	4.095(2)	
			Cs4–I6	4.099(2)	
			Cs4–I4	4.110(2)	

[a] The distances involving Cs1 and Cs3 correspond to an average of the local distances between empty and full site.

observed in Nb_6X_{18}-based unit compounds. Indeed, the Nb_6 cluster is located inside a polyhedron formed by the inner ligands to which it is bonded. It results in a steric hindrance around the niobium atoms that makes difficult its approach by apical ligands [3,5]. The Nb–I^i bond lengths (2.750(9)–2.818(10) Å) are slightly larger than those found in the edge bridged $Nb_6Cl_{10.8}I_{3.2}$ (2.631(3) and 2.760(3) Å) [12].

The large discrepancy between the ionic radii of iodine and fluorine ligands induces a significant distortion of the Nb_6 cluster. The I-bridged Nb–Nb bond lengths (2.923(2) Å, 2.932(2) Å) are larger than the F-bridged Nb–Nb ones that spread within the range 2.810(2)–2.813(2) Å. The later ones are close to those found in Nb_6F_{15} (2.80 Å) in spite of different valence electron count per Nb_6 (16 in the title compound and 15 in Nb_6F_{15}). Owing to the low I7/F7 and I8/F8 ratio, the Nb–Nb bonds randomly edge bridged by fluorine and

iodine (2.805(3) Å, 2.811(2) Å) have a length close to the F-bridged ones.

The cohesion of the structure is ensured by coulombic interactions between the anionic units and four cesium cations. This cationic stoichiometry leads to 16 valence electrons per Nb_6 cluster; it corresponds to full-filled metal–metal bonding states of the Nb_6L_{18} molecular orbital diagram.

Cs2 and Cs4 (Figs. 3b and c respectively) cations fully occupy their positions and are located in XII and IX coordination sites respectively built from ligands that are not affected by a I/F random distribution. The environment of Cs2 is constituted by six apical iodine atoms and six inner iodine atoms belonging to six adjacent clusters (each of them brings one apical iodine and one inner iodine to the coordination sphere of cesium) and is similar to that found in $CsNb_6I_{11}$.
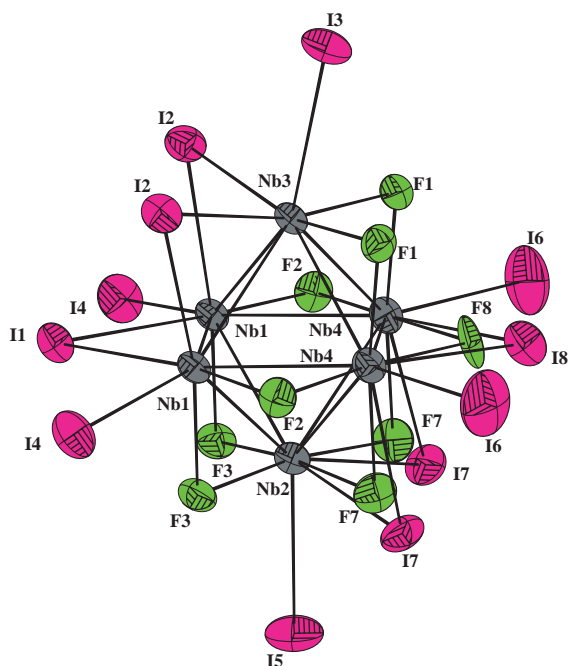
Fig. 1. $Nb_6F^i_{8.5}I^i_{3.5}I^a_6$ discrete unit. Only one of the two represented F8 and I8 as well as F7 and I7 positions are locally occupied. Displacement ellipsoids are shown at the 50% probability level.
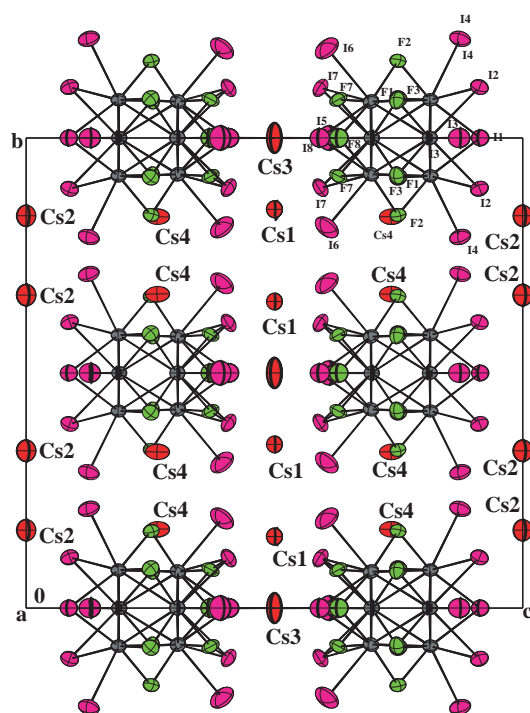

Fig. 2. Projection of the structure along the [100] direction. Only one of the two represented F8 and I8 as well as F7 and I7 positions are locally occupied. Displacement ellipsoids are shown at the 50% probability level.

Fig. 3. (a) Cs1 environment. (b) Cs2 environment (c) Cs4 environment: displacement ellipsoids are shown at the 50% probability level. For sake of clarity, only the ligands of the clusters belonging to the cesium coordination sphere are represented.

The site of Cs4 is original and is constituted by three fluorine and six iodine ligands belonging to three adjacent units. The cesium cation is located at the center of a fluorine triangle with two triangles of apical iodine lying above and below it. It can be compared to the site of lanthanum and uranium cations in $Cs_2LaTa_6Br_{15}O_3$ [22] and $Cs_2UNb_6Cl_{15}O_3$ [23] built from three inner oxygens and six apical halogens. The

Cs–F and the Cs–I bond lengths vary within the range 3.063(8)–3.072(8) Å and 4.057(2)–4.110(2) Å, respectively, and are larger than sum of the ionic radii Cs–F = 2.955 Å and Cs–I = 3.87 Å [24].

Cs1 (Fig. 3a) and Cs3, that do not fully occupy their crystallographic positions, exhibit both a VIII coordination number. Their environments involve six apical iodines and two inner ligands F7/I7 or F8/I8 belonging to four adjacent units. The very short Cs1–I7 (2.114(10) Å) and Cs3–I8 distances (2.129(21) Å) indicate a correlation between the occupancies of Cs1 and Cs3 and those of I7 and I8. In other words, the presence of I7 on the L7 inner site implies an empty Cs1 site and the presence of I8 on the L8 inner site implies an empty Cs3 site. The respective occupancies observed for Cs1/(F7, I7) and Cs3/(F8, I8) agree with the latter assumption. Indeed, the refined occupancies found for Cs1 and I7 correspond to 1.31(2) Cs1 vacancies and 1.21(5) I7 occupancies per formula whereas the refined occupancies found for Cs3 and I8 correspond to 0.57(2) Cs3 vacancies and 0.46(3) I8 occupancies per formula. Consequently, Cs1 and Cs3 are located in an ordered environment constituted by six iodine and two fluorine ligands.

4. Discussion, conclusion

As stressed above, the disordered $Nb_6F_{8.5}^iI_{3.5}^iI_6^a$ unit deduced from X-ray structural determination should correspond to the coexistence of ordered $Nb_6F_9^iI_3^iI_6^a$ and $Nb_6F_6^iI_6^iI_6^a$ units with a 5:1 ratio. An identical ordering of oxygen and chlorine leading to a $Nb_6O_6^iCl_6^iCl_6^a$ unit has ever been observed in $PbLu_3Nb_6Cl_{15}O_6$ [25], but the new $Nb_6F_9^iI_3^iI_6^a$ unit with a I_3^i, F_3^i, F_3^i, F_3^i sequence is entirely original.

Despite lower discrepancies between chlorine and oxygen radii, the Nb_6 cluster is submitted to stronger distortions in oxychlorides than in the title compound. For instance, in $PbLu_3Nb_6Cl_{15}O_6$, one of the Nb_6 oxyhalides that contains the highest O^i/Nb_6 ratio, the Nb–Nb bond lengths spread within the range 2.7900(8)–3.0173(9) Å (average: 2.9036 Å) compared to 2.805(2)–2.932(2) Å (average: 2.840 Å) in the title compound. This finding indicates that despite of similar ionic radii, the electronic effect of oxygen ligand on Nb_6 cluster distortion is stronger than that of fluorine ligand.

To conclude, $Cs_4Nb_6F_{8.5}I_{9.5}$, obtained via solid state synthesis by the reaction of Nb_6F_{15}, CsI and I_2 at 570°C in niobium container, has been isolated and structurally characterized. This novel cluster halide is based on cluster units containing for the first time terminal I^a ligands together with ordered μ_2-I^i and μ_2-F^i ligands on nine inner positions, whilst the three last ones are slightly affected by a I/F random occupancy. The reaction of Nb_6F_{15} with chosen alkali salt should lead

to the $Nb_6F_{12}^i$ excision by the formation of $Nb_6F_{12}^iX_6^a$ units (X = F, Cl, Br, I). Since the synthesis and characterization of Nb_6F_{15}, this fluoroiodide is the niobium cluster compound that contains the highest F^i/Nb_6 ratio.

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