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Article

Synthesis, Crystal Structure, and Characterization of the First Nb_3 Triangular Cluster Compound Bonded to Fluorine Ligands: Association of $Nb_3I^iF^i_3F^a_8L^a$ Units and $Nb^{IV}L_6$ Octahedra with L = O and F

S. Cordier,*,[†] O. Hernandez,[†] J.-Y. Thépot,[‡] A. I. Shames,[§] and C. Perrin[†]

Laboratoire de Chimie du Solide et Inorganique Moléculaire (LCSIM), Institut de Chimie de Rennes, UMR 6511 CNRS-Université de Rennes 1, and Laboratoire d'Organométalliques et Catalyse: Chimie et Electrochimie Moléculaire, Institut de Chimie de Rennes, UMR 6509 CNRS-Université de Rennes 1, Avenue du Général Leclerc, 35042 Rennes Cedex, France, and Department of Physics, Ben-Gurion University of the Negev, P.O. Box 653, 84 105 Be'er-Sheva, Israel

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The synthesis and the crystal structure of the first compound containing Nb_3 triangular clusters bonded to fluorine ligands are presented in this work. The structure of $Nb_3IF_7L(NbL_2)_{0.25}$ with L = O and F, determined by single-crystal X-ray diffraction, is based on a $Nb_3I^iF^i_3F^a_8L^a$ unit and a NbL_6 octahedron (tetragonal, space group $I4/m$, $a = 13.8638(3)$ Å, $c = 8.9183(2)$ Å, $V = 1714.14(7)$ Å^3, $Z = 8$). Two crystallographic positions (noted L5 and L6) are randomly occupied by fluorine and oxygen with two different F:O occupancies. These L ligands build an octahedral site for a single niobium atom, located between the units. The four L5 ligands of the NbL_6 octahedron are shared with four Nb_3 cluster units, while the two other L6 ligands are terminal. The Nb_3 cluster is face-capped by one iodine and edge-bridged by three fluorine ligands. Two of the three niobium atoms constituting the cluster are bonded to three additional apical fluorine ligands, while the third one is bonded to two fluorines and one L5 ligand. The Nb_3 cluster is linked to six adjacent ones via all the apical fluorine ligands. The developed formula of the unit is therefore $Nb_3I^iF^i_3F^{a-a}{}_{8/2}L^a$ according to the Schäfer and Schnering notation. The oxidation state of the single niobium and the random distribution of fluorine and oxygen on the two L sites will be discussed on the basis of structural analysis, the bond valence method, and IR and EPR measurements. The structural results will be compared to those of previously reported niobium compounds containing NbF_6 or $Nb(F,O)_6$ octahedra.

Introduction

The various properties and potential applications of the transition-metal cluster compounds—e.g., superconductivity at a high critical field,[1] catalysis,[2] or redox intercalation processes[3]—have stimulated the research of many groups in the world for several decades. The compounds built from M_3X_{13} units (X = halogen), obtained in solid-state chemistry, constitute one aspect of this cluster research field.[4] Such compounds contain a triangular M_3 cluster with metal—metal bonds, face- and edge-capped by one μ_3-X^i ligand and three μ_2-X^i ligands, respectively, while nine terminal X^a ligands complete the coordination of the cluster. The three Nb_3X_8 (X = Cl, Br, I) binary halides were isolated a long time ago. They crystallize in two structure types characterized by different stackings of layers constituted by interconnected Nb_3 clusters.[5,6] More recently, mixed-ligand Nb_3YX_7 compounds (Y = chalcogen, X = halogen) were obtained by the introduction of divalent ligands in the Nb/X systems.[7,8]

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* Author to whom correspondence should be addressed. E-mail: stephane.cordier@univ-rennes1.fr. Fax: (33) 2 99 63 57 04.

[†] UMR 6511 CNRS-Université de Rennes 1.

[‡] UMR 6509 CNRS-Université de Rennes 1.

[§] Ben-Gurion University of the Negev.

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The next step was to use oxygen instead of sulfur, selenium, or tellurium; this has allowed the stabilization of $Nb_3O_2Cl_5$, in which the smaller size of the oxygen ligand compared to that of chlorine gives access to distorted triangular Nb_3 clusters bonded to one another via original μ_3-O^{i-a} interunit bridges.[9] Another way to obtain M_3X_{13} and related cluster compounds with original structural features is to synthesize mixed-halide compounds with a large ionic radius discrepancy, such as fluorine associated with another halogen. However, only niobium octahedral clusters have been found hitherto in the chlorofluoride and bromofluoride chemistry with a random distribution of fluorine and chlorine (or bromine) on the different ligand sites.[10-12] It is shown in the present paper that the combined use of iodine and fluorine has allowed the stabilization of the $Nb_3IF_7L(NbL_2)_{0.25}$ ($L =$ O, F) oxyhalide characterized by NbL_6 octahedra that share four of their apexes with four $Nb_3I^iF^i_3F^a_8L^a$ units. The oxidation state of the niobium cation will be specified on the basis of F/O disorder, IR and EPR data, and simple theoretical considerations.

Experimental Section

Synthesis and Chemical Analyses. Single crystals of the title compound were initially obtained as a byproduct from a reaction designed to obtain a fluoroiodide compound with sodium countercations, "$Na_2Nb_7F_{16}I_5$", that could have been isostructural to the $Na_2Nb_7F_{21-y}X_y$ series ($X =$ Cl, Br). Indeed, a starting mixture of NaI (Prolabo, Rectapur), NbF_5 (Aldrich, 98%), Nb (Ventron, m2N8), and I_2 (bisublimated) in the ratio $Na_2Nb_7F_{16}I_5$, handled under an inert atmosphere, was ground and formed as a pellet. Then, it was introduced into a niobium container (Plansee) which was subsequently welded under argon and encapsulated in an evacuated silica ampule. After 3 days of reaction at 800 °C, the final product was obtained as a black microcrystalline powder. The strongest lines of the powder X-ray diffraction pattern showed the presence of Nb_6F_{15}[13] and Nb_6I_{11},[14] whereas the smallest ones indicated a new phase. Single crystals of the title compound, needle-shaped or plate-shaped, suitable for X-ray diffraction studies, were formed during this reaction.

A preliminary chemical analysis by energy dispersive spectrometry (EDS), using a scanning electron microscope JEOL JSM 6400 equipped with a microprobe EDS OXFORD LINK ISIS, showed that all the single crystals contained the expected Nb, F, and I elements in a ratio close to the title stoichiometry. A weak oxygen peak was also observed but was not quantified at this stage because it could have resulted from a contamination. One of these single crystals was used for the structural determination. A first structural refinement, assuming that the title phase did not contain any trace of oxygen, led to the "$Nb_3I^iF^i_3F^{a-a}_{8/2}F^a(Nb^{II}F_2)_{0.25}$" formula. After this first structural refinement, the presence of oxygen in the structure was taken into account for obvious reasons developed in the Discussion and was subsequently verified by accurate WDS−EPMA (wavelength dispersive X-ray spectrometry−electron probe microanalyzer) measurements using a Camebax SX 50 microprobe, equipped with five spectrometers and a variety of crystals to make accessible the radiation characteristics of the full range of elements (atomic weight greater than He). Seven needle-shaped single crystals of the title compound from the same preparation were embedded in epoxy resin and polished down to 0.25 mm diamond grade, to obtain a perfect plane surface. The measurements were performed on several points of each crystal (total of 223 points), each of them exhibiting Nb, I and F, as well as oxygen element in a smaller amount. For the sake of accuracy, due to the low oxygen content, it was checked that no trace of oxygen was detected in a standard sample free of this element using the same conditions of analysis. It turned out that the compositions of the seven crystals were very close to each other. The experimental average atomic percentage composition determined using all these measurements is reported in Table 1. For comparison, the refined stoichiometry ($Nb_{3.25}F_{8.32}I_1O_{0.18}$) deduced from the structural determination (Crystal Data Collection and Refinement) as well as the two theoretical limit formulas ($Nb_{3.25}IF_8O_{0.5}$ and $Nb_{3.25}IF_{7.75}O_{0.75}$) (Discussion) are also given. Note that the F amount was slightly overestimated and the Nb amount slightly underestimated, which might be explained by an imprecise mass absorption coefficient of F Kα in Nb.

Table 1. Atomic Percentage Compositions

	% O	% I	% F	% Nb
WDS−EPMA[a]	2.5(5)	7.2(2)	66.9(9)	23.4(6)
"$Nb_{3.25}F_{8.32}I_1O_{0.18}$" [b]	1.4	7.8	65.2	25.5
"$Nb_{3.25}IF_8O_{0.5}$" [c]	3.9	7.8	62.7	25.5
"$Nb_{3.25}IF_{7.75}O_{0.75}$" [d]	5.9	7.8	60.7	25.5

[a] WDS−EPMA analysis. [b] For comparison, refined stoichiometry deduced from the structural determination. [c] Limit formula $Nb_{3.25}IF_8O_{0.5}$. [d] Limit formula $Nb_{3.25}IF_{7.75}O_{0.75}$.

Once the presence of oxygen was indicated, several syntheses were performed from NbF_5, Nb_2O_5 (Merck, Optipur), Nb (Ventron, m2N8), and I (bisublimated) with different O/F ratios at different temperatures to optimize the purity of the compound. According to the X-ray powder patterns measured after each reaction, a pure dark-brown powder, with only very slight amounts of unidentified secondary phases, could be obtained starting from the "$Nb_{3.25}IF_8O_{0.5}$" stoichiometry maintained at 570 °C for 3 days. However, it must be pointed out that the oxygen traces contained in the starting products as well as on the niobium container are enough to obtain the title compound with an appreciable yield without using Nb_2O_5.

Crystal Data Collection and Refinement. A suitable single crystal of the title compound was mounted on a Nonius KappaCCD X-ray area-detector diffractometer with Mo Kα radiation ($\lambda = 0.71073$ Å). Once the data processing was performed by the KappaCCD analysis software,[15] the cell parameters were refined as follows: $a = 13.8638(3)$ Å, $c = 8.9183(2)$ Å, $V = 1714.14(7)$ Å^3. A multiscan absorption correction was performed through SORTAV.[16] The lattice, according to the observed systematic extinctions, is body-centered. The structure was solved in the *I*4/*m* space group by direct methods (SIR97 program[17]) combined with

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Table 2. Crystal Data and Structural Refinement Parameters for $Nb_3IF_7L(NbL_2)_{0.25}$

empirical formula	$Nb_{3.25}F_{8.32}I_1O_{0.18}$	Z	8
fw	589.797	μ (cm^{-1})	79.51
D_{calcd} (g cm^{-3})	4.5725	total no. of reflns collected	19223
T (°C)	20	no. of unique reflns	1991
cryst dimens (mm)	0.03 · 0.04 · 0.21	R_{int}	0.0311
λ (Å)	0.71073	no. of obsd reflns [$I > 3\sigma(I)$]	1048
cryst syst	tetragonal	no. of refined params	67
space group	$I4/m$ (No. 87)	$R(F_o)$ (obsd reflns)^a	0.0227
a (Å)	13.8638 (3)	$R_w(F_o)$ (obsd reflns)^b	0.0244
c (Å)	8.9183 (2)	$\Delta\rho_{min}/\Delta\rho_{max}$ (e Å^{-3})	−1.08/1.14
V (Å^3)	1714.14 (7)		

^{a} $R(F_o) = \sum_{hkl}[||F_o| - |F_c||]/\sum_{hkl}[|F_o|]$. ^{b} $R_w(F_o) = [\sum_{hkl}[w(i)\,(F_o - F_c)^2]/\sum_{hkl}[w(i)\,F_o^2]]^{1/2}$.

Table 3. Selected Geometric Parameters (Bond Lengths, Å; Angles, deg)

I1−Nb1	2.8215(7)	Nb1−I1−Nb2	58.50(2)
I1−Nb2 × 2	2.7934(5)	Nb1−I1−Nb2	58.50(2)
Nb1−Nb2 × 2	2.7438(6)	Nb2−I1−Nb2	58.87(2)
Nb2−Nb2	2.7457(9)	Nb2−Nb1−Nb2	60.05(2)
Nb1−F2 × 2	2.064(3)	Nb1−Nb2−Nb2	59.98(1)
Nb1−F3 × 2	2.041(3)	Nb2−F4−Nb2	148.7(2)
Nb1−L5	2.120(4)	Nb1−F2−Nb2	167.3(2)
Nb2−F1	2.057(3)	F5−Nb3−F5	90.000
Nb2−F2	2.066(3)	O6−Nb3−O6	180.00
Nb2−F3	2.045(3)	Nb1−F5−Nb3	140.5(2)
Nb2−F4	2.046(3)		
Nb2−F4	2.119(3)		
Nb3−L5 × 4	2.041(4)		
Nb3−L6 × 2	1.849(7)		

Fourier difference syntheses and refined against F (CRYSTALS program[18]). First, the refinement was successfully carried out assuming the absence of oxygen; i.e., all the F ligands were assumed to fully occupy their crystallographic sites. All the atoms, in particular the fluorine ones, were refined anisotropically, leading to the $Nb_3F_8I(NbF_2)_{0.25}$ formula ($R = 2.26\%$, $\Delta\rho_{min} = -1.06$ e Å^{-3}, $\Delta\rho_{max} = 1.14$ e Å^{-3}, 1048 independent reflections used versus 67 least-squares parameters). Subsequently, to describe the oxygen/fluorine statistical disorder affecting the fluorine ligand sites (see the Discussion and chemical analyses), the assumption of fully occupied fluorine ligand sites was released. Oxygen was thus systematically introduced on each of the six fluorine ligand sites with arbitrary initial occupancies of 50%, in the same position and with the same isotropic displacement parameter as the associated fluorine atom. The constrained refinement of the occupancies of the latter sites revealed that only the L5 and L6 sites were affected by a F/O statistical disorder (0.47(4)/0.03(4) and 0.19(3)/0.06(3), respectively). This effect, i.e., the presence of oxygen only on both L ligand sites of the NbL_2 entity, is as a matter of fact extremely weak from a crystallographic point of view ($R = 2.27\%$, $\Delta\rho_{min} = -1.08$ e Å^{-3}, $\Delta\rho_{max} = 1.14$ e Å^{-3}, 1048 independent reflections used versus 67 least-squares parameters, to be compared to the aforementioned values) but is corroborated by simple theoretical arguments (based upon the bond valence method, BVM) and experimental measurements (IR and EPR) (see the Discussion). Crystal data and details of the final refinement are given in Table 2. Selected geometric parameters are summarized in Table 3.

EPR Measurements. EPR spectra of a polycrystalline sample were obtained using a Bruker EMX 8/2.7 spectrometer (X-band, $\nu = 9.5$ GHz) equipped with an Oxford Instruments cryogenic unit.

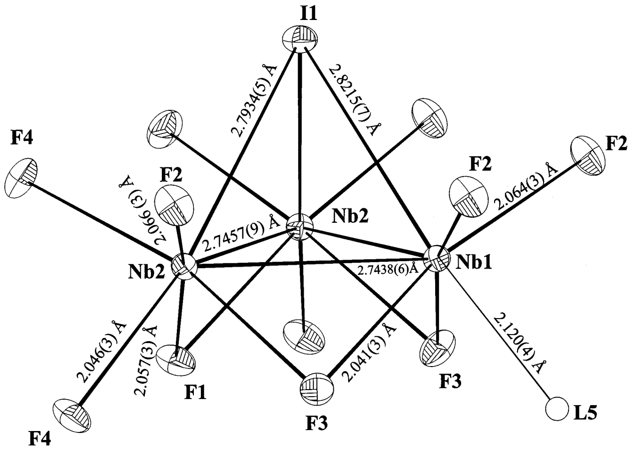

Figure 1. Representation of the $Nb_3I^iF^i_3F^a_8L^a$ unit. Displacement ellipsoids are shown at the 50% probability level.

Processing and simulation of EPR spectra were done using Bruker's WIN-EPR and SimFonia software.

IR Measurements. The IR spectrum was collected using an FTIR Bruker Equinox 55 spectrophotometer. The powdered sample was formed as a pellet with KBr salt.

Results

$Nb_3IF_7L(NbL_2)_{0.25}$ crystallizes in an original structure type built from interconnected $Nb_3IF_{11}L$ units and NbL_6 entities with L = O and F. In the $Nb_3IF_{11}L$ unit represented in Figure 1, the triangular cluster constituted by two independent niobium atoms is face-capped by one iodine ligand (μ_3-I^i) and edge-capped by three fluorine (μ_2-F^i) ones: F1 and F3. Three apical fluorine ligands, one F2 and two F4 atoms, complete the pseudooctahedral environment of Nb2, whereas the pseudooctahedral environment of Nb1 is completed by two F2 atoms and fluorine and oxygen atoms randomly distributed on one L ligand site with the following refined F:O ratio: 94:06. The occupation of the face-capping and edge-bridging positions by iodine and fluorine ligands, respectively, corroborates previous studies performed on Nb_3YX_7 (Y = chalcogen, X = halogen) series for which it has been found that the μ_3-X^i position is preferentially occupied by the most electropositive element.[4] In addition, the great discrepancy between I and F radii implies preferentially the face-capping position instead of the edge-bridging one for the iodine according to steric considerations. Moreover, in niobium cluster chemistry, it was found that I appears either in face-capping or edge-bridging cluster positions, for instance in Nb_3I_8[6] or Nb_6I_{11},[14] while F is only found, up to now, in edge-bridging positions like in Nb_6F_{15}[13] and related compounds.

The $Nb_3IF_{11}L$ units are interconnected by sharing apical fluorine atoms with six adjacent clusters, according to the arrangement represented in Figure 2. The apical ligand position (L5) randomly occupied by fluorine and oxygen is not involved in these intercluster connections. Finally, the developed formula of the units is $Nb_3(\mu_3\text{-}I^i)(\mu_2\text{-}F^i)_3F^{a-a}_{8/2}L^a$ according to the Schäfer and Schnering notation.[19]

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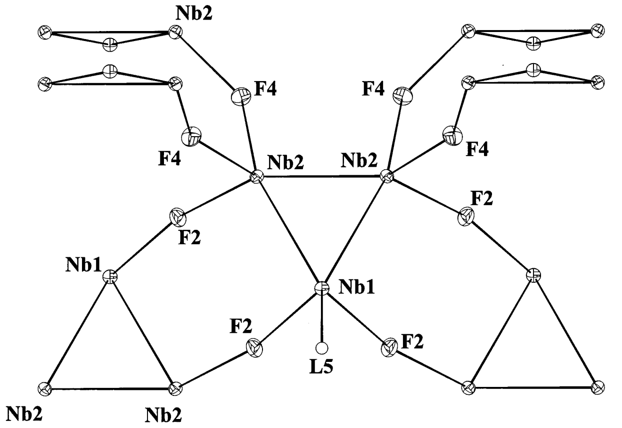

Figure 2. Interconnection of the $Nb_3IF_{11}L$ units. Displacement ellipsoids are shown at the 50% probability level. For the sake of clarity, only the Nb_3 clusters and the F^{a-a} and L5 ligands are represented.

Additional Nb3 and L6 atoms are located in channels generated by the unit arrangement represented in Figure 3. The respective F:O refined ratio for the L6 ligand is 76:24. The octahedral coordination of this Nb3 niobium is completed by four other L5 ligands of the Nb_3 cluster units—belonging to four adjacent clusters—that form an $(L5)_4$ square plane arrangement perpendicular to the L6−L6 direction (see Figure 4). The Nb3 niobium atom of the distorted NbL_6 octahedron is located at the origin and at the center of the unit cell. Finally the formula of the compound can be written as $Nb_3IF_7L\text{-}(NbL_2)_{0.25}$.

EPR spectra of a polycrystalline sample were observed within a wide range between room and liquid He temperatures. At all temperatures these spectra show multicomponent patterns centered close to $g \approx 1.9$ (Figure 5). Such a pattern is typical for the powder-like EPR spectrum of a single d^1 paramagnetic ion ($S = 1/2$) located within an axially distorted octahedral complex. Well-resolved low- and high-field hyperfine components indicate that the unpaired electron is centered at the metal ion with nuclear spin $I = 9/2$. All these features allow correlation of the observed EPR spectrum with a single niobium atom in the +4 valence state ($4d^1$, $S = 1/2$; ^{93}Nb, 100% abundance, $I = 9/2$). Computer simulation was successfully done for the parallel hyperfine components of the powder-like spectrum (see Figure 5). It was found that $g_{\parallel} = g_{zz} = 1.862 \pm 0.005$ and $A_{\parallel} = A_{zz} = 35.4 \pm 0.5$ mT. Unfortunately, very broad lines ($\Delta H_{pp} \approx 20$ mT, by simulation) prevented the reliable fitting of the perpendicular component of that pattern. Thus, within a very rough experimental error, it may be stated that $g_x \approx g_y = g_{\perp} = 1.91 \pm 0.01$ and $A_x \approx A_y = A_{\perp} < \Delta H_{pp}$.

Discussion

Niobium Oxidation State in Relation to Oxygen Content. The valence electron count (VEC) per the Nb_3 cluster in the Nb_3L_{13}-based compounds lies between 6 and 8; for instance, VEC = 6 for $Nb_3Cl_{10}(PEt_3)_3$[20] and $Nb_3O_2Cl_5$,[9] VEC = 7 for $CsNb_3SBr_7$[21] and Nb_3Cl_8,[5] and VEC = 8 for $Nb_3Cl_7(P(CH_3)(C_6H_5)_2)_6$[22] and $NaNb_3Cl_8$.[23] Several molecular orbital and band structure calculations performed on M_3L_{13} units and derived compounds suggest that, for an eight-electron system, the HOMO level is a filled $2a_1$ orbital with M−M bonding and M−L antibonding character and that the LUMO is a 2e orbital (see ref 23 and references therein). It has been stated that strong π interactions in the M−L edge-bridging bonds favor stronger antibonding character in the $2a_1$ orbital, favoring a VEC of 6 as illustrated by the example of $Zn_2Mo_3O_8$.[24]

Regardless of the NbF_2 entity, formally, the "$Nb_3F^i_3I^i\text{-}F^{a-a}_{4/2}F^a(NbF_2)_{0.25}$" formula obtained after a first refinement, in which no oxygen was taken into account, leads to a calculated valence electrons per cluster of 6. However, the oxidation state for the isolated Nb3 niobium atom deduced from charge transfer should be +2, which is not consistent with an isolated niobium cation. The oxidation state of Nb3 deduced from the BVM[25] using the Nb3−F bond lengths obtained after this first structural refinement ($d_{Nb3-F5} = 2.040$ Å × 4 and $d_{Nb3-F6} = 1.850$ Å × 2) is calculated to be 4.05 (bond valence sum calculated as follows:[25a] $V_i = \sum_j v_{ij}$, where V_i is the valence of atom i and v_{ij} is the valence of the bond between two atoms, i and j ($v_{ij} = \exp([(R_{ij} - d_{ij})/b])$ ($b = 0.37$, R_{ij} is the bond valence parameter calculated according to ref 25b: $R_{NbF} = 1.821$ Å and $R_{NbO} = 1.924$ Å, and d_{ij} is the experimental distance between i and j))). The contradiction between these two results clearly indicates that some divalent oxygen atoms must substitute some fluorine sites. Indeed, such an occupancy would not significantly affect the Nb3−(F,O) bond lengths and should lead to a realistic Nb3 oxidation state deduced from charge transfer.

The refinement of the O:F ratio using X-ray diffraction data cannot be made with a high precision considering the almost identical atomic scattering factor of both atoms even though it is well established that oxygen is present in the structure. However, as explained above in the Crystal Data Collection and Refinement, the high quality of the X-ray diffraction data gave evidence that oxygen is located only on two crystallographic sites (L5, L6) that form an octahedral site for the single Nb3 atom.

Furthermore, we have to point out that the presence of oxygen mainly on the L6 position (the occupancy of the L5 position being very weak) is also supported by an absorption band of small intensity observed at 902 cm^{-1} in the IR spectra. A vibration at a close frequency was attributed to a stretching Nb−O mode in metal oxide fluoride anions that contain a $Nb(O,F)_6$ octahedron.[26] This vibration involves a necessary Nb−terminal oxygen bond and not a Nb−O−Nb one that should give an absorption band at lower frequency.

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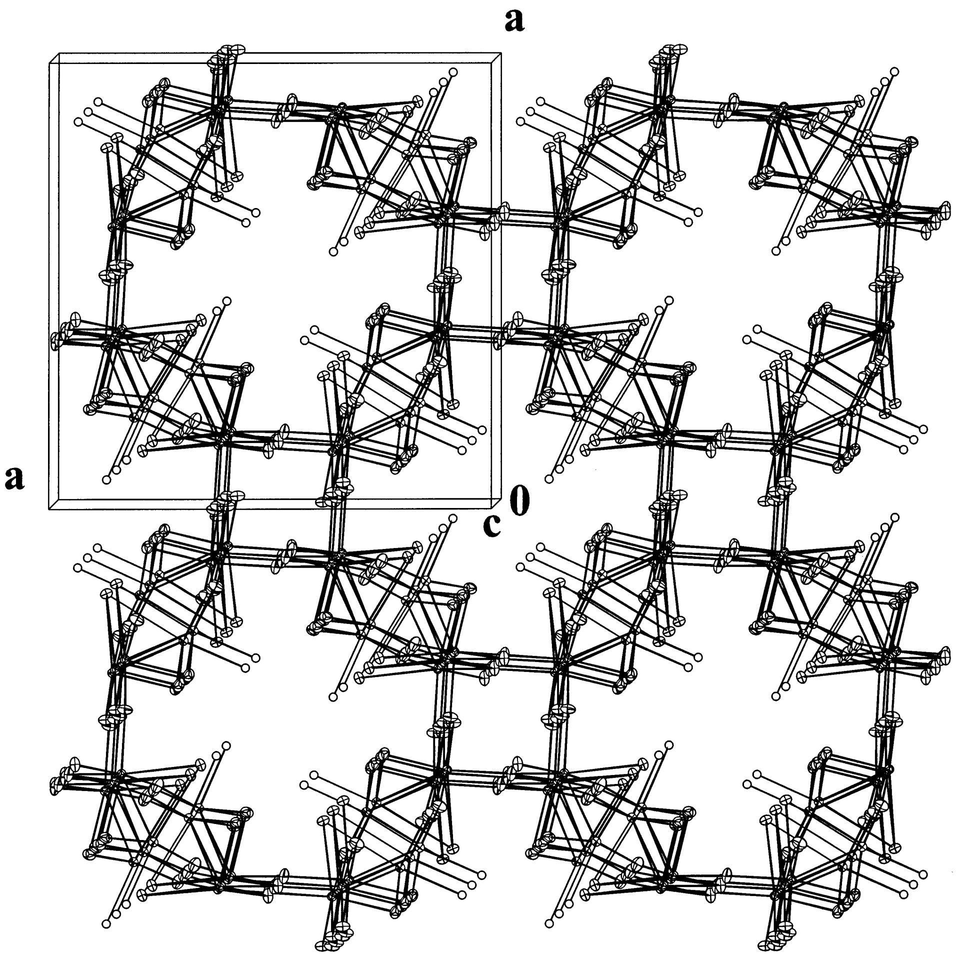

Figure 3. Representation of the crystal packing. Displacement ellipsoids are shown at the 50% probability level. For the sake of clarity, Nb3 and L6 ligands are not represented.

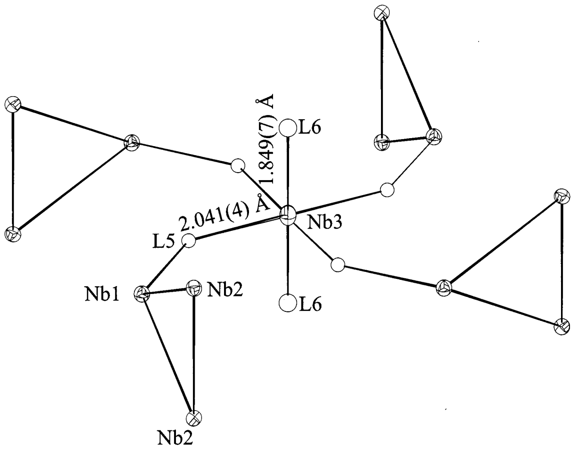

Figure 4. Representation of the Nb3L5$_{4/2}$L6$_2$ octahedron. Displacement ellipsoids are shown at the 50% probability level. For the sake of clarity, only the triangular clusters and the L6 and L5 ligands forming the octahedral coordination of Nb3 are represented.

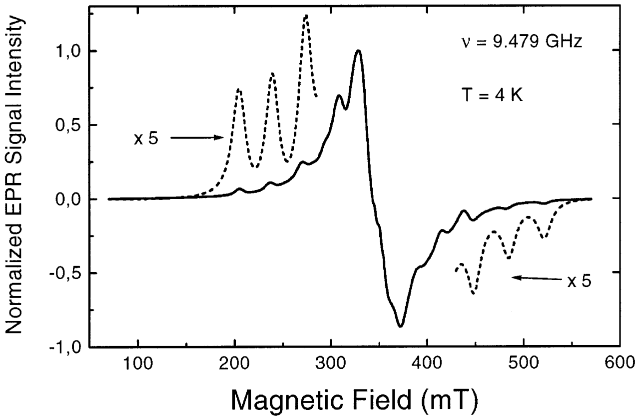

Figure 5. X-band EPR spectrum of polycrystalline $Nb_3IF_7L^a(NbL_2)_{0.25}$ recorded at $T = 4$ K: solid line, experimental spectrum; dashed line, computer simulation of the parallel hyperfine structure using the following parameters: $g_{\parallel} = 1.862$, $A_{\parallel} = 35.4$, and $\Delta H_{pp} = 20$ mT. For clarity, the simulated pattern was multiplied by a factor of 5.

As is clearly seen from the aforementioned results, the EPR spectra unambiguously indicate single Nb3 atoms in the valence state +4. Anisotropy of both the *g*-factor and hyperfine structure is in good agreement with the crystallographic data. Since no reliably detected splitting of perpendicular components was observed, the Nb(IV) atom is located within the nondistorted L5 square plane and also coordinated by the L6−L6 axis. Since no superhyperfine structure was observed, no definite conclusions on whether oxygen or fluorine occupies the L6 sites can be drawn. On the other hand, the fact that individual EPR lines remain very broad even at liquid He temperatures points out the possible structural origin of this broadening, in particular O/F disorder. Indeed, taking into account the abnormally large value for the parallel hyperfine splitting parameter $A_{\|}$ (see, for example ref 23), its variations may cause significant line broadening. These variations may be due to the distribution of L6−Nb3−L6 distances, usually observed for polycrystalline samples, as well as due to irregularity in the oxygen and fluorine locations at the L6 sites.

In summary, from a chemical point of view the oxygen content must be correlated to the niobium oxidation state (VEC = 6) of the cluster and to that of the Nb3 single atoms (+4). However, it leaves open the question of whether some kind of charge transfer occurs between the isolated niobium and the cluster and whether the Nb3 site could be statistically occupied by Nb(IV) and Nb(V) in relation with O/F disorder. Nevertheless, taking into account that the VEC per cluster is 6, two theoretical limit formulas can be obtained depending on whether Nb3 has a +4 or +5 oxidation state: $Nb_{3.25}IF_8O_{0.5}$ (VEC = 6 and $Nb3^{IV}$) and $Nb_{3.25}IF_{7.75}O_{0.75}$ (VEC = 6 and $Nb3^{V}$). The existence of a strong Nb^{IV} EPR signal combined with the chemical analyses and since the compound is obtained in high yield using the $Nb_{3.25}IF_8O_{0.5}$ starting stoichiometry give evidence that the formula of the compound does not deviate far from $Nb_{3.25}IF_8O_{0.5}$.

Comparison to Other Clusters or NbF_6-Based Compounds. Let us recall that, in cluster chemistry, numerous compounds in which highly oxidized Nb cations coexist with Nb_3 or Nb_6 clusters, for instance, in $Nb_7S_2I_{19}$[4] or $LaNb_7O_{12}$,[24] are reported. More recently, the $Na_2Nb_7F_{21-x}X_x$ series have been isolated (X= Cl, Br), their structures consisting of a $Nb_6F^i_{12-x}X_xF^{a-a}_{6/2}$ unit network, sodium countercations, and isolated NbF_6 octahedra.[25] In these series, the oxidation state of the niobium in the octahedra is +5 and the bond order sum deduced from the six equivalent Nb−F distances (d_{Nb-F} = 1.85(5) Å) is calculated to be 5.54, giving confidence in the calculations performed using the BVM in the present work. Furthermore, in the $Na_2Nb_7F_{21-x}X_x$ series, the NbF_6 octahedra are isolated and consequently the six Nb−F distances are equivalent.

A useful comparison of the bond lengths in the studied compound can be made with those of NbF_4.[13] The structure of this simple fluoride (SnF4 type[30]) is based on NbF_6 octahedra sharing four of their apexes with other octahedra to form infinite $NbF_2F_{4/2}$ planes. In such an arrangement, two terminal fluorine atoms remain unshared. This topology can be related to that of the $Nb3L6_2L5_{4/2}$ octahedron in $Nb_3I^iF^i_3F^{a-a}_{8/2}L^a(NbL_2)_{0.25}$: the two L6 ligands are unshared, and the four L5 ligands are shared with the $Nb_3I^iF^i_3F^{a-a}_{8/2}L^a$ unit. It is noteworthy that the Nb3−L5 bond length (2.041(4) Å) is the same as the Nb−F planar one in NbF_4 (2.04 Å) and the terminal Nb3−L6 length is slightly smaller than that observed in NbF_4 (1.849(7) and 1.877[31] Å, respectively). The oxidation state for Nb deduced from the BVM in NbF_4 is calculated to be 4.01 and fully agrees with that found by charge transfer. Recently, in the oxide fluoride NbF_4-derived compound, namely, $NbOF_3$,[31] the presence of an oxygen/fluorine statistical occupancy on both anion sites has been shown (by Rietveld refinement from powder X-ray diffraction data, combined with IR and RMN experiments). The title compound is another example of an oxide fluoride with an oxygen/fluorine distribution around a niobium cation.

In conclusion, the title compound displays an original topology characterized by the coexistence of two different networks built from a triangular Nb_3 cluster and from isolated niobium cations in a high oxidation state.[11,29] Besides the case of Nb_6F_{15},[13] the present work yields a new example of metal−metal bonds with fluorine ligands and the first example where a triangular Nb_3 cluster is associated with a fluorine bridging ligand. The insertion of a small alkali metal in a similar architecture is now in progress to obtain a triangular Nb_3 paramagnetic cluster (VEC = 7) that could interact with the single Nb^{4+}.

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Supporting Information Available: An X-ray crystallographic file of $Nb_{3.25}F_{8.32}I_1O_{0.18}$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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