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Structural Studies of Indium and Thallium Insertion into the Framework of the Cluster Compound $Ti_2Nb_6Cl_{14}O_4$

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We have investigated the possibility of altering the electronic configuration of the niobium oxochloride cluster compound $Ti_2Nb_6Cl_{14}O_4$ **(I)** by doping this material with monovalent cations that can fit into cavities present in its cluster framework. The doping of **I** with In^+ and Tl^+ ions resulted in the formation of $M_xTi_2Nb_6Cl_{14-x}O_{4+x}$ ($M = In$, $x = 0.10, 0.20, 0.27$; $M = Tl$, $x = 0.10, 0.20$) in which the M^+ ions partially occupy these cavities. The crystal structure analysis indicated that the additional charge provided by M^+ ions is compensated by substitution of chlorine by oxygen, which leads to the cluster electronic configuration being intact. Crystal data: $In_{0.272}Ti_2Nb_6Cl_{13.728}O_{4.272}$, space group $C2/c$ (No. 15), $a = 12.679(2)$ Å, $b = 14.567(2)$ Å, $c = 12.632(3)$ Å, $\beta = 95.26(2)°$, $Z = 4$; $Tl_{0.196}Ti_2Nb_6Cl_{13.804}O_{4.196}$, space group $C2/c$ (no. 15), $a = 12.732(1)$ Å, $b = 14.607(2)$ Å, $c = 12.662(2)$ Å, $\beta = 95.28(1)°$, $Z = 4$.

Introduction

Formation of clusters via metal−metal bonding is a characteristic feature of many compounds with early transition metals in low oxidation states.[1] In reduced niobium halides and oxides, the most common structural motif is the cluster unit $[(Nb_6L^{i}_{12})L^{a}_{6}]^{n-}$ (L = F, Cl, Br, O).[2−4] It is based on an octahedron of Nb atoms, surrounded by 12 “inner” (L^i) and 6 “outer” (L^a) ligands. Experimental and theoretical investigations have shown that in these compounds valence electrons available for metal−metal interactions are distributed among a_{1g}, t_{1u}, t_{2g}, and a_{2u} energy states.[3,5] The character of the a_{2u} state is determined by the balance between its Nb−Nb bonding character and Nb−L antibonding character. In niobium halides, a_{2u} is overall nonbonding and is partially or fully occupied, leading to compounds with valence electron concentration (VEC) of 15 or 16. The 16-electron configuration is more stable and leads to a diamagnetic cluster $(Nb_6X_{18})^{4-}$ (X = Cl, Br), whereas compounds with 15-electron clusters $(Nb_6X_{18})^{3-}$ are paramagnetic. Recent efforts in the investigation of niobium cluster halides focused on the preparation of compounds in which these paramagnetic clusters can interact with each other or with other magnetically active centers, such as rare earth or transition metal cations or organic species.[3] However, such interactions have been found to be weak, if present at all.[6−8] This is due, in particular, to the steric effect of halide ligands causing large separations between the clusters and the magnetic counterions (4.8−5.2 Å). Hence, the use of ligands with smaller size such as fluorine or oxygen constitutes one of the simplest and the most obvious strategy to decrease the ligand’s matrix effect and allow better cluster−cluster and cluster−cation interactions. Recently, Cordier et al. reported the synthesis of $ScNb_6Cl_{13}O_3$ and the series $RETa_6Br_{13}O_3$.[9,10] The structural analysis of these compounds shows that they are characterized by short distances between niobium and RE^{3+} counterion (Nb−Sc = 3.391 Å and Ta−RE = 3.585 Å) (RE = rare earth).

Our systematic investigation of niobium oxochloride cluster compounds containing magnetically active transition metal ions recently led to the synthesis and structural characterization of the compound $Ti_2Nb_6Cl_{14}O_4$.[11] It crystallizes in a novel structural type in which niobium clusters form *perovskite*-like layers linked to each other via zigzag chains of edge-sharing $[TiCl_4O_2]$ octahedra (Figure 1). Short Nb−Ti distances of 3.3657(7) Å characterize this compound. The valence electron concentration in these oxohalide cluster compounds is 14, as observed in most niobium oxide cluster compounds.[4] This can be explained by the increase in niobium−ligand antibonding interactions upon substitution of halogen by oxygen, which results in an overall antibonding character of the a_{2u} orbital. However, a few 15-electron compounds are known among niobium cluster oxides as is the case for $LaNb_8O_{14}$ and $Rb_4Al_2Nb_{35}O_{70}$.[12,13]

The main goal at the origin of this report was to change the electronic configuration of the cluster in $Ti_2Nb_6Cl_{14}O_4$ (**I**) by increasing its VEC from 14 to 15 in order to obtain paramagnetic clusters and to study magnetic interactions between Ti(III) and the cluster unit. The presence of empty cavities (one per cluster)

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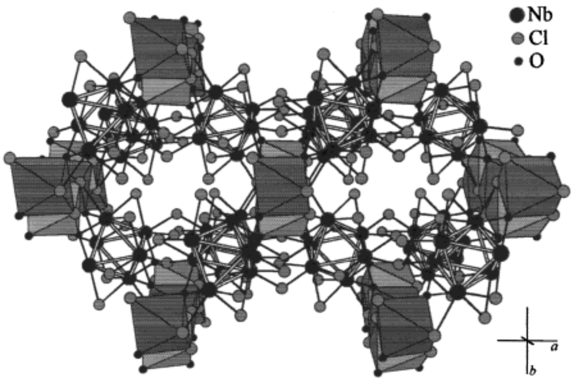

Figure 1. Fragment of the crystal structure of $Ti_2Nb_6Cl_{14}O_4$ showing the cluster layers connected via zigzag chains of edge-shared $TiCl_4O_2$ octahedra.

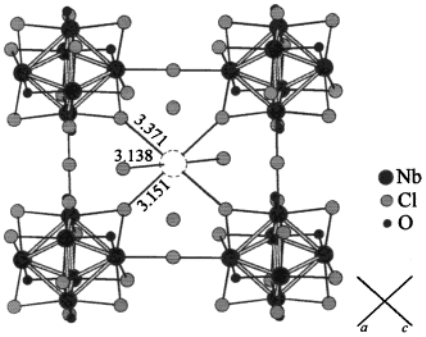

Figure 2. Fragment of the perovskite-like cluster layer showing the octahedral cavity within the layer in the $Ti_2Nb_6Cl_{14}O_4$ framework. The empty sphere represents the center of the cavity.

within the pseudosquare cluster layers in $Ti_2Nb_6Cl_{14}O_4$ (Figure 2) and low-lying empty energy states suggested that reduction of the cluster in this compound can be achieved by filling these cavities with monovalent cations of suitable size, such as In^+ or Tl^+. Herein, we describe the synthesis and crystal structure of a new series obtained as a result of our investigation, namely, $M_xTi_2Nb_6Cl_{14-x}O_{4+x}$ (M = In, $x = 0.10, 0.20, 0.27$; M = Tl, $x = 0.10, 0.20$).

Experimental Section

Synthesis. The compound $In_{0.272}Ti_2Nb_6Cl_{13.728}O_{4.272}$ (**II**) was initially obtained in low yield as black monoclinic crystals from a reaction designed for the preparation of $InTi_2Nb_6Cl_{14}O_4$. Subsequently, the compounds $In_xTi_2Nb_6Cl_{14-x}O_{4+x}$ ($x = 0.10, 0.20, 0.27$) were prepared from a stoichiometric mixture of Nb powder (Alfa Aesar, 99.8%), $NbCl_5$ (Alfa Aesar, 99%), Nb_2O_5 (Johnson Matthey, 99.5%), Ti foil (Alfa Aesar, 99.9%), and In metal (Johnson Matthey, 99.9%), handled in argon atmosphere. The mixtures were placed into a quartz tube (outer diameter 9 mm, inner diameter 7 mm, length 4 cm), sealed under vacuum, and heated at 750 °C for 96 h followed by controlled cooling to room temperature in 96 h. The presence of In, Nb, Ti, and Cl in the crystals was confirmed by energy-dispersive X-ray analysis (EDAX). The actual compositions of the compounds with $x = 0.2$ and 0.27 were determined from the structural analysis using single-crystal X-ray diffraction.

To compare the structural effects of M^+ cations of different sizes, the compounds $Tl_xTi_2Nb_6Cl_{14-x}O_{4+x}$ ($x = 0.1$ and 0.2) were synthesized under the same conditions, using TlCl (Johnson Matthey, 99.999%) as a source of thallium. These phases were obtained in high yield (>90%) and were characterized by EDAX and single-crystal X-ray diffraction analyses. The reactions carried out at higher temperature (860 °C) and followed by quenching did not lead to significant changes in the amount of In/Tl in the final products according to EDAX analysis.

Table 1. Crystal Data and Structure Refinement for $M_xTi_2Nb_6Cl_{14-x}O_{4+x}$

formula	$In_{0.272}Ti_2Nb_6Cl_{13.728}O_{4.272}$	$Tl_{0.196}Ti_2Nb_6Cl_{13.804}O_{4.196}$
fw, g mol^{-1}	1241.20	1250.54
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (no.15)	*C*2/*c* (no.15)
a, Å	12.679(2)	12.732(1)
b, Å	14.567(2)	14.607(2)
c, Å	12.632(3)	12.662(2)
β, deg	95.25(2)	95.28(1)
V, Å^3	2323.3(7)	2344.9(5)
Z	4	4
temp, K	293	293
λ, Å	0.710 73	0.710 73
μ (Mo Kα), mm^{-1}	5.361	6.416
ρ_{calcd}, g cm^{-3}	3.549	3.542
R_1 [a] ($I > 2\sigma(I)$)	0.0181	0.0346
R_1 [a] (all data)	0.0228	0.0589
wR2 [b] (all data)	0.0395	0.0629

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR^2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = (\max(F_o^2,0) + 2F_c^2)/3$, with $a = 0.0146$, $b = 8.805$ for $In_{0.272}Ti_2Nb_6Cl_{13.728}O_{4.272}$ and $a = 0.0237$, $b = 0$ for $Tl_{0.196}Ti_2Nb_6Cl_{13.804}O_{4.196}$.

Elemental Analysis. Crystals of the phases prepared were analyzed using EDAX. The spectra were obtained using a Philips 515 scanning electron microscope equipped with a microprobe.

Crystal Structure Determination. (a) $In_{0.272}Ti_2Nb_6Cl_{13.728}O_{4.272}$ (II). A black columnlike crystal was selected for X-ray diffraction analysis and mounted in a glass capillary under an inert atmosphere. The intensity data were collected on a Brüker P4 diffractometer using Mo Kα radiation. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on ψ scans was applied. The extinction conditions were found to be consistent with the space groups *C*2/*c* and *Cc*. The intensity statistics indicated a centrosymmetric space group; thus the structure was solved in *C*2/*c*. Initial atomic positions of Nb, Ti, and Cl were determined using direct methods (Shelxs-86).[14] Subsequently, oxygen and indium atoms were located from Fourier difference maps generated after least-squares refinement cycles (Shelxl-93).[15] The low intensity of the indium peak indicated that it is partially occupied. In addition, unreasonably short distances between indium and Cl7 indicated that the indium position can only be occupied when Cl7 is absent. The larger thermal parameter of Cl7 compared to those of the other chlorine ligands and the presence of a small peak in its vicinity with an environment consistent with that of inner oxide ligand suggested that the Cl7 position is partially occupied by chlorine and oxygen (Cl7 and O7). The distance between indium and O7 agrees with typical In^I−O distances. The occupancies of Cl7 and O7 were refined with the restriction that they add up to a 100% occupancy of the site. Subsequent refinement showed that In1 position is split into two sites, In(1a) and In(1b) with separation of about 0.4 Å. A Fourier difference map revealed a small residual peak at 1.81 Å from Cl5. The distances between this peak and other nearest chlorines were consistent with In^I−Cl distances. This peak was assigned to indium (In2), which is present when the Cl5 site is occupied by oxygen. However, the small occupancy of the In2 site did not allow resolution of the position of Cl5 into chlorine and oxygen. In the final refinement stages, all atoms but indium and O7 were refined anisotropically, resulting in $R_1 = 0.0228$ and wR2 = 0.0395 based on F^2 for all data. Subsequent refinement of the structure in the noncentrosymmetric space group *Cc* did not lead to new features or lower residuals.

(b) $Tl_{0.196}Ti_2Nb_6Cl_{13.804}O_{4.196}$. A black monoclinic parallelepiped-like crystal was selected for X-ray diffraction analysis and mounted in a glass capillary in the drybox. The intensity data were collected on a Brüker P4 diffractometer using Mo Kα radiation. The data were

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Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for M$_x$Ti$_2$Nb$_6$Cl$_{14-x}$O$_{4+x}$

	In$_{0.272}$Ti$_2$Nb$_6$Cl$_{13.728}$O$_{4.272}$					Tl$_{0.196}$Ti$_2$Nb$_6$Cl$_{13.804}$O$_{4.196}$				
	x	*y*	*z*	U_{eq}	SOF	*x*	*y*	*z*	U_{eq}	SOF
Nb(1)	0.2051(1)	0.1292(1)	0.4383(1)	0.008(1)		0.2050(1)	0.1293(1)	0.4383(1)	0.009(1)	
Nb(2)	0.1357(1)	0.3108(1)	0.3912(1)	0.009(1)		0.1355(1)	0.3109(1)	0.3911(1)	0.010(1)	
Nb(3)	0.1347(1)	0.2300(1)	0.6083(1)	0.008(1)		0.1346(1)	0.2300(1)	0.6085(1)	0.010(1)	
Ti(1)	0	0	0.5	0.010(1)		0	0	0.5	0.012(1)	
Ti(2)	0	0.1080(1)	0.25	0.012(1)		0	0.1077(1)	0.25	0.013(1)	
Cl(1)	0	0.2067(1)	0.75	0.021(1)		0	0.2065(1)	0.75	0.021(1)	
Cl(2)	0	0.3844(1)	0.25	0.028(1)		0	0.3850(1)	0.25	0.025(1)	
Cl(3)	0.1101(1)	−0.0162(1)	0.3504(1)	0.012(1)		0.1100(1)	−0.0162(1)	0.3505(1)	0.013(1)	
Cl(4)	0.3312(1)	0.1198(1)	0.3008(1)	0.015(1)		0.3309(1)	0.1196(1)	0.3007(1)	0.016(1)	
Cl(5)	−0.0119(1)	0.3062(1)	0.5035(1)	0.017(1)		−0.0115(1)	0.3064(1)	0.5037(1)	0.017(1)	
Cl(6)	0.3304(1)	0.0293(1)	0.5471(1)	0.015(1)		0.3300(1)	0.0292(1)	0.5473(1)	0.016(1)	
Cl(7)	0.2470(1)	0.3360(1)	0.2502(2)	0.018(1)	0.907(9)	0.2472(1)	0.3359(1)	0.2498(2)	0.018(1)	0.93(1)
O(7)	0.257(3)	0.325(3)	0.298(5)	0.03(1)	0.093(9)	0.247(4)	0.322(4)	0.293(7)	0.01(1)	0.07(1)
Cl(8)	0.1179(1)	0.1008(1)	0.1087(1)	0.016(1)		0.1179(1)	0.1010(1)	0.1086(1)	0.017(1)	
O(1)	0.0953(2)	0.1876(2)	0.3320(2)	0.011(1)		0.0954(3)	0.1876(2)	0.3319(3)	0.013(1)	
O(2)	0.0919(2)	0.1076(2)	0.5408(2)	0.010(1)		0.0926(3)	0.1079(2)	0.5411(3)	0.011(1)	
M(1a)	0.267(1)	0.280(1)	0.1074(5)	0.021(3)	0.068(8)	0.266(1)	0.276(1)	0.0948(5)	0.024(2)	0.052(7)
M(1b)	0.250(2)	0.301(2)	0.1050(8)	0.024(4)	0.046(8)	0.252(2)	0.295(2)	0.0941(7)	0.026(4)	0.034(7)
M(2)	−0.150(2)	0.295(1)	0.525(2)	0.044(7)	0.022(2)	−0.165(3)	0.293(3)	0.527(3)	0.06(1)	0.012(1)

Table 3. Selected Bond Lengths (Å) for M$_x$Ti$_2$Nb$_6$Cl$_{14-x}$O$_{4+x}$

	M = In	M = Tl
(Nb$_6$Cl$_{14}$O$_4$) Cluster Unit		
Nb(1)−Nb(3)	2.8138(6)	2.8232(7)
Nb(1)−Nb(2)	2.8336(6)	2.8429(7)
Nb(1)−Nb(2)′	2.9470(8)	2.9573(7)
Nb(1)−Nb(3)′	2.9844(6)	2.9950(7)
Nb(2)−Nb(3)′	2.9715(7)	2.9867(7)
Nb(2)−Nb(3)	2.9852(7)	2.9967(7)
Nb−Cl^i:		
Nb(1)−Cl(4)	2.470(1)	2.478(1)
Nb(1)−Cl(6)	2.475(1)	2.485(1)
Nb(2)−Cl(7)	2.401(2)	2.413(2)
Nb(2)−Cl(5)	2.450(1)	2.456(1)
Nb(2)−Cl(6)	2.482(1)	2.489(1)
Nb(3)−Cl(7)	2.424(2)	2.431(2)
Nb(3)−Cl(5)	2.447(1)	2.452(1)
Nb(3)−Cl(4)	2.491(1)	2.499(1)
Nb−Cl^a:		
Nb(1)−Cl(3)	2.631(1)	2.640(1)
Nb(2)−Cl(2)	2.5944(9)	2.603(1)
Nb(3)−Cl(1)	2.6062(6)	2.6133(6)
Nb−O^i:		
Nb(1)−O(1)	2.030(3)	2.036(4)
Nb(1)−O(2)	2.044(3)	2.045(4)
Nb(2)−O(1)	1.993(3)	1.999(4)
Nb(2)−O(7)	2.04(5)	1.95(7)
Nb(3)−O(2)	2.028(3)	2.029(3)
Nb(3)−O(7)	1.91(6)	2.03(7)
Ti Environment		
Ti(1)−O(2)	1.992(3), 2×	2.008(3), 2×
Ti(1)−Cl(8)	2.428(1), 2×	2.437(1), 2×
Ti(1)−Cl(3)	2.461(1), 2×	2.468(1), 2×
Ti(2)−O(1)	1.910(3), 2×	1.918(4), 2×
Ti(2)−Cl(8)	2.433(1), 2×	2.441(1), 2×
Ti(2)−Cl(3)	2.550(1), 2×	2.555(2), 2×
M Environment		
M(1a)−Cl(8)	3.22(1)	3.190(9)
M(1a)−Cl(1)	3.32(1)	3.42(1)
M(1a)−Cl(3)	3.38(1)	3.46(1)
M(1a)−Cl(4)	3.42(2)	3.51(2)
M(1a)−Cl(5)	3.43(2)	3.38(2)
M(1a)−Cl(5)′	3.44(2)	3.39(1)
M(1a)−Cl(8)	3.655(7)	3.571(7)
M(1a)−O(7)	2.50(6)	2.63(8)
M(1b)−Cl(5)	3.20(2)	3.20(2)
M(1b)−Cl(3)	3.22(2)	3.31(2)
M(1b)−Cl(8)	3.37(2)	3.32(2)
M(1b)−Cl(1)	3.51(2)	3.57(2)
M(1b)-Cl(8)′	3.60(1)	3.53(1)
M(1b)−Cl(4)	3.70(3)	3.73(3)
M(1b)−Cl(5)′	3.73(3)	3.64(3)
M(1b)−O(7)	2.45(7)	2.55(8)
M(2)−Cl(8)	3.34(2)	3.37(4)
M(2)−Cl(6)	3.44(2)	3.46(4)
M(2)−Cl(1)	3.52(2)	3.59(4)
M(2)−Cl(8)′	3.55(2)	3.41(4)
M(2)−Cl(7)	3.63(2)	3.63(4)
M(2)−Cl(4)	3.73(2)	3.69(4)
M(2)−Cl(7)′	3.75(2)	3.65(4)
Other Important Distances		
Nb(1)−Ti(1)	3.3586(6)	3.3705(5)
Nb(1)−Ti(2)	3.3734(8)	3.3841(7)
Shortest M−M Distances		
M(1a)−M(1a)′	2.84(1)	2.51(1)
M(1b)−M(1b)′	3.04(3)	2.72(3)
M(2)−M(2)′	2.86(4)	2.54(7)
M(1a)−M(2)′	2.14(2)	1.93(4)
M(1b)−M(2)	1.98(2)	1.81(4)
M(1a)−Cl(7)	2.02(1)	2.18(1)
M(1b)−Cl(7)	1.91(1)	2.07(1)
M(2)−Cl(5)	1.81(2)	2.02(4)

corrected for Lorentz and polarization effects, and an analytical (face-indexing) absorption correction was applied. The extinction conditions were consistent with space groups *C*2/*c* and *Cc*. The atomic positions obtained for **II** were used at the initial stages of refinement. At the final stage, all atoms but thallium and O7 were refined anisotropically. The occupancies of Cl7 and O7 were refined with the restriction that the total occupancy of the site is 100%. The final refinement yielded $R_1 = 0.0588$ and wR2 = 0.0632 based on all data. The refinement of the structure in the noncentrosymmetric space group *Cc* did not lead to new features or lower residuals.

Details of data collection and crystal data for In$_{0.272}$Ti$_2$Nb$_6$Cl$_{13.728}$O$_{4.272}$ and Tl$_{0.196}$Ti$_2$Nb$_6$Cl$_{13.804}$O$_{4.196}$ are summarized in Table 1. Atomic positions and equivalent isotropic parameters are given in Table 2, and selected bond distances and angles are in Table 3.

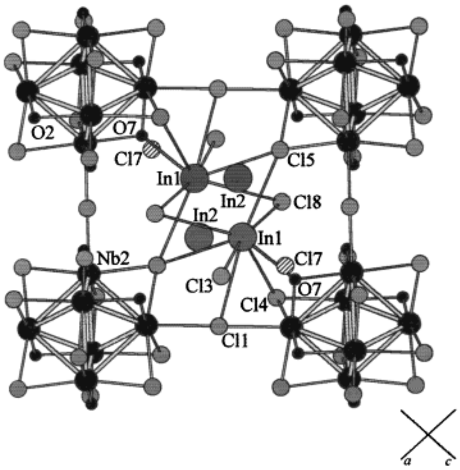

Figure 3. Fragment of $M_xTi_2Nb_6Cl_{14-x.728}O_{4+x}$ structure showing the location of the sites occupied by the M atoms. The hatched spheres represent Cl7 positions that are not occupied when In1 is present. The In2−Cl bonds are omitted for clarity.

Results and Discussion

Synthesis. To determine the maximum amount of indium that can be inserted in the $Ti_2Nb_6Cl_{14}O_4$ framework, the composition $InTi_2Nb_6Cl_{13}O_5$, which corresponds to one In^+ cation per cluster and takes into account the substitution of one chlorine by one oxygen ligand to compensate for the charge difference, was studied. The product based on the $Ti_2Nb_6Cl_{14}O_4$ framework was obtained in low yield (about 20%) and was found to contain 0.263(4) indium atoms per cluster according to single-crystal X-ray diffraction analysis, similar to compound (**II**). The products of reactions with higher indium amounts (two per cluster) did not contain the $In_xTi_2Nb_6Cl_{14-x}O_{4+x}$ phase. Subsequently, the compounds $In_xTi_2Nb_6Cl_{14-x}O_{4+x}$ ($x = 0.1$ and 0.2) were prepared in high yield (>90%). The product of the reaction corresponding to $x_{\mathrm{initial}} = 0.2$ was analyzed by EDAX and single-crystal X-ray diffraction. The structure analysis resulted in crystallographic data and atomic positions identical to those found for **II**. The total occupancy of indium sites was found to be 0.210(3) per cluster. In the case of $x_{\mathrm{initial}} = 0.1$, the product was analyzed by EDAX analysis, which showed that the intensities of the indium peaks were approximately 2 times lower than those in the case of $x_{\mathrm{initial}} = 0.2$.

For the thallium phases EDAX analysis confirmed the presence of thallium in ca. 2:1 ratio for $x_{\mathrm{initial}} = 0.2$ and $x_{\mathrm{initial}} = 0.1$. The structure analysis showed these phases to be isotypic with the $In_xTi_2Nb_6Cl_{14-x}O_{4+x}$ compounds and to contain 0.196(2) and 0.102(2) thallium atoms per cluster for $x_{\mathrm{initial}} = 0.2$ and $x_{\mathrm{initial}} = 0.1$, respectively.

Crystal Structure. A fragment of the crystal structure of the compounds $M_xTi_2Nb_6Cl_{14-x}O_{4+x}$ (M = In, Tl) is shown in Figure 3. The main structural motif of $Ti_2Nb_6Cl_{14}O_4$ remains essentially intact as the M^+ cations enter the cavities within the cluster layers. However, for every cation M^+ inserted in the $Ti_2Nb_6Cl_{14}O_4$ framework, one chloride (Cl7 for M1 position, and Cl5 for M2 position) is substituted by an oxide ligand. Therefore, the insertion of In^+ or Tl^+ ions does not lead to an increase in the number of valence electrons available for Nb−Nb interactions within the clusters. These results confirm the stability of the VEC of 14 in niobium oxochlorides. In addition to retaining the stable electronic configuration, substitution of Cl7 by oxygen allows the cations M^+ to shift from the center of the octahedral cavity (Figure 2) to occupy two crystallographically independent sites M1 and M2 with higher coordination number (CN = 8). Both of these sites and their inversion-related equivalents are located within the same cavity. The distance between M1 and M2 (1.98(2) Å) is too short for these positions to be simultaneously occupied. The asymmetric coordination environments of In1 and In2 and the larger separation between the inversion-related indium positions (d(In1−In1) = 2.84(1) and d(In2−In2) = 2.86(4) Å) suggest that formation of indium dimers is possible. Indeed, $In^{I}-In^{I}$ dimers with an In−In distance of 2.864 Å were found in $In_6La_{10}O_6S_{17}$.[16] However, the short Tl1−Tl1 distance (2.51(1) Å) found in the compound $Tl_xTi_2Nb_6Cl_{13-x}O_{4+x}$ ruled out the simultaneous presence of two M atoms in the same cavity, since $Tl^{I}-Tl^{I}$ separation is usually much larger, 3.2−3.9 Å.[17] Thus, the maximum amount of M^+ cations that can in principle be incorporated in the $Ti_2Nb_6Cl_{14}O_4$ framework is one per cluster, which corresponds to the stoichiometry $MTi_2Nb_6Cl_{13}O_5$. However, the highest total M site occupancies that could be experimentally achieved was $x = 0.272$ (for M = In) per cluster. Our investigations show that for higher values of x_{initial}, other phases with new structural types based on similar octahedral clusters are formed besides the compounds reported here. The investigation of their structural and physical properties is underway.

Conclusion

Our studies show that In^+ and Tl^+ ions can be incorporated in the framework of the niobium oxochloride $Ti_2Nb_6Cl_{14}O_4$ under high-temperature conditions. The presence of two ligands with different charge and size allows for the insertion to occur without changing the electronic properties of the material. The number of valence electrons per cluster is maintained through simultaneous substitution of chlorine by oxygen. The substitution could probably be avoided in a low-temperature intercalation process, but the cavities within the cluster layers cannot be accessed by large cations without bond breaking. Intercalation of small cations such as Li^+ or Cu^+ into the empty channels present between the cluster layers in $Ti_2Nb_6Cl_{14}O_4$ is currently under investigation using “soft chemistry” techniques.

Supporting Information Available: One X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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