Articles

A New Quasi-One-Dimensional Niobium Oxychloride Cluster Compound $Cs_2Ti_4Nb_6Cl_{18}O_6$: Structural Effects of Ligand Combination

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The new niobium oxychloride cluster compound, $Cs_2Ti_4Nb_6Cl_{18}O_6$, was obtained by solid-state synthesis techniques in the course of our systematic investigation of metal oxychloride systems aimed at the preparation of low-dimensional cluster compounds. $Cs_2Ti_4Nb_6Cl_{18}O_6$ crystallizes in the trigonal system, with unit cell parameters $a = 11.1903(7)$, $c = 15.600(2)$ Å, space group $P\bar{3}1c$, $Z = 2$. Its crystal structure was determined by single-crystal X-ray diffraction techniques. The full-matrix least-squares refinement against F^2 converged to $R_1 = 0.048$ ($F_o > 4\sigma(F_o)$), $wR_2 = 0.069$ (all data). The structure is based on an octahedral cluster unit $(Nb_6Cl^i_6O^i_6)Cl^a_6$ in which the six edge-bridging oxide ligands are arranged in two sets of three on opposite sides of the Nb_6 octahedron. Ti^{3+} ions link the clusters through O^i and Cl^a ligands to form linear chains running along the c axis. The location of titanium ions correlates with the arrangement of oxide ligands around the Nb_6 metal core. The chains interact with each other through additional Ti^{3+} and Cs^+ ions. Interchain interactions are significantly weaker than intrachain interactions, resulting in a quasi-one-dimensional character of the overall structure.

Introduction

Low-dimensional materials containing transition metals have attracted significant attention due to their remarkable structural and physical properties and a wide range of applications in catalysis, ionic transport, and redox intercalation processes.[1−4] Recently, we began investigating a new approach to the design and preparation of low-dimensional materials containing octahedral metal clusters. Our strategy is based on creating anisotropic bonding preferences of the cluster units by changing the charge distribution around the metal core using a combination of ligands with large difference in their charge density. Previous research efforts focused on developing a strategy for modifying the cluster framework dimensionality by adjusting the metal-to-ligand ratio.[5−7] Our systematic investigation of niobium oxychlorides containing octahedral Nb_6 clusters recently led to the preparation of two layered materials, $[Tl_5(Ti_2Cl_9)][(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$ and $Cs_2Ti_3(Nb_6Cl_{12.5}O_4)_2Cl_2$, which have unique hexagonal-bronze-type and graphite-type cluster connectivity, respectively.[8,9] Here we describe a new oxychloride $Cs_2Ti_4Nb_6Cl_{18}O_6$ (**I**) in which discrete niobium clusters are strongly bonded to each other through Ti^{3+} ions to form chains, resulting in quasi-one-dimensional character of the overall structure.

Experimental Section

Synthesis. The title compound forms in high yield (>95%) as black (dark-brown when ground) air-stable needles with hexagonal cross-section in a reaction of stoichiometric amounts of Nb powder (Alfa, 99.8%), Ti foil (Alfa, 99.99%), CsCl (Alfa, 99.9%), Nb_2O_5 (Alfa, 99.5) and $NbCl_5$ (Alfa, 99.9%). The mixture (0.2 g) was prepared under argon atmosphere, placed in a silica tube (OD 9 mm, ID 7 mm, length 4 cm), sealed under vacuum, heated for 4 days at 720 °C and cooled to 500 °C in 4 days, followed by radiative cooling to room temperature. The purity of the product was confirmed by X-ray powder diffraction, and elemental composition was verified by semiquantitative energy-dispersive X-ray analysis.

Crystal Structure Determination. A black needlelike crystal was selected for X-ray diffraction analysis and mounted in a glass capillary under inert atmosphere. The intensity data were collected at room temperature on a Bruker P4 diffractometer using Mo Kα radiation. The unit cell parameters were refined based on 39 centered reflections to give a hexagonal unit cell with $a = 11.1903(7)$, $c = 15.600(2)$ Å. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on 10 ψ scans with $17.3° \leq 2\theta \leq 31.7°$ was applied. The Laue symmetry and the extinction conditions were found to be consistent with the space groups $P\bar{3}1c$ and $P31c$. The structure was solved in $P\bar{3}1c$ as the intensity statistics indicated a centrosymmetric space group. Initial atomic positions of all atoms except Cs(2) were determined using direct methods (Shelxs-86).[10] Isotropic least-squares refinement (Shelxl-93)[11] of the model converged to $R_1 = 0.096$ for 727 data with $F_o > 4\sigma(F_o)$ and $R_1 = 0.156$, $wR_2 =$

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10.1021/ic010392q CCC: $20.00

Table 1. Crystal Data and Structure Refinement for $Cs_2Ti_4Nb_6Cl_{18}O_6$

formula	$Cs_2Ti_4Nb_6Cl_{18}O_6$
a (Å)	11.1903(7)
c (Å)	15.600(2)
V (Å^3)	1691.7(3)
Z	2
fw (g/mol)	1748.98
space group	$P\bar{3}1c$ (No. 163)
T	298(1) K
λ(Å)	0.71073
ρ_{calcd} (g cm^{-3})	3.433
μ (cm^{-1})	64.05
$R_1{}^a$ ($I > 2\sigma(I)$)	0.048
$wR_2{}^b$ (all data)	0.069

[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 $w = 1/[\sigma^2(F_o^2) + (0.0127P)^2]$, $P = (\max(F_o^2, 0) + 2F_c^2)/3$.

Table 2. Atomic Coordinates and Equivalent Isotropic Displacement Parameters (Å^2) for $Cs_2Ti_4Nb_6Cl_{18}O_6$

	x	y	z	$U_{eq}{}^a$	occupancy
Nb	0.11860(9)	0.95692(9)	0.08007(5)	0.0116(2)	
Cl(1)	0.0816(2)	0.7450(2)	0.0064(1)	0.0181(5)	
Cl(2)	0.2890(2)	0.9422(3)	0.1853(1)	0.0192(5)	
Cl(3)	0.4851(2)	0.3187(3)	0.1596(1)	0.0206(6)	
Ti(1)	0.2903(2)	0.1451(1)	0.25	0.0138(6)	
Ti(2)	0.6667	0.3333	0.25	0.0134(9)	
O	0.1666(6)	0.1220(6)	0.1553(3)	0.010(1)	
Cs(1a)	0.3333	0.6667	0.0514(8)	0.038(5)	0.38(8)
Cs(1b)	0.3333	0.6667	0.077(3)	0.088(5)	0.57(8)
Cs(2)	0.3333	0.6667	0.25	0.11(2)	0.069(7)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $Cs_2Ti_4Nb_6Cl_{18}O_6{}^a$

($Nb_6Cl_{14}O_4$) Cluster Unit:			
Nb−Nb:			
$Nb-Nb^1{}_{(oxide-bridged)}$	2.811(1)	$Nb^1-Nb-Nb^3$	61.85(2)
$Nb-Nb^2{}_{(chloride-bridged)}$	2.979(1)	$Nb^3-Nb-Nb^2$	56.30(4)
$Nb-Cl^i$:			
Nb−Cl(1)	2.477(2)	$Nb-Cl(1)-Nb^3$	73.31(7)
$Nb-Cl(1)^2$	2.512(2)		
$Nb-Cl^a$:			
Nb−Cl(2)	2.583(2)		
$Nb-O^i$:			
Nb−O	2.021(5)	$Nb-O-Nb^4$	88.0(2)
$Nb-O^1$	2.025(6)		
Ti Environment:			
Ti(1)−O	1.951(5) 2×	$O-Ti(1)-O^5$	104.2(3)
Ti(1)−Cl(2)	2.478(2) 2×	$O^5-Ti(1)-Cl(2)$	95.9(2)
Ti(1)−Cl(3)	2.506(3) 2×	$O-Ti(1)-Cl(2)$	83.8(2)
		$Cl(2)-Ti(1)-Cl(2)^5$	179.4(2)
		$O^5-Ti(1)-Cl(3)^5$	87.8(2)
		$O-Ti(1)-Cl(3)^5$	164.7(2)
		$Cl(3)-Ti(1)-Cl(3)^5$	85.54(9)
		$Cl(2)^5-Ti(1)-Cl(3)^5$	94.91(9)
		$Cl(3)^5-Ti(1)-Cl(3)$	82.2(1)
Ti(2)−Cl(3)	2.410(2) 6×	$Cl(3)^6-Ti(2)-Cl(3)^7$	86.2(1)
		$Cl(3)^6-Ti(2)-Cl(3)^8$	89.24(8)
		$Cl(3)^7-Ti(2)-Cl(3)^8$	95.7(1)
		$Cl(3)^8-Ti(2)-Cl(3)^5$	173.3(1)
Cs Environment:			
Cs(1a)−Cl(1)	3.416(3) 3×		
Cs(1a)−Cl(3)	3.83(1) 3×		
Cs(1a)−Cl(2)	3.956(7) 3×		
Cs(1b)−Cl(1)	3.52(2) 3×		
Cs(1b)−Cl(2)	3.76(2) 3×		
Cs(1b)−Cl(3)	4.17(5) 3×		
Cs(2)−Cl(2)	3.508(2) 6×		
Other Important Distances			
Nb−Ti(1)	3.333(1)		
Ti(1)−Ti(2)	3.648(2)		
Cs(1a)−Cs(1b)	0.39(5)		
Cs(1a)−Cs(2)	3.10(1)		
Cs(1b)−Cs(2)	2.71(5)		

[a] Symmetry transformation used to generate equivalent atoms: #1 $-x + y, -x, z$; #2 $x - y, x, -z$; #3 $y, -x + y, -z$; #4 $-y, x - y, z$; #5 $x, x - y, -z + {}^1/_2$; #6 $-y + 1, x - y, z$; #7 $-x + y + 1, y, -z + {}^1/_2$; #8 $-x + y + 1, -x + 1, z$.

0.253 for all data. Subsequent anisotropic refinement yielded highest residual electron density peak of 2.83 e/Å^3 at the special position (1/3, 2/3, 1/4) located at 2.91 Å from Cs(1) (2×) and 3.51 Å from Cl(2) (6×). This environment is consistent with a partially occupied oxygen atom or a cesium atom that is present when Cs(1) position is not occupied. Assigning this electron density to oxygen O(2) and refining its occupancy led to the SOF(O(2)) = 0.06(1). The possibility of the alternative assignment of this electron density to a cesium atom Cs(2) was indicated by the refined value of SOF(Cs(1)) of 0.310(3). The refinement of the occupancy of Cs(2) led to SOF(Cs(2)) = 0.013(2). The latter model was selected based on its better charge balance. Anisotropic refinement of Cs(2) position resulted in an unrealistic U_{33} value of 0.4(1) Å^2 which could be caused by low coordination number of Cs(2) or its low occupancy. Therefore, in all consecutive refinement cycles, an isotropic model for the Cs(2) position was applied. The highest residual electron density peak of 2.59 e/Å^3 remaining after this stage of the refinement was found on the 3-fold axis at 0.91 Å from Cs(1) which indicated the splitting of this cesium position. In the consequent cycles, Cs(1) was refined as being disordered over two closely spaced positions Cs(1a) and Cs(1b). Their SOF values refined to 0.13(3) and 0.19(3), respectively. In the final cycles, an extinction correction was applied, and refinement converged to $R_1 = 0.048$ ($F_o > 4\sigma(F_o)$), $wR_2 = 0.069$ (all data). Subsequent refinement of the structure in the noncentrosymmetric space group $P31c$ did not lead to new features or lower residuals. Details of crystal data and data collection for $Cs_2Ti_4Nb_6Cl_{18}O_6$ are summarized in Table 1. Atomic positions and equivalent isotropic thermal parameters are given in Table 2, selected bond distances and angles are listed in Table 3.

Magnetic Measurements. Magnetic susceptibility measurements as a function of temperature (2−300 K) were taken at 0.5 and 4 T, using a Quantum Design MPMS superconducting quantum interference device (SQUID) magnetometer. The crystalline sample was contained in a gelatin capsule fixed inside a plastic straw for immersion into the SQUID. No diamagnetic correction was made for the sample container because its signal was insignificant relative to the sample.

Results

The new oxychloride compound $Cs_2Ti_4Nb_6Cl_{18}O_6$ crystallizes in an original structure type based on $(Nb_6Cl^i_6O^i_6)Cl^a_6$ clusters linked through ($TiCl_4O_2$) octahedra to form linear chains. The chains interact with each other through ($TiCl_6$) octahedra and cesium ions (Figure 1). The $(Nb_6Cl^i_6O^i_6)Cl^a_6$ cluster unit (Figure 2) is based on a Nb_6 octahedron in which all edges are bridged by chloride or oxide ligand ("inner" ligands, L^i), and six other chloride ligands attach to the Nb_6 octahedron in apical positions ("outer" ligands, Cl^a). The six oxide ligands selectively occupy "inner" positions arranged in two sets of three on opposite sides of the Nb_6 octahedron. The ligand arrangement results in an anisotropic cluster unit with symmetry close to D_{3d} (crystallographically imposed symmetry S_6). The intracluster bond distances, $Nb-Nb_{(oxide-bridged)} = 2.811(1)$ and $Nb-Nb_{(chloride-bridged)} = 2.979(1)$ Å, are similar to those found in other niobium oxychlorides.[8,9,12−15]

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(11) Sheldrick, G. M. *SHELXL93, Program for the Refinement of Crystal Structures*; University of Göttingen: Germany.

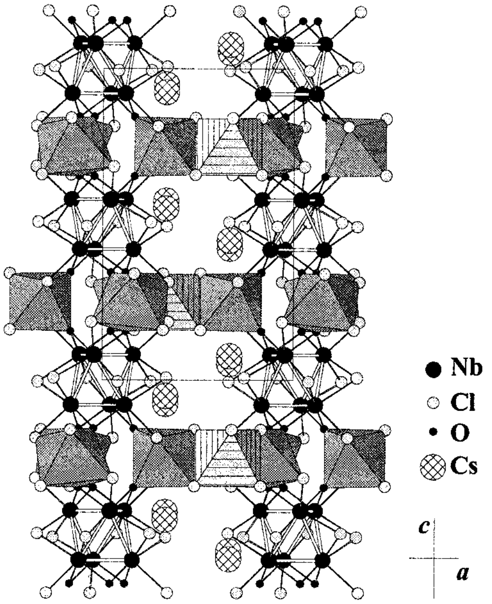

Figure 1. A fragment of the structure of $Cs_2Ti_4Nb_6Cl_{18}O_6$ (gray and hatched octahedra represent $(Ti(1)Cl_4O_2)$ and $(Ti(2)Cl_6)$ octahedra, respectively).

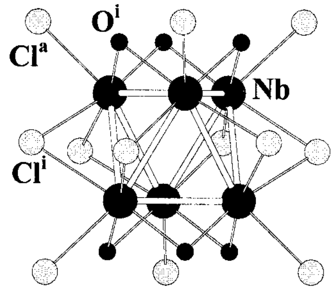

Figure 2. A view of the $(Nb_6Cl^i_6O^i_6)Cl^a_6$ cluster unit.

Each cluster is connected to two adjacent clusters through titanium Ti(1) to form chains running in the $\vec{c}$ direction (Figure 1). The linkage between two neighboring clusters is provided by three Ti(1) atoms, every one of which coordinates to one O^i and one Cl^a ligands from each cluster. The coordination sphere of Ti(1) is completed to an octahedron by two additional chloride ligands (Cl3) that do not belong to the clusters. The $(Ti(1)Cl_4O_2)$ octahedron thus formed has two O^i and two Cl(3) ligands in *cis*-positions and two Cl^a ligands in *trans*-positions. The repeating unit along the chain contains two clusters and two sets of three $(Ti(1)Cl_4O_2)$ octahedra. The two clusters are related by a *c*-glide plane, which leads to a difference of about 30° in their orientation with respect to the 3-fold axis. The effect of this *c*-glide plane on the two sets of three $(Ti(1)Cl_4O_2)$ octahedra is an approximate rotation of these groups with respect to each other by 60° around the 3-fold axis.

The chains are connected to each other through titanium ions Ti(2) located on a special position (D_3 symmetry) and coordinated to six Cl(3) ligands belonging to three $(Ti(1)Cl_4O_2)$ octahedra from three different chains (Figure 1). This linkage leads to the formation of tetrameric propeller-like $(Ti_4Cl_{12}O_6)$ units built from four (TiL_6) octahedra sharing edges (Figure 3). The Ti(1)−Ti(2) distance is 3.648(2) Å.

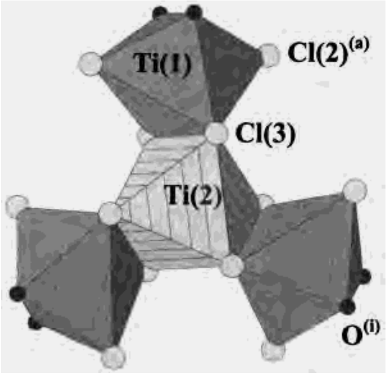

Figure 3. A view of the tetrameric propeller-like $(Ti_4Cl_{12}O_6)$ units built from four (TiL_6) octahedra that share edges.

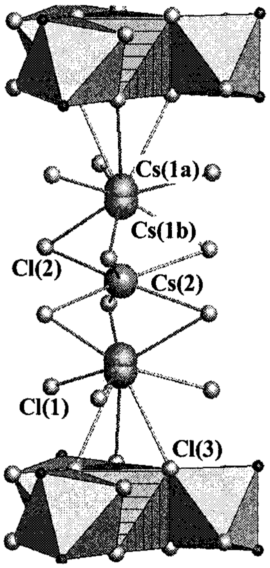

Figure 4. The environment of cesium in $Cs_2Ti_4Nb_6Cl_{18}O_6$.

Cesium ions are located on the 3-fold axes between the chains and are distributed among three sites, Cs(1a), Cs(1b), and Cs(2) in the elongated cavities formed between $(Ti_4Cl_{12}O_6)$ units (Figure 4). The closely spaced Cs(1a) and Cs(1b) sites coordinate to nine chlorines and are partially occupied, 38(8)% and 57(8)%, respectively.[16] The site Cs(2), located at the special position with D_3 symmetry, is coordinated to six chlorines and is occupied when Cs(1a) and Cs(1b) sites are empty. Since Cs(1) and Cs(2) sites cannot be simultaneously occupied due to their small separation (Cs(1a)−Cs(2) = 3.10(1) Å, Cs(1b)−Cs(2) = 2.71(5) Å), the total amount of cesium ions per formula unit cannot exceed $2 - x$, where x is the occupancy of Cs(2). The value of x refines to only 0.069(7), which does not lead to a significant deviation of the refined stoichiometry from $Cs_2Ti_4Nb_6Cl_{18}O_6$.

The total number of *d* electrons per formula unit based on this stoichiometry is 18. The observed intracluster bond distances indicate that 14 of these electrons belong to the cluster,[17] as is

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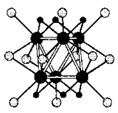
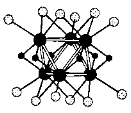
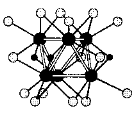
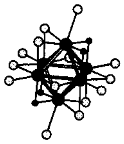
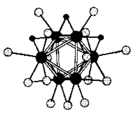
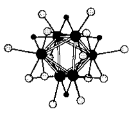
(16) The large standard deviations of Cs(1a) and Cs(1b) occupancies result from a close separation of these sites. The refined occupancy of Cs(1) site without taking its splitting into account is 93.0(9)% which agrees well with 6.9(7)% occupancy of Cs(2) which is present when Cs(1) is not occupied.

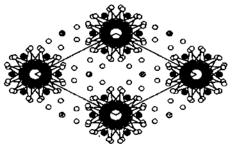
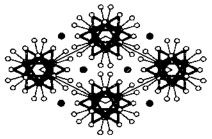
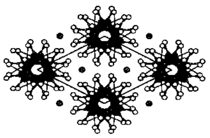
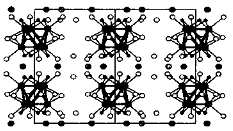
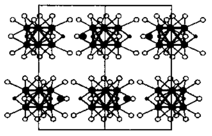
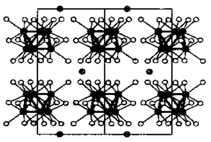
(17) Perrin, C.; Cordier, S.; Ihmaïne, S.; Sergent, M. *J. Alloys Compounds* **1995,** *229*, 123−133 and references therein.

Table 4. Relationships between Ligand Arrangement and Cluster Connectivity in Niobium Oxychlorides

	Cluster Units with Equivalent Niobium Atoms			Cluster Units with Differentiation of Niobium Atoms		
Ligand Arrangement[a]						
Compound	$Cs_2Ti_4Nb_6Cl_{18}O_6$	$KLu_3Nb_6Cl_{15}O_6$	$Cs_2UNb_6Cl_{15}O_3$	$Ti_2Nb_6Cl_{14}O_4$, $Tl_5Ti_8Nb_{18}Cl_{53}O_{12}$	$ScNb_6Cl_{13}O_3$	$Cs_2Ti_3Nb_{12}Cl_{27}O_8$
Ref.	this work	15	14	12, 8	13	9
Cluster Connectivity		Discrete clusters		2D net	3D net	2D net

[a] Large black spheres, small black spheres, and light-gray spheres represent niobium, oxygen, and chlorine, respectively.

Table 5. Comparison between Crystal Structures of $Cs_2Ti_4Nb_6Cl_{18}O_6$, $Cs_2UNb_6Cl_{15}O_3$, and $CsTiNb_6Cl_{18}$

	$Cs_2Ti_4Nb_6Cl_{18}O_6$	$Cs_2UNb_6Cl_{15}O_3$	$CsTiNb_6Cl_{18}$
Unit cell dimensions (Å)	$a = 11.190$ $c = 15.600$	$a = 9.208$ $c = 17.095$	$a = 9.108$ $c = 17.002$
View in [001] direction[a]			
View in [110] direction[b]			
Environment of M^{3+} cations	Ti(1): 2 O^i, 2 Cl^a, 2 Cl Ti(2): 6 Cl	3 O^i, 6 Cl^a	6 Cl^a
Number of clusters linked by M^{3+} cation	2	3	6
Overall dimensionality	Quasi-1D	2D	3D

[a] Large black spheres, niobium; small black spheres, oxygen; light-gray spheres, chlorine; hatched dark-gray spheres, M^{3+} atoms linking the clusters; unhatched dark-gray spheres, Ti(2) in (**I**). Cesium atoms and $M^{3+}-Cl$ and $M^{3+}-O$ bonds are omitted for clarity. [b] The origins of the unit cells of $Cs_2Ti_4Nb_6Cl_{18}O_6$ and $CsTiNb_6Cl_{18}$ are shifted in the [001] direction by 1/4 *c* compared to the standard setting.

the case for most other niobium oxychloride cluster compounds with more than two inner oxide ligands.[8,9,13,14] This cluster electronic configuration corresponds to all titanium atoms being present as Ti^{3+}. The oxidation state +3 for titanium is confirmed by magnetic measurements which show Curie behavior with an effective magnetic moment of 3.24 μ_B per formula unit (Figure 5) which is close to the expected value for four unpaired electrons of 3.46 μ_B. and by bond valence sum calculations[18] (BVS(Ti1) = 3.14; BVS(Ti2) = 3.28).

Discussion

The new compound $Cs_2Ti_4Nb_6Cl_{18}O_6$ (**I**) is the second example of a niobium oxychloride based on octahedral Nb_6 clusters with six oxide ligands. The $(Nb_6Cl^i_6O^i_6)Cl^a_6$ cluster unit in (**I**) and that in the previously reported $KLu_3Nb_6Cl_{15}O_6$ (**II**)[15] have the same symmetry, but different ligand arrangement. The oxide inner ligand positions in (**I**) are occupied by chloride ligands in (**II**), and vice versa. The occurrence of cluster units with equal number, but different arrangement of oxide ligands, also observed for oxychloride clusters with three[13,14] and four[8,9,12] oxide ligands, indicates the potential for a versatile structural chemistry of metal oxychloride cluster compounds yet to be discovered.

The title compound complements the previously reported examples of niobium oxychloride cluster materials[8,9,15] that illustrate the relationships between the ligand arrangement and cluster connectivity in this class of compounds (Table 4). The absence of direct intercluster cluster connectivity, in other words, the nonbridging functionality of all outer ligands, Cl^a, correlates with the equivalent coordination of all niobium atoms. Similar relationship is observed in $KLu_3Nb_6Cl_{15}O_6$ [15] and $Cs_2UNb_6Cl_{15}O_3$ [14] that are also based on clusters with equivalent niobium atoms. In contrast, in compounds based on clusters in which niobium atoms have different environment, the Cl^a ligands have different functionalities (bridging and nonbridging) leading to anisotropic cluster frameworks.[8,9,12,13]

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(18) O'Keeffe M.; Brese, N. E. *J. Am. Chem. Soc.* **1991**, *113*, 3226−3229.

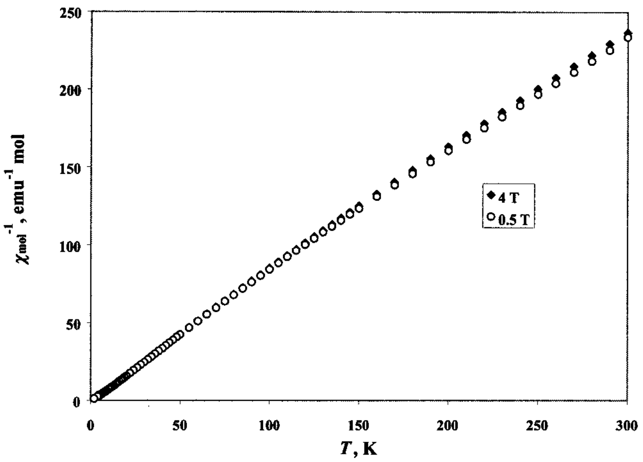

Figure 5. Inverse molar magnetic susceptibility of $Cs_2Ti_4Nb_6Cl_{18}O_6$ as a function of temperature at 0.5 and 4 T.

Even though the use of a combination of oxide and chloride ligands in the title compound does not induce anisotropic cluster connectivity through the outer ligands, it affects the dimensionality of the overall structure. The oxide ligands, distributed in two sets of three on opposite sides of the cluster unit, define the directions of linkages between the clusters and titanium ions, leading to the formation of one-dimensional chains. The electrostatic interactions within the chains through Ti(1), oxide and chloride ions are significantly stronger than the interchain interactions involving Ti(2), Cs, and chloride ions, thus the overall structure can be considered quasi-one-dimensional. This conclusion is supported by the experimental observation that the crystals of the title compound easily split into fibers along the $\vec{c}$ axis.

The influence of the presence of oxide ligands and their arrangement on the location of counterions is evidenced by comparing the structure of the title compound to that of $Cs_2UNb_6Cl_{15}O_3$ [14] and $CsTiNb_6Cl_{18}$ [19] which are also based on discrete clusters, and crystallize in the same space group $P\bar{3}1c$ with two clusters per unit cell (Table 5). In contrast to (**I**), the compound $Cs_2UNb_6Cl_{15}O_3$ has three oxide ligands in inner positions around the clusters' waists, and the U^{3+} cations are located in the plane containing the inner oxide ligands. Each U^{3+} ion links three clusters through their O^i and Cl^a ligands. These linkages occur in two directions only, leading to a layered character of the overall structure. In the case of $CsTiNb_6Cl_{18}$, the titanium ions coordinate to six outer chlorines from six adjacent clusters, with Ti−Cl^a linkages extending in three dimensions.

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Supporting Information Available: Tables of details of data collection and refinement and anisotropic displacement parameters and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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