Layered niobium titanium oxychloride cluster compounds with six-member ring opening channels

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Abstract

New niobium oxychloride cluster compounds corresponding to the general formula, $A_5Ti_8Nb_{18}Cl_{53}O_{12}$ ($A =$ K, In), have been prepared in sealed quartz tubes from a mixture containing $NbCl_5$, Nb_2O_5, Nb, Ti, and KCl or In by solid-state reactions at 750°C. Their structure was determined using single-crystal X-ray diffraction; Crystal data: trigonal, $P\bar{3}$ml (No. 164) (for K: $a = 16.8303(11)$ Å, $c = 9.0510(8)$ Å, $V = 2220.3(3)$ Å^3 and $Z = 1$; for In: $a = 16.889(2)$ Å, $c = 9.0684(2)$ Å, $V = 2240.0(6)$ Å^3 and $Z = 1$). The full-matrix least-squares refinement of all data against F^2 converged to $R_1 = 0.044$, w$R_2 = 0.088$ for K, and $R_1 = 0.050$, w$R_2 = 0.140$ for In. The structure consists of octahedral $(Nb_6Cl_8^iO_4^i)Cl_6^a$ cluster units that share four outer chloride ligands with four adjacent clusters to form a two-dimensional framework that generates six- and three-member rings similar to those found in hexagonal tungsten bronze. Additional linkages within the same layer are provided by $Ti_3Cl_7O_6$ trimers. Adjacent layers are stacked in registry with each other leading to the formation of six-member ring openings channels parallel to the [001] direction in which a disordered $[A_5(Ti_2Cl_9)]^{2+}$ species are located. Magnetic susceptibility studies show paramagnetic behavior with a magnetic moment of 3.74 μ_B per formula unit.

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1. Introduction

Transition metal clusters exhibit a wide variety of nuclearity and molecular architectures [1,2]. In solid-state chemistry, the most common cluster units are octahedral M_6L_{14} and M_6L_{18} clusters. These cluster units are different in the ways the metal octahedral core is surrounded by ligands. In M_6L_{14}-type clusters, typical for molybdenum and rhenium halides, chalcogenides, and chalcohalides, eight "inner" ligands (L^i) cap the octahedron faces and six "outer" ligands (L^a) are located in the apical positions [3,4].[1] For metals with smaller number of valence electrons, the M_6L_{18}-type clusters in which 12 "inner" ligands bridge the edges of the M_6 octahedron, and six "outer" ligands occupy apical positions, predominate. These units are found in reduced zirconium, niobium, tantalum, and rare earth halides, and niobium, tantalum, molybdenum and tungsten oxides [5–9]. Depending on the number of ligands, the clusters can connect to each other through inner and/or outer ligands, or by direct condensation of the metal octahedra, to form a variety of frameworks. In compounds containing octahedral clusters, the framework dimensionality is directly dependent on the number of ligands. For compounds containing octahedral M_6L_{18}-type clusters, the cluster framework dimensionality increases from 0D (discrete clusters) to 3D as the number of ligands per cluster decreases from 18 to 15. As the number of ligands decreases, the charge of the cluster framework decreases and is compensated by adjusting the charge of counterions or by changing the charge of the cluster unit using a combination of ligands of different charges. This "ligand-combination" approach was well developed in molybdenum and rhenium cluster chemistry [10,11].

Our work in this area attempts to prepare and characterize low-dimensional and open-framework materials containing octahedral transition metal clusters

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[1] The notation employed here was initially defined in Ref. [4].

combining ligands of different charge and different size to affect the cluster framework dimensionality not only through changing the overall charge of the cluster unit, but also through the formation of cluster units with uneven surface charge distribution which can define preferred directions of intercluster linkages. The anisotropy in the bonding preferences of the cluster unit favors the formation of non-isotropic, i.e. low-dimensional or open-framework materials. In addition, stabilizing clusters with chiral ligand arrangements may lead to the formation of chiral cluster frameworks, which constitutes a significant challenge for materials chemists. We chose the combination of oxide and chloride as ligands in niobium M_6L_{18} clusters, because the following criteria are simultaneously satisfied: (i) large difference in ligand charge density which decreases the trend of statistical ligand distribution observed in other mixed-ligand systems such as molybdenum and rhenium chalcohalides [12–14] and niobium bromofluorides [15,16]; (ii) the frameworks of reduced niobium oxides and chlorides are based on the same cluster type (M_6L_{18}) [8,17]; (iii) the chlorides are usually characterized by discrete cluster units, while oxides have dense cluster frameworks; and (iv) predominance of low-dimensional structures in metals oxychlorides, such as FeOCl [18] and $NbOCl_2$ [19] which are layered, and $NbOCl_3$ which has a 1D framework [20]. Explorative synthesis of niobium oxychlorides containing titanium as a counterion led to the preparation of a number of phases with low-dimensional character [21]. Here we describe the synthesis and crystal structure of a new series of 2D oxychloride cluster compounds with the idealized composition $A_5Ti_8Nb_{18}Cl_{53}O_{12}$ (A = K, In). Their crystal structure is based on an octahedral Nb_6 cluster core coordinated by eight inner chlorine, four inner oxygen, and six outer chlorine ligands: $(Nb_6Cl_8^iO_4^i)Cl_6^a$. These clusters share outer chlorine ligands to form layers characterized by large six-member ring openings containing $[Ti_2Cl_9]^{3-}$ dimers surrounded by potassium or indium cations.

2. Experimental

2.1. Syntheses

The compounds with the idealized formula $A_5Ti_8Nb_{18}Cl_{53}O_{12}$ (A = K, In) were prepared quantitatively from a stoichiometric mixture of KCl (Alfa, 99.9%) or In shots (Alfa, 99.9%), Ti foil (Alfa, 99.9%), Nb powder (Alfa 99.8%), $NbCl_5$ (Alfa, 99.5%) and Nb_2O_5 (Alfa, 99.8%). The mixtures were handled under argon-filled inert atmosphere and heated in an evacuated sealed silica tube at 750°C for 5 days and slowly cooled down to 500°C in 2 days. The heating and cooling ramps were 10°C/h and 5°C/h, respectively. The

products were obtained as thin black trigonal plates of size up to 1 mm in diameter, which were found to undergo partial degradation upon long exposure to air. The minor impurities were Nb_3Cl_8 and $NbOCl_2$ as identified by powder X-ray diffraction. Energy-dispersive X-ray spectrometry (EDS) carried out on selected crystals indicated the presence of titanium, potassium or indium, niobium and chlorine in all crystals analyzed.

2.2. Magnetic measurements

The magnetic susceptibility of $A_5Ti_8Nb_{18}Cl_{53}O_{12}$ was measured using a Quantum Design MPMS XL SQUID magnetometer. For the magnetic measurements, loose crystals of $A_5Ti_8Nb_{18}Cl_{53}O_{12}$ were placed into a gelatin capsule, which was placed inside a plastic straw. Samples were measured under both zero-field-cooled (zfc) and field-cooled (fc) conditions. In either case, the magnetization was measured in the temperature range of 2–300 K at an applied field of 5 kG. In addition, a field sweep at applied fields between −40 and 40 kG was measured at 5 K. The very small diamagnetic contribution of the gelatin capsule containing the sample had a negligible contribution to the overall magnetization, which was dominated by the sample signal.

2.3. Crystal structure determination

The crystal data collection and refinement for the two phases were the same so that only the procedures for the potassium phase will be described. The crystallographic details for the two phases can be found in the combined CIF file submitted as supporting information.

A black trigonal plate-like crystal of size $0.20 \times 0.15 \times 0.02$ mm^3 was selected under an inert atmosphere and placed in a sealed glass capillary for X-ray diffraction analysis. Intensity data were collected on a Bruker SMART CCD diffractometer using Mo$K\alpha$ radiation. The unit-cell parameters were refined based on 15831 reflections of which 1879 were unique to give a trigonal unit cell $a = 16.8303(11)$ Å, $c = 9.0510(8)$ Å. Axial photographs taken using Bruker P4 diffractometer confirmed the unit-cell dimensions. Intensity statistics indicated $\bar{3}m$ Laue symmetry and a centrosymmetric space group, and extinction conditions were consistent with space groups $P\bar{3}m1$ and $P3m1$. The structure was solved in $P\bar{3}m1$ by direct methods. The framework atoms: two Nb, one Ti, one O and seven Cl were first located from difference Fourier maps and anisotropic least-squares refinement of these atoms with fixed full occupancies led to $R_1 = 0.082$, w$R_2 = 0.304$ for all data. The highest residual electron density peak of 22.82 e Å^{-3} at special position $(0, 0, 1/2)$ was assigned to Ti(2) due to its octahedral environment consistent with Ti–Cl distance of 2.33 Å; however, the large value of thermal parameter ($U_{eq} = 0.088(2)$ Å^2) indicated

possible partial occupancy of this site. Refinement of SOF(Ti(2)) led to the occupancy of 50(4)% and U_{eq}(Ti(2)) = 0.041(2) Å^2. The presence of a peak of 2.29 e Å^{-3} in the vicinity of Cl(6) and the large value of thermal parameter of Cl(6) (U_{eq} = 0.047(2) Å^2) compared to those of the chlorines belonging to the cluster indicated that Cl(6) position is simultaneously occupied by chlorine and oxygen (O(6)). Refinement of the occupancies of Cl(6) and O(6) with the restriction that they add up to the full occupancy of the site resulted in 60(2)% occupancy by chlorine and 40(2)%

Table 1
Crystal data and structure refinement for [K$_5$(Ti$_2$Cl$_9$)][(Nb$_6$Cl$_{12}$O$_4$)$_3$(Ti$_3$Cl$_4$)$_2$]

Empirical formula	K$_{4.96}$Ti$_{6.5}$Nb$_{18}$Cl$_{46.32}$O$_{12.84}$
Formula weight	3850.82
Wavelength (Å)	0.71073
Temperature (K)	293(2)
Crystal system	Trigonal
Space group	$P\bar{3}m1$ (No. 164)
a (Å)	16.8303(11)
C (Å)	9.0510(8)
Volume (Å^3)	2220.3(3)
Z	1
ρ_{cal}(g cm^{-3})	3.047
Total reflections	15857
Abs. coefficient(mm^{-1})	4.25
T_{min} and T_{max}	0.2153 and 0.9166
θ range (deg)	1.4–27.51
Independent reflections	1879 [R(int) = 0.0462]
R indices (all data)[a,b]	R_1 = 0.042, wR_2 = 0.088
Goodness of fit[c] on F^2	1.11

[a] $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; [b] w$R_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$, where w $= 1/[\sigma^2(F_o^2) + (0.0266P)^2 + 44.5P]$, $P = (\max(F_o^2, 0) + 2F_c^2)/3$; [c] GOF $= [\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{parameter})]^{1/2}$.

Table 2
Selected interatomic distances (Å) and angles (deg) in [K$_5$(Ti$_2$Cl$_9$)][(Nb$_6$Cl$_{12}$O$_4$)$_3$(Ti$_3$Cl$_4$)$_2$]

[Nb$_6$Cl$_8$O$_4$]Cl$_6$ unit			
Nb − Nb$_{oxide-bridged}$	2.8104(7)	Nb–Nb–Nb	56.76(1)–62.11(2)
Nb − Nb$_{chloride-bridged}$	2.9703(7)	Nb–Nb–Nb	59.99(1)–63.78(1)
Nb(1)–O(1)	2.016(3)		
Nb(2)–O(1)	1.989(3)		
Nb(1)–Cl(1)	2.474(1)		
Nb(1)–Cl(2)	2.635(2)		
Nb(2)–Cl(1)	2.480(1)		
Nb(2)–Cl(3)	2.5790(9)		
Nb(2)–Cl(4)	2.433(1)		
Nb(2)–Cl(5)	2.422(1)		
Ti environment			
Ti(1)–O(1)	1.967(3)	Cl(3)–Ti(1)–Cl(7)	92.90(8)
Ti(1)–O(6)	2.213(9)	Cl(3)–Ti(1)–O(1)	82.3(1)
Ti(1)–Cl(6)	2.430(4)		
Ti(1)–Cl(3)	2.590(2)		
Ti(1)–Cl(7)	2.293(3)		

occupancy by oxygen. The final refinement cycles resulted R_1 = 0.042, wR_2 = 0.088 for all data. The highly disordered species in the hexagonal channels could not be modeled satisfactorily. A number of crystals of the potassium and the indium phases from different reactions were studied and refinements always showed a high disorder of the species inside the channel. However, the phases are isostructural with the previously reported thallium analog(21b) and the compounds are obtained from reactions loaded with the same stoichiometry. Refinement in the acentric space group $P3m1$ did not lead to new features or statistically significant changes in reliability factors or GOF. Further details regarding data collection and refinement parameters, and bonding parameters are listed in Tables 1 and 2, respectively.

3. Results and discussion

The framework (Fig. 1) of the title compounds is formed of (Nb$_6$Cl$_8^i$O$_4^i$)Cl$_6^a$ cluster units (Fig. 2) which has eight chlorines and four oxygens as inner-, and six other chlorines ligands in apical positions. The inner ligands have the same arrangement as that found in the cluster unit in Ti$_2$Nb$_6$Cl$_{14}$O$_4$(21a). The intracluster bond lengths (d_{Nb-Nb} = 2.8104(7) − 2.9703(7) Å, d_{Nb-Cl^a} = 2.422(1) − 2.480(1) Å, d_{Nb-Cl^a} = 2.5790(9) − 2.635(2) Å, d_{Nb-O} = 1.989(3) − 2.016(3) Å) are similar to those found in other niobium oxychloride cluster compounds. Each cluster shares four outer chloride ligands with four adjacent clusters to form a 2D framework that generates six- and three-member rings (Fig. 3) similar to those found in hexagonal tungsten bronze [22]. The cluster connectivity formula (Nb$_6$Cl$_8^i$O$_4^i$)Cl$_{4/2}^{a-a}$Cl$_2^a$ is the same as that found in Ti$_2$Nb$_6$Cl$_{14}$O$_4$(21a); however, the layer's topology is dramatically different from that in the latter oxychloride. Additional linkages between clusters within the same layer are provided by Ti$_3$Cl$_7$O$_6$ trimers (d(Ti–Ti) = 3.667(2) Å) built from three TiCl$_4$O$_2$ octahedra that share one vertex and three edges. Each trimer connects three clusters through O^i and Cl^a ligands. Trimeric Ti$_3$L$_{13}$ units have been reported for other reduced titanium chlorides and are prone to metal–metal bond formation [23]. The six-member cluster ring openings contain highly disordered species that is attributed to [Ti$_2$Cl$_9$]$^{3-}$ dimers surrounded by K$^+$ or In$^+$ ions as is the case in the thallium analog. Similar [Ti$_2$Cl$_9$]$^{3-}$ dimers surrounded by A^+ ions are found in the series A_3Ti$_2$Cl$_9$ (A = Cs, In) [24]. The ordering of this species observed in the case of the thallium phase leads to superstructure (2c) in which the layers differ only in the orientation of the [Tl$_5$Ti$_2$Cl$_9$]$^{2+}$ units. In contrast, the repeating unit in the potassium and indium phases consists of one layer in which the A^+ cations are statistically distributed over 12 sites (occupied by ca.
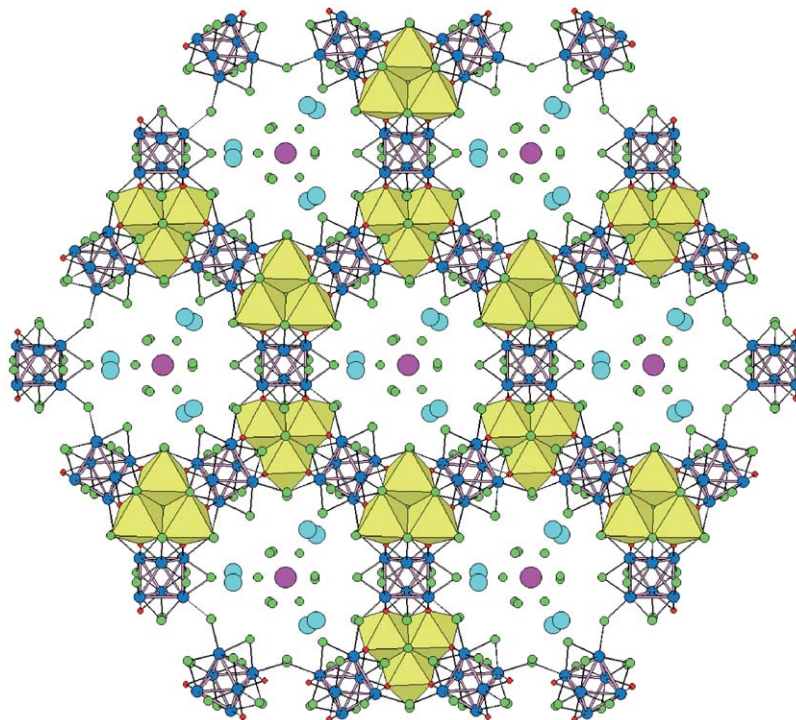
Fig. 1. A projection of one layer of $[A_5(Ti_2Cl_9)][(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$ structure on the (ab) plane (blue octahedra: $(Nb_6Cl_8^iO_4^i)Cl_6^a$ clusters, yellow: $Ti_3Cl_7O_6$ trimers).
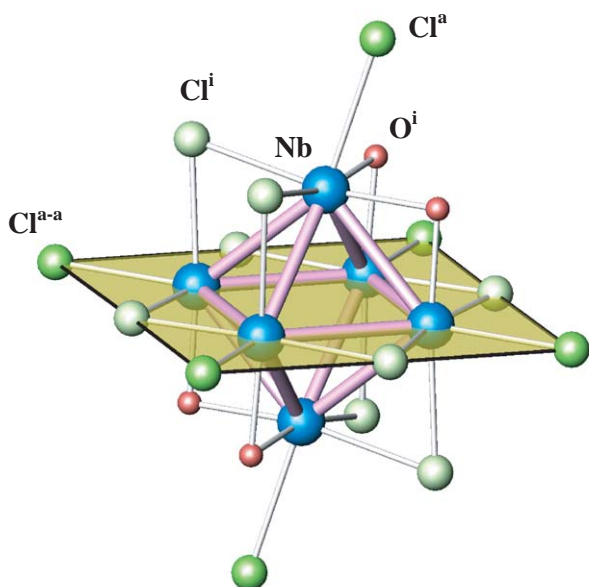
Fig. 2. View of the cluster unit in $[A_5(Ti_2Cl_9)][(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$ showing the plane containing outer chlorine ligands that connect the clusters into a 2D network.

25% and 32% for $A = K$ and In, respectively) that correspond to juxtaposition of the two different orientations of the trigonal prisms formed by the Tl^+ sites. While in the thallium structure, the six Tl^+ sites encapsulate well-defined $[Ti_2Cl_9]^{3-}$ dimers, no reliable model of the electron density in the centers of the

channels in the potassium and indium compounds could be developed due to high degree of disorder. Adjacent layers in the potassium and indium phases are the same and stack in registry with each other leading to the formation of six-member ring openings channels parallel to the [001] direction (Fig. 1) in which the disordered species are located. As in the case of $[Tl_5(Ti_2Cl_9)]$ $[(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$, the formation of the honeycomb-like cluster framework is probably due to the presence of the $[A_5(Ti_2Cl_9)]^{2+}$ units which plays the role of a template around which the six-member cluster ring is assembled. The templating effects are supported by the fact that in $Ti_2Nb_6Cl_{14}O_4$, where no templating units are present, the same clusters form a framework with different topology and smaller openings. A similar templating effect was observed in other cluster compounds, such as $Cs_3(ZrCl_5)Zr_6Cl_{15}Mn$ [25] in which the $[ZrCl_5]^-$ units stabilize a 3D framework formed by octahedral $Zr_6Cl_{18}(Mn)$ clusters, and $Nb_7S_2I_{19}$ [26] in which NbI_5 acts as a template leading to the formation of a graphite-like framework formed by triangular $Nb_3I_{10}S$ clusters. Fig. 4 shows a comparison between the structures of cluster compounds templated by inorganic species.

3.1. Magnetic properties and electron distribution

The compounds $A_5(Ti_2Cl_9)[(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$ contain 50 d-electrons per formula unit. The observed
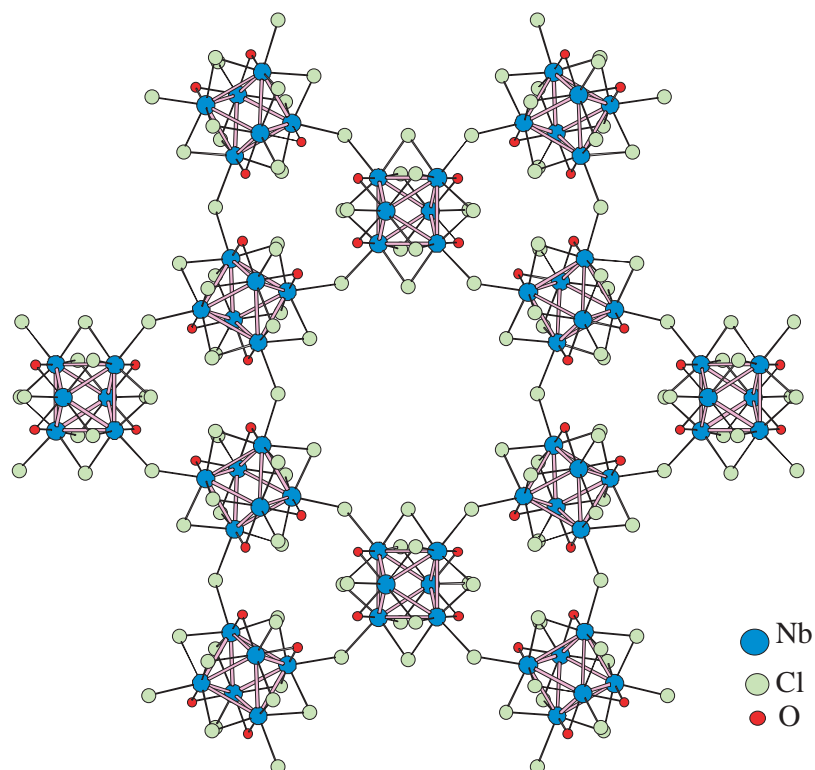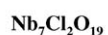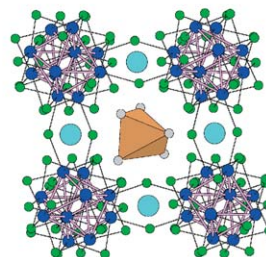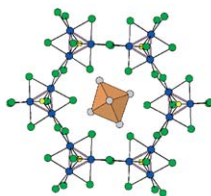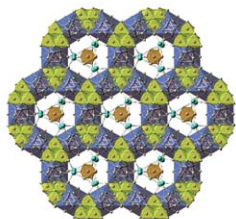
Fig. 3. Cluster framework in $[A_5(Ti_2Cl_9)][(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$. Niobium (blue), chlorine (green), oxygen (red).
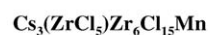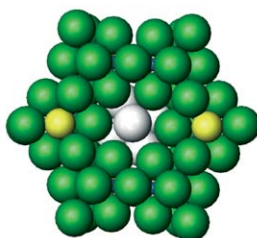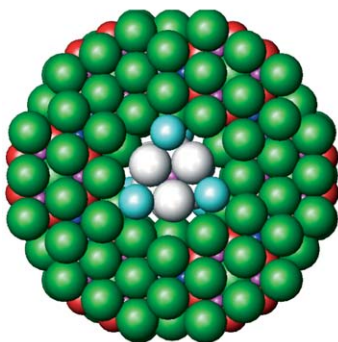

Fig. 4. Comparison between the crystal structures of $[A_5(Ti_2Cl_9)][(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$, $Nb_7S_2I_{19}$, and $Cs_3(ZrCl_5)Zr_6Cl_{15}$ illustrating templating effects. The templating units are shown as orange polyhedra. Color code: dark-green: halide atoms of the framework; gray: halide atoms of the templating units; dark-blue: Nb or Zr; light-blue: Tl, In, K or Cs; red: O; purple: Ti; yellow polyhedra: $Ti_3Cl_7O_6$ trimers; yellow spheres: S.

intracluster bond distances indicate that each cluster in the formula unit has 14 electrons [27,28]. The remaining eight electrons belong to eight titanium atoms, which corresponds to all titanium atoms being present in the oxidation state $+3$. The magnetic measurements show Curie–Weiss behavior with an effective magnetic moment of $3.74\,\mu_B$ per formula unit, which is lower than that expected for eight Ti^{3+}. However, this value is close to that derived for a model of antiferromagnetically coupled Ti^{3+} ions in the $[Ti_2Cl_9]^{3-}$ dimers as was observed in $Cs_3Ti_2Cl_9$ [23] and six non-interacting Ti^{3+} ions in two $Ti_3Cl_7O_6$ trimers ($4.24\,\mu_B$).

4. Conclusion

New niobium oxychloride cluster compounds have been prepared. Their structures are based on octahedral oxychloride cluster units linked to each other to form honeycomb-like layered framework. Trimeric $Ti_3Cl_7O_6$ units built from three $TiCl_4O_2$ octahedra that share one vertex and three edges support the framework. The layers contain six-member ring openings where disordered $[A_5(Ti_2Cl_9)]^{2+}$ units are located.

Acknowledgments

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