Towards the Design of Open-Framework Cluster Materials: A Novel Layered Niobium Oxochloride with a Honeycomblike Structure**

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In memory of Jean Rouxel

Open-framework compounds have numerous technological applications as heterogeneous catalysts, ion exchangers, and as molecular sieves.[1] Research in this field focuses on the preparation of open-framework materials containing redox-active centers which leads to a considerable increase of their catalytic potential.[2] The use of metal clusters as redox-active centers is of special importance due to the remarkable catalytic properties of cluster compounds compared to mononuclear metal complexes.[3] Our systematic investigation of reduced niobium oxochlorides containing octahedral Nb_6 clusters led to the preparation of the layered material described herein. Its crystal structure is based on an octahedral Nb_6 cluster core coordinated by eight inner chloride, four inner oxide, and six outer chloride ligands: $[(Nb_6Cl^i_8O^i_4)Cl^a_6]$ (Figure 1). These clusters share outer chloride ligands to form layers characterized by large six-membered rings. The ring openings contain units of $[Ti_2Cl_9]^{3-}$ dimers surrounded by thallium cations. The two-dimensional character of this material is favored by the arrangement of the oxide and chloride ligands which results in an anisotropic charge distribution around the Nb_6 cluster core.

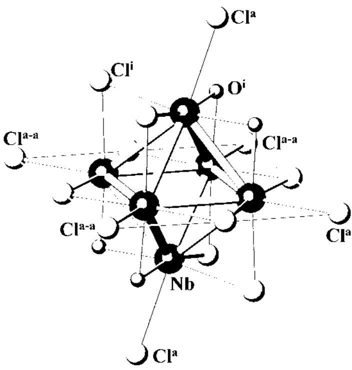

Figure 1. View of the $[(Nb_6Cl^i_8O^i_4)Cl^a_6]$ cluster unit in **1** highlighting the plane containing outer chloride ligands (Cl^{a-a}) that connect the clusters into a two-dimensional network.

The novel, layered niobium oxochloride $[\{Tl_5(Ti_2Cl_9)\}\{(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2\}]$ (**1**) crystallizes in the space group $P\bar{3}c1$, with two formula units per unit cell. Its structure[4] is composed of layers shown in Figure 2. The basic cluster unit is a Nb_6 octahedron in which every edge is bridged by a chloride or oxide ligand ("inner" Cl^i and O^i ligands), and six other chloride ligands attach to the Nb_6 octahedron in apical positions ("outer" ligands, Cl^a). The cluster has the same ligand arrangement and similar bond distances as those found in $Ti_2Nb_6Cl_{14}O_4$[5] (selected bond lengths [Å]: Nb–Nb 2.8164(10)–2.9824(9), Nb–Cl^i 2.427(2)–2.484(2), Nb–Cl^a 2.585(2)–2.652(2), Nb–O 1.992(5)–2.033(5)). Each cluster shares four outer chlorines (Cl^{a-a} in Figure 1) with four adjacent clusters to form a two-dimensional network which generates six- and three-membered rings similar to those found in hexagonal tungsten bronzes (HTB).[6] Additional linkages between clusters within the same layer are provided by $[Ti_3Cl_7O_6]$ trimers[7] (Ti–Ti 3.792(3) Å) built from three $[TiCl_4O_2]$ octahedra that share one vertex (Figure 3a). Each trimer connects three clusters through inner and outer

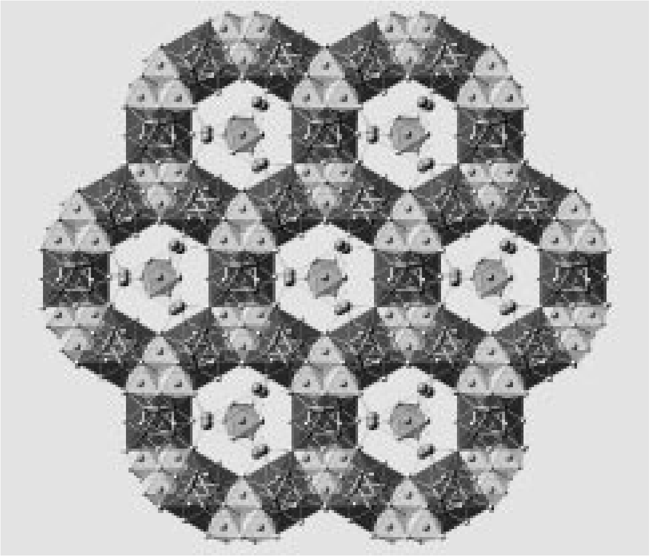

Figure 2. A projection of one layer in **1** on the *ab* plane. Dark gray octahedra of $[(Nb_6Cl^i_8O^i_4)Cl^a_6]$ clusters and light gray $[Ti_3Cl_7O_6]$ trimers form a honeycomblike framework with cavities containing $[Ti_2Cl_9]^{3-}$ dimers surrounded by Tl ions.

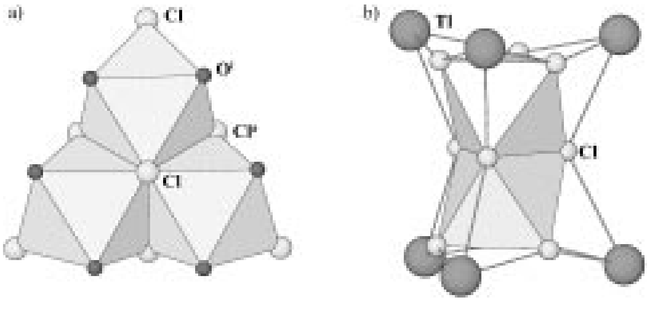

Figure 3. a) $[Ti_3Cl_7O_6]$ trimer built from three $[TiCl_4O_2]$ octahedra that share one vertex; b) $[Ti_2Cl_9]^{3-}$ dimer surrounded by thallium ions.

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chloride ligands. The $[Ti_3L_{13}]$ units are common in reduced titanium chlorides and are prone to metal–metal bond formation.[8] For example, $Na_2Ti_3Cl_8$[8a] contains $[Ti_3Cl_{13}]$ trimers, and undergoes a phase transition resulting in the formation of triangular titanium clusters and a decrease in Ti–Ti distances from 3.717 to 2.996 Å.

The openings of the six-membered cluster rings contain $[Ti_2Cl_9]^{3-}$ dimers surrounded by Tl^+ ions (Figure 3b). The dimers are formed from two $[TiCl_6]$ octahedra sharing one face (Ti–Ti 2.977(8) Å) and are aligned along the [001] direction. Each dimer is surrounded by five Tl^+ ions statistically distributed over six crystallographic sites. Similar $[Ti_2Cl_9]^{3-}$ dimers surrounded by A^+ ions are found in the series $A_3Ti_2Cl_9$ (A = Cs, In).[9]

Adjacent layers are stacked perfectly on top of each other and differ only in the orientation of Tl^+ and $[Ti_2Cl_9]^{3-}$ ions. The ring openings in individual layers merge into channels parallel to the [001] direction.

Layered frameworks similar to that found in **1** are present in non-cluster compounds such as $K[Al(OH)_2]_3(SO_4)_2$ (alunite),[10] $K_3(SbO_2)_3(PO_4)_2$,[11] and $(NH_4)(VO_2)_3(SeO_3)_2$.[12] Their anionic frameworks have the general formula $M_3T_2O_x^{n-}$ and consist of HTB-type layers made up of corner-sharing $[MO_6]$ octahedra and $[TO_3]$ or $[TO_4]$ polyhedra. In the structure of **1**, the $[Nb_6Cl^i_8O^i_4]$ cluster core plays the role of the metal M, outer chloride ligands correspond to oxide ligands of $[MO_6]$, and $[Ti_3Cl_7O_6]$ trimers correspond to the $[TO_4]$ or $[TO_3]$ units. In contrast to **1**, the layers in these $M_3T_2O_x^{n-}$ examples are shifted with respect to each other resulting in the absence of channels.

The formation of the HTB-type cluster framework in **1** is favored by the presence of $[Ti_2Cl_9]^{3-}$ units which play the role of a template around which the six-membered cluster ring is assembled. A similar templating effect was observed in the case of $Nb_7S_2I_{19}$,[13] in which triangular $[Nb_3I_{10}S]$ clusters form a graphite-like network stabilized by $[NbI_5]$ molecules. Attempts to remove $[NbI_5]$ led to the decomposition of the phase.[13a] This decomposition is probably due to the fact that the size of the ring opening fits only one iodide ligand. In the case of **1**, however, a cluster-ring opening can accommodate an entire $[Tl_5(Ti_2Cl_9)]^{2+}$ unit. Removal of $[Ti_2Cl_9]^{3-}$ dimers or the whole $[Tl_5(Ti_2Cl_9)]^{2+}$ template could be possible due to the electronic flexibility of the framework. Attempts to remove or exchange these units are underway.

Compound **1** contains 50 valence electrons per formula unit. The observed intracluster bond distances and the analogy with other niobium oxochloride cluster compounds,[5, 14] indicate that each cluster has 14 electrons, and 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[15] (Figure 4) show Curie behavior with an effective magnetic moment of 3.96 μ_B per formula unit which corresponds to 5.2 unpaired electrons.[16] This value is consistent with the model of noninteracting Ti^{3+} ions in the $[Ti_3Cl_7O_6]$ trimers (two trimers per formula unit), and antiferromagnetically coupled Ti^{3+} ions in the $[Ti_2Cl_9]^{3-}$ dimers (one dimer per formula unit) as is the case in $Cs_3Ti_2Cl_9$.[17]

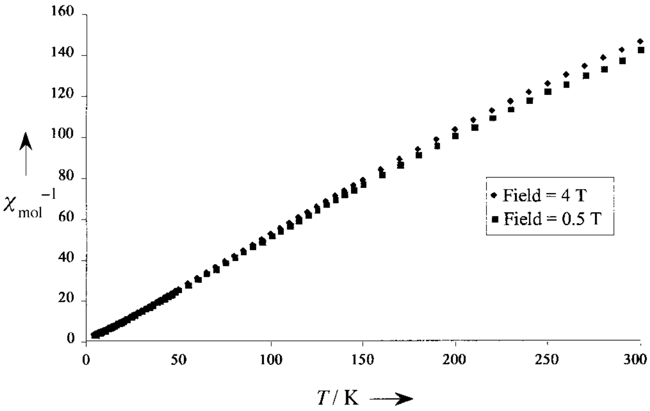

Figure 4. Reverse molar magnetic susceptibility χ_{mol}^{-1} (mol emu^{-1}) of **1** over the temperature range 2–300 K.

Compound **1** represents the first example of a layered HTB-type framework in cluster chemistry. Its layered structure confirms the relationship between the ligand arrangement in the cluster unit and the cluster framework dimensionality. These correlations and the structural analogies with noncluster framework prototypes can serve as a basis for future design of open-framework compounds containing octahedral clusters.

Experimental Section

Compound **1** was initially obtained from the composition $TlTi_2Nb_6Cl_{15}O_4$ corresponding to the addition of one equivalent of TlCl to the starting stoichiometry of the parent compound $Ti_2Nb_6Cl_{14}O_4$. After the composition of the new phase was established from the crystal structure analysis, the compound $[\{Tl_5(Ti_2Cl_9)\}\{(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2\}]$ was obtained quantitatively from stoichiometric amounts of Nb powder, Ti foil, TlCl, Nb_2O_5, and $NbCl_5$. The mixture (handled under an inert atmosphere) was placed in a silica tube, sealed under vacuum, heated for 4 d at 720 °C, and cooled to 500 °C over 4 d, followed by radiative cooling to room temperature. The product was obtained as black hexagonal plates up to 2 mm in diameter.

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[4] Crystal structure data for **1**: trigonal, space group $P\bar{3}c1$, (no. 165), $a = 16.8990(5)$, $c = 18.0422(7)$ Å, $V = 4462.1(3)$ Å^3, $Z = 2$, $\rho_{calcd} = 3.772$ g cm^{-3}, $F(000) = 4560$, $\lambda(Mo_{K\alpha}) = 0.71073$ Å, $\mu(Mo_{K\alpha}) = 13.198$ mm^{-1}, $T = 153$ K. A black hexagonal plate-like crystal ($0.1 \times 0.1 \times 0.01$ mm^3) was selected under an inert atmosphere, sealed in a glass capillary, and used for data collection. The data were collected using Siemens SMART diffractometer equipped with a CCD area detector. A total of 24153 reflections were collected over the range $2.78° \leq 2\theta \leq 55.00°$; 3424 were independent. Lorentz, polarization, and empirical absorption corrections ($T_{min} = 0.26$, $T_{max} = 0.78$) were applied, and the structure was solved and refined against F^2 with 3409 reflections ($I > 0\sigma(I)$) using the SHEXTL V5.1 package. Thallium sites are disordered over two closely spaced (0.35(4) Å) sites. The refinement of the central ligand position in the $[Ti_3Cl_7O_6]$ units showed that it is 80(2)% occupied by a chlorine and 20(2)% by an oxygen (O7)

atom. The [Ti_2Cl_9] units are present about 90% of the time, so that the net stoichiometry is $Tl_{4.87(16)}Ti_{7.81(3)}Nb_{18}Cl_{51.51(16)}O_{12.40(4)}$. The highest residual electron-density peak (1.724 e Å^{-3}) is located between the two titanium atoms that form the dimers. Anisotropic refinement of all atoms except for O7 converged to $R_1 = 0.064$, $wR_2 = 0.102$. Further details of the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-410776.

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[15] The magnetic measurements were performed using a SQUID magnetometer at 0.5 and 4 T in the temperature range 4–300 K.

[16] The Curie constant was obtained from the linear fit of χ_{mol} versus T^{-1} at temperatures >20 K, based on the Curie law $\chi_{mol} = C/T$. The linear fit gives $C = 1.956$ emu mol^{-1}, and a small diamagnetic contribution of 6.0×10^{-5} emu mol^{-1}. The expected magnetic moment for six unpaired electrons is $\mu_{6e} = \sqrt{6} \times \mu_{1e} = 4.24\ \mu_B$.

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Molecular Beacons: A Novel Approach to Detect Protein–DNA Interactions[**]

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Protein–DNA interactions are known to play an important role in a wide variety of biological processes. Binding of proteins to genomic DNA is involved in various biological processes including DNA replication, transcription, recombination, and repair.[1] To study these protein–DNA binding events, a variety of techniques such as band shift and footprinting assays, affinity chromatography, fluorescence analysis, and microscopy visualization have been developed.[2–5] While all of these techniques provide insight into one specific aspect of protein–DNA binding, optical and fluorescence methods offer significant advantages in analytical sensitivity and simplicity. Here we describe a new approach to study protein–DNA binding and to quantify proteins using a recently developed oligonucleotide probe that serves as a molecular beacon (MB).[6–11]

The molecular beacon is designed in such a way that it can report the presence of a specific complementary nucleic acid in homogeneous solutions.[6] The molecular beacon is labeled with a fluorophore at one end and a nonfluorescent quencher at the opposite end. In solution, the molecular beacon forms a hairpin loop which brings the fluorophore and quencher close enough to allow quenching to occur by fluorescence resonance energy transfer. Upon hybridization to a complementary sequence, the hairpin loop is broken and the fluorophore and quencher are separated, resulting in the restoration of fluorescence. The molecular beacon approach has great advantages over other DNA probes, including the ability to detect single-base mismatches, the capability of studying biological processes in real time, and the possibility for in vivo analysis. There have been several applications of molecular beacons, such as sensitive monitoring of the polymerase chain reaction,[7] real-time detection of DNA–RNA hybridization in living cells,[8] DNA mutation analysis,[9] and even detection of pathogenic retroviruses.[10] Recently, a biotinylated single-stranded DNA (ssDNA) molecular beacon was designed and used for DNA-hybridization studies at a liquid–solid interface and for the development of ultrasensitive DNA sensors.[11] Molecular beacons hold great promise in studies in genetics and disease mechanisms as well as in disease diagnostics. So far, however, all applications have been based on the hybridization between a molecular beacon and DNA or RNA molecules. The use of a molecular beacon for studying protein–DNA interactions could be of great benefit for understanding the many important biological processes that require ultrasensitive and specific protein detection. Herein, we report for the first time the interactions between proteins and a molecular beacon.

The molecular beacon synthesized for this study is shown in Figure 1. It was designed with tetramethylrhodamine (TAMRA; Molecular Probes, Eugene, OR) as the fluorophore and 4-(4′-dimethylaminophenylazo)benzoic acid (DABCYL; Molecular Probes) as the quencher. The molecular beacon was synthesized by using DABCYL-derivatized controlled pore glass (CPG) as the starting material. The synthesis was started from the 3′ end. The nucleotides were added sequentially by using standard cyanoethylphosphoramidite chemistry. The 5′ end nucleotide is conjugated to a $(CH_2)_6$-NH linker arm, producing a primary amine group at the 5′-end. This amino group was used to attach tetramethylrhodamine. The product was purified by gel filtration chromatography and reverse-phase high-pressure liquid chromatography (RP-HPLC). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry was used to confirm the synthesis of the designed molecular beacon (data not shown). In the absence

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