A new layered niobium oxochloride cluster compound with novel framework topology†

Ekaterina V. Anokhina, Cynthia S. Day and Abdessadek Lachgar*

Department of Chemistry, Wake Forest University, Winston-Salem, NC 27109 USA. E-mail: lachgar@wfu.edu

Received (in Irvine, CA, USA) 15th March 2000, Accepted 12th May 2000
Published on the Web 19th July 2000

The asymmetric arrangement of chloride and oxide ligands around the octahedral Nb_6 cluster core and their electrostatic interaction with Ti^{3+} counterions play an important role in the formation of a novel 2D framework with cluster connectivity unprecedented in compounds containing octahedral clusters.

Low-dimensional materials containing transition metals have significant importance due to their remarkable physical properties and a wide range of applications in catalysis, ionic transport, and redox intercalation processes.[1] Thus, extensive research efforts have been spent on the design, preparation and characterization of these materials. Investigation of early transition metal cluster materials led to development of a strategy for controlling the cluster-framework dimensionality by adjusting the number of intercluster bridging ligands.[2]

Recently, we began investigating a new approach to the design and preparation of low-dimensional materials containing octahedral metal clusters. The methodology being explored is the modification of the environment of the metal core to form building blocks with well-defined anisotropic bonding preferences using a combination of ligands that create anisotropic charge distribution. In addition, a combination of counterions with large difference in their charge-to-radius ratios and, thus, different coordination preferences, is used to enhance the effects of anisotropic ligand distribution. Our systematic investigation of niobium oxochlorides containing octahedral Nb_6 clusters recently led to the preparation of the layered material $[Tl_5(Ti_2Cl_9)][(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$ which has a unique hexagonal-bronze-type cluster connectivity.[3] Here we describe a novel layered oxochloride $Cs_2Ti_3(Nb_6Cl_{12.5}O_4)_2Cl_2$ **1** in which each octahedral Nb_6 cluster is connected to three adjacent clusters through chloride ligands to form layers with graphite-type topology.[4] The factors leading to its unusual structural properties are proposed.

Compound **1** was initially obtained as black elongated rectangular plates in a reaction designed to prepare the caesium analogue of $[Tl_5(Ti_2Cl_9)][(Nb_6Cl_{12}O_4)_3(Ti_3Cl_4)_2]$ **2**. The crystals were analyzed by energy-dispersive X-ray analysis, and the crystal structure of **1** was determined by single crystal X-ray diffraction.‡ Subsequently, **1** was obtained in high yield in the reaction of stoichiometric amounts of Nb powder, Ti foil, CsCl, Nb_2O_5 and $NbCl_5$. The mixture (handled under argon atmosphere) was placed in a silica tube, sealed under vacuum, heated for 4 d at 750 °C and cooled to 500 °C in 4 d, followed by radiative cooling to room temperature. The product purity was confirmed by X-ray powder diffraction.

The main building block of the two-dimensional structure of **1** (Fig. 1) is an octahedral cluster unit $(Nb_6Cl^i_8O^i_4)Cl^a_6$,[5] in which four oxide ligands selectively occupy 'inner' positions arranged in sets of three ('triad') and one on opposite sides of the Nb_6 octahedron (Fig. 2). The ligand arrangement results in an anisotropic chiral cluster unit with symmetry close to C_2. Octahedral niobium oxochloride clusters with four oxide ligands were also encountered in **2** and in $Ti_2Nb_6Cl_{14}O_4$ **3**,[6] however in contrast to **1**, the O^i ligands in the latter oxochlorides are arranged centrosymmetrically in two sets of two, leading to a different isomer with symmetry close to C_{2h}. A cluster unit in which the oxide ligands are arranged in a 'triad' similar to that in **1**, is found in the previously reported oxochloride $ScNb_6Cl_{13}O_3$ **4** which has three oxide ligands per cluster.[7] The bond distances in the cluster in **1** are similar to those found in compounds **2**–**4** and are consistent with the presence of 14 valence electrons per cluster.[3,6–8] Each cluster shares three of its six Cl^a ligands with three adjacent clusters to form layers with topology similar to that of graphite (Fig. 3). The connectivity formula can be written as $(Nb_6Cl^i_8O^i_4)Cl^{a-a}_{3/2}Cl^a_3$. Layered frameworks based on octahedral clusters, typically, have pseudo-square topology with connectivity formula $(M_6L^i_n)L^{a-a}_{4/2}L^a_2$ (M = Zr, Nb, n = 12; M = Mo, Re, n = 8).[9] The graphite-type connectivity found here is especially surprising for cluster units with C_2 symmetry, for which one would expect an even number of bridging ligands. This could be the result of optimizing the electrostatic interactions between the ligands and Ti^{3+} ions. In the presence of highly charged counterions, the oxide and chloride ligands tend to segregate to form aggregates of oxide ions surrounded by chlorides, as illustrated by the structures of typical ternary transition metal oxochlorides such as layered MOCl (M = Ti^{3+}, Fe^{3+}, Yb^{3+})[10] and $VOCl_2$,[11] and the 1D material $NbOCl_3$.[12] In these structures, chloride ions form the surface of the layers or chains, while oxide and metal ions are

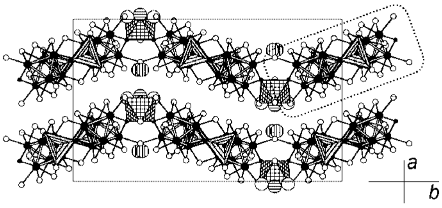

Fig. 1 A view of the crystal structure of **1** in the [001] direction. Large black, small black and small light-gray spheres represent Nb, O, and Cl, respectively. Hatched and light cross-hatched polyhedra represent $[Ti(1)Cl_2O_3]$ trigonal bipyramids and $[Ti(2)Cl_4O_2]$ octahedra, respectively. Caesium atoms are shown as large gray spheres: vertically hatched - Cs(1), horizontally hatched - Cs(2a), not hatched - Cs(2b). The dotted curve outlines the $[Ti(Nb_6Cl_{13}O_4)]$ chain running in the [001] direction.

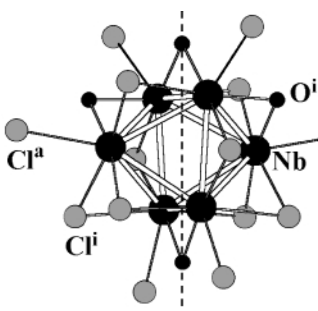

Fig. 2 The cluster unit in **1**. The dashed line shows the pseudo two-fold symmetry axis. Bond distances (Å): Nb–Nb 2.776(1)–3.028(1), Nb–Cl^i 2.430(3)–2.503(2), Nb–Cl^a 2.605(3)–2.636(2), Nb–O^i 1.963(7)–2.061(6).

---

† Electronic supplementary information (ESI) available: 3D interactive versions of the structure of **1**. See http://www.rsc.org/suppdata/cc/b0/b002147o/

DOI: 10.1039/b002147o

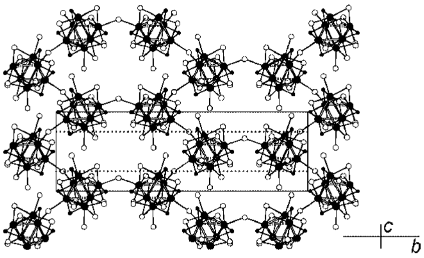

Fig. 3 A view of the graphite-type layered cluster framework in **1**; for labelling, see Fig. 1. Dotted lines represent the *a*-glide plane perpendicular to $\vec{c}$ that relates adjacent layers.

located inside. Similar ion segregation is observed in the cluster compounds **1**–**4**. The ligand arrangement in the cluster unit of **1** favors the formation of [$Ti(Nb_6Cl_{13}O_4)$] zig-zag chains (Fig. 4) in which the clusters are connected through Ti^{3+} ions (Ti(1)) and Cl^a ligands so that oxide ligands forming the 'triads' are shielded by chlorides. Each Ti(1) connects three clusters and has a distorted trigonal-bipyramidal environment formed by three O^i and two Cl^a ligands (bond distances: $d_{Ti–Cleq}$ = 2.411(3) and 2.423(3), $d_{Ti–Oeq}$ = 1.876(6), $d_{Ti–Oax}$ = 2.035(7) and 2.037(7) Å). Bond-valence sum calculations[13] confirm the oxidation state +3 for Ti(1). The chains connect to each other through an additional titanium (Ti(2)) and Cl^a ligands to form layers, so that the remaining oxide ligands (O(4)) are shielded by chlorides (Fig. 1). This linkage type results in the wave-like geometry of the layers and novel graphite-like cluster framework topology. The titanium Ti(2) coordinates to two O^i and two Cl^a ligands, arranged in a distorted square-planar geometry. Its coordination environment is completed to octahedral or square-pyramidal by additional chloride or oxide ligands[14] (bond distances: $d_{Ti–Cl}$ = 2.36(3)–2.570(9), $d_{Ti–O}$ = 1.84(2)–2.02(1) Å). The anion segregation argument allows us to rationalize the formation of the complex 3D cluster framework and the unusual trigonal-bipyramidal coordination of scandium ions in **4** which is based on clusters with the same 'triad' of O^i ligands as that found in **1**. The clusters and the Sc^{3+} ions form chains similar to the one shown in Fig. 4, where the O(4) atoms are substituted by chlorines. These chains are connected to each other through Cl^a ligands in a tetragonal 'woodpile'-fashion to form a chiral 3D framework.

Adjacent layers in **1** are related by an *a*-glide plane perpendicular to $\vec{c}$ (Figs. 1 and 3) and interact through caesium ions that are distributed over three independent sites (Cs(1), Cs(2a), Cs(2b)) located on the layers' surface on each side of cone-shaped openings generated by six-member cluster rings (Fig. 1). The site Cs(1) is fully occupied and is coordinated by 9 chlorides within 4 Å. The Cs(2a) and Cs(2b) sites, separated by 1.29 Å, are located in the channels running between the layers in the $\vec{b}$ direction. These two sites are partially occupied (Cs(2a) 41(2)%, Cs(2b) 18.8(9)%), and are coordinated by 8 and 7 chlorines within 4 Å, respectively. The number of caesium ions per cluster was refined to 0.89(2) which agrees with the oxidation states assigned to the transition metals and the refined occupancies of Cl(14), L(15), and Cl(16) sites.

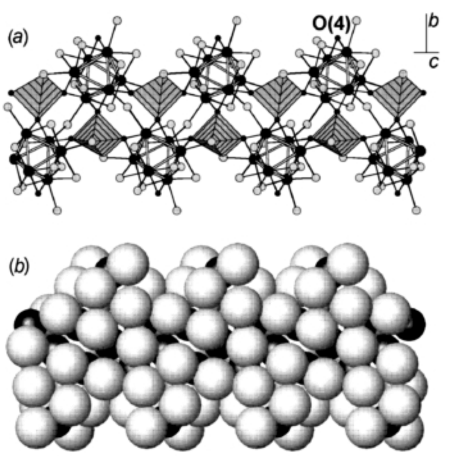

Fig. 4 (*a*) A ball-and-stick view of the [$Ti(Nb_6Cl_{13}O_4)$] chain in **1**. For labelling, see caption to Fig. 1. (*b*) Space-filling representation of anions in the same fragment (black - O, gray - Cl).

The structural properties of the new oxochloride $Cs_2Ti_3(Nb_6Cl_{12.5}O_4)_2Cl_2$ demonstrate the effectiveness of using a combination of ligands to prepare low-dimensional cluster materials. The interplay between the effects of anisotropic charge distribution around the cluster core and the trend for the anion segregation in the overall structure is conducive for the formation of diverse structural types with low-dimensional or open-framework character. These effects seem to have a greater influence on the framework dimensionality than the total number of ligands which is the primary structure-determining factor in cluster compounds with one ligand type or statistical ligand distribution.

Notes and references

‡ *Crystal data* for **1**: refined stoichiometry $Cs_{1.79(3)}Ti_3Nb_{12}Cl_{26.51(3)}O_{8.14(2)}$, orthorhombic, space group *Pnma* (No.62), a = 17.546(2), b = 29.323(3), c = 9.1556(7) Å, V = 4710.5(8) Å^3, T = 298 K, Z = 4, M = 2565.97, $\mu(Mo_{K\alpha})$ = 6.17 mm^{-1}, 7411 reflections measured, 6011 unique (R_{int} = 0.051) which were used in all calculations. Least-squares refinements were based on F^2 and converged to R_1 = 0.054, wR_2 = 0.106 (($I > 2\sigma(I)$), R_1 = 0.101, wR_2 = 0.117 (all data). CCDC 182/1667. See http://www.rsc.org/suppdata/cc/b0/b002147o/ for crystallographic data in .cif format.

1 See for example: *Magnetic Properties of Layered Transition Metal Compounds*, ed. L. J. De Jongh, Kluwer, Dordrecht, 1990; *Physics and Chemistry of Low-Dimensional Inorganic Conductors*, ed. C. Schlenker, J. Dumas and M. Greenblatt, Plenum, New York, 1996; *Progress in Intercalation Research*, ed. W. Müller-Warmuth and R. Schöllhorn, Kluwer, Dordrecht, 1994.

2 C. Perrin, *J. Alloys Compd.*, 1997, **262**, 10; J. R. Long, L. S. McCarty and R. H. Holm, *J. Am. Chem. Soc.*, 1996, **118**, 4603 and references therein.

3 E. V. Anokhina, C. S. Day, M. W. Essig and A. Lachgar, *Angew. Chem., Int. Ed.*, 2000, **39**, 1047.

4 A framework based on $Re_6Se_{11}Cl_3$ clusters which has a graphite-type topology, but different from **1** cluster connectivity is reported in J. R. Long, A. S. Williamson and R. H. Holm, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 226.

5 The subscripts 'i' and 'a' refer to the ligands bridging the edges of the metal octahedron ('inner' ligands), and the ligands located in the apical positions ('outer' ligands), respectively.

6 E. V. Anokhina, M. W. Essig and A. Lachgar, *Angew. Chem., Int. Ed.*, 1998, **37**, 522.

7 S. Cordier, C. Perrin and M. Sergent, *Eur. J. Solid State Inorg. Chem.*, 1994, **31**, 1049.

8 C. Perrin, S. Cordier, S. Ihmaïne and M. Sergent, *J. Alloys Compd.*, 1995, **229**, 123 and references therein.

9 R. P. Ziebarth and J. D. Corbett, *Inorg. Chem.*, 1989, **28**, 626; B. Baján and H.-J. Meyer, *Z. Allg. Anorg. Chem.*, 1997, **623**, 791; H. Schäfer, H. G. von Schnering, J. Tillack, F. Kuhnen, H. Wöhrle and H. Baumann, *Z. Allg. Anorg. Chem.*, 1967, **353**, 281; H. G. von Schnering, W. May and K. Peters, *Z. Kristallogr.*, 1993, **208**, 368; A. Perrin, L. Leduc and M. Sergent, *Eur. J. Solid State Inorg. Chem.*, 1991, **28**, 919.

10 E. M. Snegireva, S. I. Troyanov and V. B. Rybakov, *Zh. Neorg. Khim.*, 1990, **35**, 1945; M. D. Lind, *Acta Crystallogr., Sect. B*, 1970, **26**, 1058; G. Brandt and R. Diehl, *Mater. Res. Bull.*, 1974, **9**, 411.

11 H. J. Seifert and J. Uebach, *Z. Allg. Anorg. Chem.*, 1981, **479**, 32.

12 D. E. Sands, A. Zalkin and R. E. Elson, *Acta Crystallogr.*, 1959, **12**, 21.

13 I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B*, 1985, **41**, 244.

14 The refinement of occupancies of the ligands not belonging to the clusters showed that coordination of Ti(2) is completed to octahedral by two chloride ligands (Cl(15) and Cl(14)), to square-pyramidal by one chloride ligand (Cl(16)), and to square-pyramidal by one oxide ligand ((O15)), 65(1), 21(1), and 14(2)% of the time, respectively.