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Straightforward Synthesis and Structure of a New Starting Material for Niobium Cluster Phases: $[Nb_6Cl^i_{12}(CH_3OH)^a_4Cl^a_2]\cdot 6CH_3OH$

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A new, fast, and straightforward synthetic route for the new cluster compound $[Nb_6Cl^i_{12}(CH_3OH)^a_4Cl^a_2]\cdot 6CH_3OH$, taking advantage of the special solubility properties of tetracyanoborate salts has been established, and the single-crystal X-ray structure of this compound, which is a promising starting material for new cluster phases, has been determined.

A characteristic feature of materials containing early transition metals in oxidation states lower than the group number is the formation of clusters via metal–metal bonding.[1] In reduced niobium halides and oxides, a common structural motif consists of the $[Nb_6X^i_{12}Y^a_6]^n$ cluster unit. The Nb_6 octahedra are edge-bridged by 12 *inner* ligands X^i = F, Cl, Br, or O. Six additional ligands occupy the terminal, so-called *outer* (aussen) positions, Y^a,[2] which can be either anionic or neutral ligands. Depending on the oxidation state of the cluster and the charge of the ligands, *n* can range from +2 to −4 for cluster complexes which are preparatively accessible. Such cluster phases are available by means of high-temperature solid-state, as well as solution-chemical, methods.[3,1e,1d] In solution, the molecular clusters give access to ligand-substitution reactions, which of course take place preferably at the outer Y^a positions. A variety of materials have been reported for niobium chlorides with Y^a = other halides,[4,5] cyanides,[6] thiocyanides,[7] azides,[8] methanolate,[9] and others.[1e] Materials prepared by such ligand-substitution reactions have eventually very interesting properties, e.g. structural, spectroscopical, catalytical, or magnetical,[10] like for example, the open-framework materials $[(CH_3)_4N]_2[MnNb_6Cl_{12}(CN)_6]$ or $[Zn(en)]_2[Nb_6Cl_{12}(CN)_6]$ (en = ethylenediamine).[6a,b]

So far, the chemistry of such Nb (or Ta) cluster materials is much less developed than that of, for example, comparable Mo or W clusters.[1e] A reason for this seems to be that inconvenient multistep procedures are needed to get suitable starting materials for Nb cluster ligand substitution reactions. In general, cluster anions $[Nb_6X_{18}]^{n-}$ (X = Cl or Br, *n* = 2−4) as alkaline metal, alkaline earth metal, rare-earth metal,[11] or Ga, In, or Tl salts,[12] which are prepared by high-

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(1) (a) Mingos, D. M. P., Wales, D. J., Eds. *Introduction to Cluster Chemistry*; Prentice Hall International, Inc.: Englewood Cliffs, NJ 1990. (b) González-Moraga, G., Ed. *Cluster Chemistry*; Springer-Verlag: Berlin, Heidelberg 1993. (c) Braunstein, P., Oro, L. A., Raithly, P. R., Eds. *Metal Clusters in Chemistry*; Wiley-VCH: Weinheim, 1999. (d) Schmid, G., Ed. *Clusters and Colloids*; VCH: Weinheim, 1994. (e) Prokopuk, N., Shriver, D. F. *Adv. Inorg. Chem.* **1999**, *46*, 1−49. (f) Simon, A. *Angew. Chem.* **1981**, *93*, 23−44. (g) Köhler, J.; Svensson, G.; Simon, A. *Angew. Chem.* **1992**, *104*, 1463−1482. (h) Corbett, J. D. In *Modern Perspectives in Inorganic Crystal Chemistry*; Parthé, E., Ed.; Kluwer: Dortrecht, The Netherlands, 1992; p 27ff. (i) Corbett, J. D. *J. Chem. Soc., Dalton Trans.* **1996**, 575−587. (j) Corbett, J. D. *Inorg. Chem.* **2000**, *39*, 5178−5191. (k) Cotton, F. A. *J. Chem. Soc., Dalton Trans.* **2000**, 1961−1968 and references cited therein.

(2) Simon, A.; von Schnering, H. G.; Wöhrle, H.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1965**, *339*, 155−170.

(3) (a) Perrin, C.; Cordier, S.; Ihmaine, S.; Sergent, M. *J. Alloys Compd.* **1995**, *229*, 123−133. (b) Meyer, H.-J.; *Z. Anorg. Allg. Chem.* **1995**, *621*, 921−924. (c) Perrin, C. *J. Alloys Compd.* **1997**, *262*, 10−21. (d) Meyer, G. *Chem. Rev.* **1988**, *88*, 93−107. (e) Simon, A. *Clusters and Colloids. From Theory to Applications*; Schmidt, G., Ed.; VCH: Weinheim, 1994.

(4) (a) Simon, A.; von Schnering, H.-G.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1968**, *361*, 235−248. (b) McCarley, R. E.; Hughes, B. F.; Cotton F. A.; Zimmermann, R. *Inorg. Chem.* **1965**, *4*, 1491−1492. (c) Koknat, F. W.; Parsons J. A.; Vongvusharintra A. *Inorg. Chem.* **1974**, *13*, 1699−1702.

(5) (a) Fleming, P. B.; Müller L. A.; McCarley, R. E. *Inorg. Chem.* **1967**, *6*, 1−4. (b) Hughes, B. G.; Meyer, J. L.; Fleming P. B.; McCarley R. E. *Inorg. Chem.* **1970**, *9*, 1343−1346. (c) Koknat, F. W.; McCarley, R. E. *Inorg. Chem.* **1972**, *11*, 812−816.

(6) (a) Naumov, N. G.; Cordier, S.; Perrin, C. *Solid State Sci.* **2003**, *5*, 1359−1367. (b) Yan, B.; Day, C. S.; Lachgar, A. *Chem. Comm.* **2004**, 2390−2391. (c) Naumov, N. G.; Cordier, S.; Gulo, F.; Roisnel, T.; Fedorov V.; Perrin, C. *Inorg. Chim. Acta* **2003**, *350*, 503−510. (d) Reckeweg, O.; Meyer, H.-J. *Z. Anorg. Allg. Chem.* **1996**, *622*, 411−416.

(7) Naumov, N. G.; Cordier, S.; Perrin, C. *Chem. Commun.* **2004**, 1126−1127.

(8) Meyer, H.-J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 921−924.

(9) Beck, U.; Simon, A.; Brničević, N.; Širac, S. *Croat. Chem. Acta* **1995**, *68*, 837−848.

(10) (a) Yaghi, O. M.; O'Keffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Jim, J. *Nature* **2003**, *423*, 705−714. (b) Kim, Y.; Choi, S. K.; Park, S. M.; Nam W.; Kim, S. J. *Inorg. Chem. Commun.* **2002**, *5*, 612−615. (c) Ströbele M.; Meyer, H.-J. *Z. Naturforsch. B* **2001**, *56*, 1025−1034. (d) Tulsky, E. G.; Crawford, N. R. M.; Baudron, S. A.; Batail, P.; Long, J. R. *J. Am. Chem.* Soc. **2003**, *125*, 15543−15553.

(11) Yan, Z.; Day, C. S.; Lachgar, A. *Inorg. Chem.* **2005**, *44*, 4499−4505.

(12) Meyer, H.-J. *Z. Anorg. Allg. Chem.* **1995**, *621*, 921−924 and references cited therein.

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temperature reactions, are dissolved in H_2O, and a compound described as $[Nb_6Cl_{12}(H_2O)_4Cl_2]\cdot 4H_2O$[13] (even though its structure is not yet known precisely) is used in the next steps. Unfortunately, the dissolution process is rather slow and the present water molecules (or hydroxide ions) cause problems during following preparative steps whenever ligands of same ligand strength are planned to be bonded to the metal core or strongly reducing/moisture sensitive materials are involved.

In this communication, we report the straightforward preparation and the crystal structure of the new compound $[Nb_6Cl^i_{12}(CH_3OH)^a_4Cl^a_2]\cdot 6CH_3OH$ (**1**), which contains the neutral $[Nb_6Cl^i_{12}(CH_3OH)^a_4Cl^a_2]$ (**2**) cluster unit with an octahedral $[Nb_6Cl^i_{12}]^{2+}$ cluster core.

1 is obtained from $K_4[Nb_6Cl_{18}]$ (or $Na_4[Nb_6Cl_{18}]$),[4,14] which is dissolved under anhydrous and inert gas (Ar) conditions in CH_3OH. Addition of $K[B(CN)_4]$ (or $Na[B(CN)_4]$)[15] to the cluster solution speeds up the formation and crystal growth of the title phase, such that ~80% of the initially used cluster phase is obtained as **1** in form of dark green crystals within 3−4 days. In this reaction, four out of the six Cl^a atoms are substituted by methanol molecules, as expressed by the following equation:

$$K_4[Nb_6Cl^i_{12}Cl^a_6] + 4CH_3OH \xrightarrow[CH_3OH]{\Delta,\ K[B(CN)_4]} [Nb_6Cl^i_{12}(CH_3OH)^a_4Cl^a_2] + 4KCl\downarrow$$

To test the influence of the added tetracyanoborate, the same reaction was tried without this salt. After much longer reaction times (11 instead of 3−4 days), which also required higher temperatures of the sand bath, **1** was obtained in low yield and poor crystallinity. This indicates clearly that the addition of the tetracyanoborate salt largely improves the synthesis of the title phase. The alkaline metal salts of the $[B(CN)_4]^-$ ion are highly soluble in polar and nonpolar solvents[15] and show a vanishing coordination ability. Furthermore, the addition of $K[B(CN)_4]$ increases the concentration of the alkaline metal cation in the cluster solution and such chloride ions originating from the exo positions of the $[Nb_6Cl_{18}]^{4-}$ clusters are precipitated as KCl. The thereby emptied coordination sites are filled with the next best available ligand, methanol molecules in this case. Moreover, the tetracyanoborate salt also increases the ionic strength of the solution what leads to better crystallinity of the title phase.

The structure of **1** consists of discrete neutral $[Nb_6Cl^i_{12}(CH_3OH)^a_4Cl^a_2]$ cluster units and cocrystallized methanol molecules. In the cluster unit, the octahedral Nb_6 core is edge-bridged by 12 *inner* chlorine atoms. Four of the six apical positions are occupied by methanol ligands, and the remaining two by additional chlorine atoms arranged in a *trans* configuration (Figure 1). The atoms of **2** are arranged such that the center of the cluster is located on an inversion center.

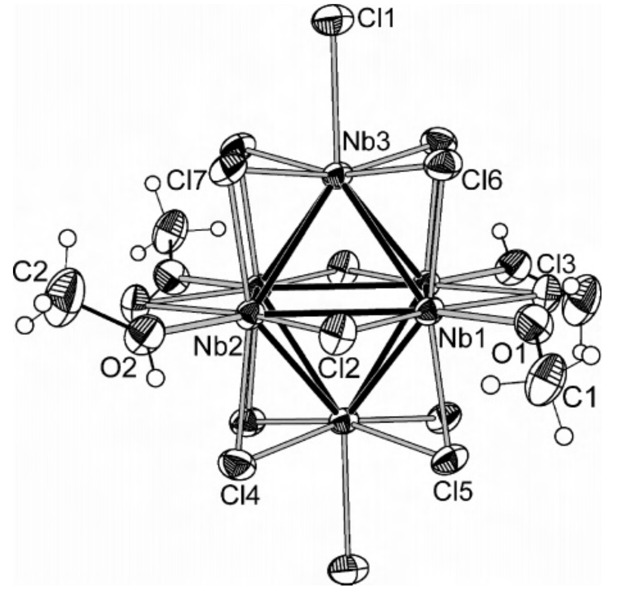

Figure 1. Molecular structure of the centrosymmetric $[Nb_6Cl^i_{12}(CH_3OH)^a_4Cl^a_2]$ cluster (**2**) in crystals of **1** with atom numbering scheme (thermal ellipsoids at the 50% probability level). Selected bond distances (Å): Nb(1)−Nb(2), 2.9044(8); Nb1−Nb2$^{\#1}$, 2.9013(8); Nb(1)−Nb(3), 2.9256(8); Nb(1)−Nb(3)$^{\#1}$, 2.9325(9); Nb(2)−Nb(3), 2.9212(9); Nb(2)−Nb(3)$^{\#1}$, 2.9345(8); Nb1−O1, 2.235(5); Nb2−O2, 2.269(5); Nb(3)−Cl1^a, 2.581(2); Nb−Cl^i (average), 2.459(2) (symmetry transformation #1: $1 - x$, $1 - y$, $1 - z$).

The average distance between the equatorial Nb atoms (Nb1 and Nb2) is 2.903 Å, and between the apical Nb3 atoms and the other two symmetry-independent metal atoms unit, the distance is 2.928 Å. The short average Nb−Nb distance is very close to that found in, for example, $[Nb_6Cl_{12}(EtOH)_6]^{2+}$ (2.904 Å),[16] whereas the average Nb(1,2)−Nb3 distance compares nicely with those Nb−Nb which are found in other cluster phases with the $[Nb_6Cl_{18}]^{4-}$ unit. Examples are the $A_4[Nb_6Cl_{12}(NCS)_6]\cdot 4H_2O$ phases (A = K, Rb, NH_4), with Nb−Nb distances around 2.930 Å.[6d] The Nb−Cl^i distances vary from 2.448(2) to 2.463(2) Å (av. 2.458 Å). The Nb3−Cl1^a distance is as expected longer with a value of 2.581(2) Å. All these distances classify the cluster as $[Nb_6Cl_{12}]^{2+}$ unit, with 16 electrons in the metal-centered cluster-based orbitals.[17]

Because of the two different types of ligands on the apical positions the metal octahedron is tetragonally elongated in the direction of the trans chloro ligands (Cl1−Nb3···Nb3$^{\#1}$−Cl1$^{\#1}$, symmetry transformation #1: $1 - x$, $1 - y$, $1 - z$). To the best of our knowledge, there have been so far only two other, comparable Nb−chloro cluster phases structurally characterized: *trans*-$[Nb_6Cl_{14}\{P(C_4H_9)_3\}_4]$[18] and $[Nb_6Cl_{12}(OH)_2(H_2O)_4]$.[19] Both have tetragonally elongated Nb_6 octahedra. This deviation from O_h symmetry can be explained

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(13) Schäfer, H.; Plautz B.; Plautz, H. *Z. Anorg. Allg. Chem.* **1972**, *392*, 10−22.

(14) Broll, A.; Juza, D.; Schäfer, H. *Z. Anorg. Allg. Chem.* **1971**, *382*, 69−79.

(15) Küppers, T.; Bernhardt, E.; Willner, H.; Rohm H. W.; Köckerling, M. *Inorg. Chem.* **2005**, *44*, 1015−1022.

(16) (a) Beck, U.; Simon, A.; Brničević, N.; Širac, S. *Croat. Chem. Acta*, **1995**, *68*, 837−848. (b) Brničević, N.; Muštović, F.; McCarley, R. E. *Inorg. Chem.* **1988**, *27*, 4532−4535.

(17) Oligaro, F.; Cordier, S.; Halet, J.-F.; Perrin, C.; Saillard J.-Y.; Sergent, M. *Inorg. Chem.* **1998**, *37*, 6199−6207 and references cited therein.

(18) Imoto,H.; Hayakawa, S.; Morita, N.; Saito, T. *Inorg. Chem.* **1990**, *29*, 2007−2014.

(19) Brničević,N.; Planinić, P.; McCarley, R. E.; Antolić, S.; Luić, M.; Kojić-Prodić, B. *J. Chem. Soc., Dalton Trans.* **1995**, *9*, 1441−1446.

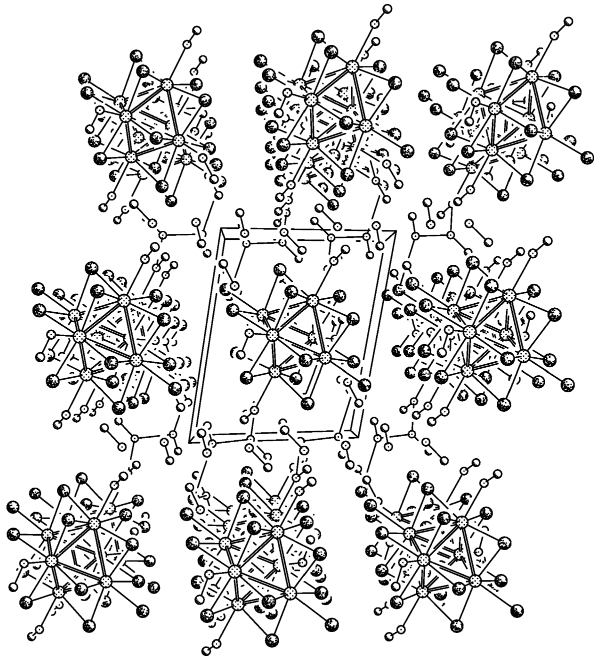

Figure 2. Layers of the neutral [Nb$_6$Cl$^i_{12}$(CH$_3$OH)$^a_4$Cl$^a_2$] clusters between which the methanol molecules are located in crystals of [Nb$_6$Cl$^i_{12}$(CH$_3$OH)$^a_4$Cl$^a_2$]·6CH$_3$OH (Nb and O regularly dotted, Cl randomly dotted, C hatched, H atoms omitted for clarity, Nb−Nb distances emphasized, unit-cell edges shown).

by the so-called *matrix effect*,[20] with the smaller (and neutral) coordinating oxygen atoms of the methanol ligands exerting a smaller matrix effect than the chloro ligands and thereby allowing for shorter (and stronger) metal−metal bonds in the equatorial plane of the Nb$_6$ unit. Besides the above-mentioned examples, some other Nb clusters with alcohol ligands have been reported in the literature, but no detailed structural data are available.[21,22]

The three-dimensional arrangement of the cluster units follows a stacking along the unit cell directions, resulting in a layered arrangement of the clusters, between which the methanol molecules are located. This layered arrangement is depicted in Figure 2.

Some preliminary tests of the solubility of the title phase in THF gave dark green solutions, indicating fair solubility. Thereby, the title phase, which is accessible by a quick and simple procedure, opens the door to a much larger chemistry with respect to new materials, catalysis, and open-framework phases, to name a few, as was accessible before with the poorly soluble water containing material.

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Supporting Information Available: Crystal data for **1** and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Corbett, J. D. *J. Solid State Chem.* **1981**, *39*(1), 56−74.

(21) Brničević, N.; Muštović, F.; McCarley, R. E. *Inorg. Chem.* **1988**, *27*, 4532−4535.

(22) Beck, U.; Simon, A.; Brničević, N.; Širac, S. *Croat. Chem. Acta*, **1995**, *68*, 837−848. This paper reports about the synthesis and structure of (C$_{18}$H$_{36}$N$_2$O$_6$Na)$_2$Na$_2$[Nb$_6$Cl$_{12}$(OCH$_3$)$_6$]·15CH$_3$OH. Unfortunately, the reported bond lengths and the color of the materials suggest this phase not to be a [Nb$_6$Cl$_{12}$]$^{2+}$, but an oxidized cluster phase.