Hexanuclear Niobium Cluster Compounds with Protonated N-Base Cations

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Dedicated to Prof. Bernd Harbrecht on the Occasion of his 70th Birthday

Abstract. Octahedral clusters of the $[M_6X_{12}]$ type offer numerous possibilities to form structural arrangements through different choices of bonding situations. In this paper a series of new cluster compounds of the transition metal niobium is described, which consist of the $[Nb_6Cl_{18}]^{2-}$, and in one case $[Nb_6Cl_{18}]^{3-}$, anion and protonated N-base cations ($[MIm-H]^+$, $[nPr_3N-H]^+$, $[TMGu-H]^+$, and $[Tzn-H]^+$). They all are prepared using water scavenger compounds $[SOCl_2$ or $(Ac)_2O]$ under oxidising conditions, resulting in two-electron (or one-electron, respectively) oxidized cluster units with respect to the starting material $[Nb_6Cl_{14}(H_2O)_4]\cdot4H_2O$. Of five members of this group single-crystal

X-ray structures were determined. The cluster anions exist in all structures as discrete units. The acidic H atoms of all N-bases are hydrogen bonded to H acceptors, in 4 cases to *outer*, exo bonded Cl atoms of the cluster unit and in one case to the O atom of a co-crystallized THF molecule. In $[TMGu-H]_2[Nb_6Cl_{18}]$ chains of cluster anions exist hydrogen-bonded through bridging $[TMGu-H]^+$ cations. ESI mass spectra of $[MIm-H]_2[Nb_6Cl_{18}]\cdot2SOCl_2$ and $[TMGu-H]_2[Nb_6Cl_{18}]$ show the expected isotopic distribution patterns for the anions together with other peaks associated to chloride mass losses and/or reduction processes.

Introduction

Compounds with discrete, hexanuclear, octahedral cluster units of group 5 metal atoms *M* with a ligand sphere of 18 chloride ions, i.e. $[M_6Cl^i_{12}Cl^a_6]^{n-}$ anions (M = Nb or Ta, Cl^i: *inner*, edge-bridging chloride ions, Cl^a outer, apical chloride ions, n = 4, 3, 2)[1] and protonated (acidic) counter cations were first published as early as 1924. *Lindner* and *Feit* reported several trinuclear tantalum and molybdenum cluster compounds with pyridinium cations.[2] Later, it was realized that the metal atom core of the anions of these cluster compounds are hexanuclear with octahedral shape. The formulas of the Ta compounds were corrected to be $[Py-H]_2[Ta_6Cl_{18}]$, and $[Py-H]_2[Ta_6Cl_{12}Br_6]$, respectively (Py = pyridine).[3] Other publications reported niobium analogues, about further cluster compounds with different halides, and about their characterization, i.e. elemental analyses, powder and single-crystal analyses, IR-, UV- spectra and susceptibility, and mass spectra.[3,4] Thermal properties and decomposition processes were investigated using TGA and DSC methods in combination with mass spectrometry.[4b] The thermal decomposition of

$[Py-H]_2[Ta_6Cl_{18}]$ is accompanied by the elimination of HCl and pyridine. The formation of $[Ta_6Cl_{16}]$ was postulated.[4a–4c] Another Ta-cluster compound, the hydrated tantalum cluster acid, "$H_2[Ta_6Cl_{18}]\cdot6H_2O$" was reported by *Mc Carley* et al. in 1970 and further investigated by *Thaxton* and *Jacobson*.[5] Heating of this cluster compounds finally also leads to the elimination of HCl. Further known compounds with $[M_6Cl_{18}]^{2-}$ anions (M = Nb or Ta) contain the acidic $[Ph_3AsOH]^+$ cation (Ph = phenyl).[6] A more reduced cluster compound with a threefold negatively charged cluster unit, $[(18Cr6)_2(H_5O_2)]_3[Nb_6Cl_{18}]$ (18Cr6 = 18-crown-6, 1,4,7,10,13,16-hexaoxacyclooctadecane), was published by *Meyer* et al.[7]

Compounds with $[Nb_6Cl^i_{12}]$ or $[Ta_6Cl^i_{12}]$ cluster units are known to be stable in three different oxidation states (see above, n = 4, 3, or 2), going along with 16, 15 or 14 electrons (CBEs, cluster based electrons) occupying the energetically highest, basically metal-metal bonding molecular orbitals.[8]

In this article we describe new compounds with the $[Nb_6Cl_{18}]^{2-}$ (and one case of $[Nb_6Cl_{18}]^{3-}$) cluster anion and protonated N-base cations. The used N-bases are 1-methyl-imidazole (MIm), tri-*n*-propylamine (nPr_3N), tetramethyl-guanidin (TMGu), and 1,3,5-triazin (Tzn). Besides the preparation, structures and physico-chemical properties, ESI mass spectra were recorded of two compounds, which indicate the formation of the chloride ion loss in the gas phase as postulated before.

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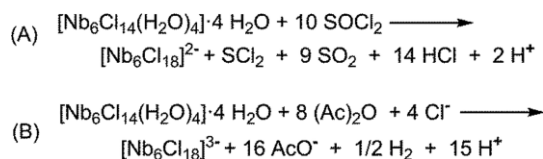 E-Mail: Martin.Koeckerling@uni-rostock.de
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Results and Discussion

Syntheses

Seven new niobium cluster compounds, which contain hexanuclear cluster anions and protonated N-base cations were pre-

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pared, **1**: [MIm-H]$_2$[Nb$_6$Cl$_{18}$]·2SOCl$_2$, **2**: [nPr$_3$N-H]$_2$[Nb$_6$Cl$_{18}$]·2CH$_2$Cl$_2$, **2B**: [nPr$_3$N-H]$_2$[Nb$_6$Cl$_{18}$], **3**: [TMGu-H]$_2$[Nb$_6$Cl$_{18}$], **3B**: [TMGu-H]$_2$[Nb$_6$Cl$_{18}$]·0.41CHCl$_3$, **4**: [Tzn-H]$_2$[Nb$_6$Cl$_{18}$]·2THF, and **5**: [nPr$_3$N-H]$_3$[Nb$_6$Cl$_{18}$]·[nPr$_3$N-H]Cl.[9]

Six samples contain the [Nb$_6$Cl$_{18}$]$^{2-}$ anion (**1–4**, **2B**, **3B**) with 14 CBEs and one the one-electron reduced version [Nb$_6$Cl$_{18}$]$^{3-}$ (**5**) with 15 CBEs. Some compounds contain besides the cluster anion and the N-base cation co-crystallized solvent molecules. In all cases the starting cluster material, [Nb$_6$Cl$_{14}$(H$_2$O)$_4$]·4H$_2$O, which contains 16 cluster based electrons (CBEs) is treated with thionyl chloride (**1–4**, **2B**, **3B**) or acetic anhydride (**5**) in the presence of a source for the protonated cation. By the reaction with SOCl$_2$ or (Ac)$_2$O all water molecules of the starting material, ligands and co-crystallized molecules are removed. The chloride ions are obtained through the reaction of the water scavenger SOCl$_2$ (**1–4**, **2B**, **3B**) or supplied by the excess of [nPr$_3$N-H]Cl in the preparation of **5**. The halide ions occupy the emptied ligand sites of the cluster, such that [Nb$_6$Cl$_{18}$]$^{n-}$ units form. Furthermore, the cluster core is oxidized by two electrons in the case of **1–4**, **2B**, **3B** and one electron in the case of **5**.[10] The overall sequence for the reaction of the cluster starting material with thionyl chloride, reaction (A), and acetic anhydride, reaction (B), is shown in Scheme 1. Under the acidic conditions the protonated base cations form, in the case of **1** [MIm-H]$^+$ from [TMS-MIm]$^+$ and of **4**, [Tzn-H]$^+$ from 1,3,5-triazine. In the other cases the protonated N-base cations are supplied with the respective starting materials.

(A) [Nb$_6$Cl$_{14}$(H$_2$O)$_4$]·4 H$_2$O + 10 SOCl$_2$ ⟶
[Nb$_6$Cl$_{18}$]$^{2-}$ + SCl$_2$ + 9 SO$_2$ + 14 HCl + 2 H$^+$

(B) [Nb$_6$Cl$_{14}$(H$_2$O)$_4$]·4 H$_2$O + 8 (Ac)$_2$O + 4 Cl$^-$ ⟶
[Nb$_6$Cl$_{18}$]$^{3-}$ + 16 AcO$^-$ + 1/2 H$_2$ + 15 H$^+$

Scheme 1. Reaction scheme for the formation of the [Nb$_6$Cl$_{18}$]$^{n-}$ cluster anions, with $n = 2$ (A) and $n = 3$ (B).

Apparently, the redox potential of H$^+$ in the formation of **5** is not strong enough for a two-electron oxidation of the 16 CBE cluster starting compound and the [Nb$_6$Cl$_{18}$]$^{3-}$ ion with 15 CBEs is formed, reaction (B) in Scheme 1. Using SOCl$_2$, the complete two-electron oxidation is observed, leading to cluster units with 14 CBEs, reaction (A) in Scheme 1.

Hypothetically, a possible side reaction between the N-base and the cluster unit with the formation of [Nb$_6$Cl$_{18-n}$(N-base)$_n$]^m ($n = 0$ to 6, $m = -4$ to +4) cluster units could happen. This is not observed, likely because of the strong acidic reaction conditions, preventing the existence of the free bases.

It is interesting to note, that so far no hexanuclear niobium cluster compound with protonated N-base cation and non oxidized, 16 CBE cluster units is known.[11] It is easy to assume, that the redox potential of H$^+$ is too strong to allow for the 16 CBE cluster to exist. But this assumption is contradicted by the fact, that the 16 CBE cluster starting material is made in acidic solutions. Thus, the synthesis of 16 CBE [Nb$_6$Cl$_{18}$] cluster compounds with protonated base cations remains a challenge.

Structures

Molecular structures in the solid state were determined of the compounds **1–5** by single-crystal X-ray diffraction. Table 1 gives selected crystal, X-ray diffraction, and refinement parameters. Table 2 lists selected atom distances. Figure 1, Figure 2, Figure 3, Figure 4, and Figure 5 show the structures of the cluster anions, the counter-cations, and the co-crystallized solvent molecules.

All compounds contain the well-known [Nb$_6$Cl$_{18}$]$^{n-}$ cluster unit with octahedral Nb$_6$ core with all edges bridged by and all apices attached to Cl atoms.[1b,1c,10] In the cases of **1** to **4** n equals 2, whereas for **5** $n = 3$. This assignment of charges complies with the number of cations per cluster unit in the crystal structures, i.e. two cations per cluster in **1** to **4** and 3 in **5**. In the refined structures of **2** and **5** some disorder is observed. In compound **2**, which contains one symmetry independent tri-n-propyl-ammonium cation, one of the three n-propyl chains (C7 – C9) has two different orientations, which are refined using a split model. In **5**, four symmetry independent [nPr$_3$N-H] cations exist, of which that around N2 has one n-propyl chain, which adopts two different orientations. As known already for a long time, the average Nb–Nb and Nb–Cl^i distances reflect the oxidation state of the cluster. In **1** to **4** the average Nb–Nb distances range from 3.0242 Å in **1** to 3.0303 Å in **4**, which is in accordance with the values found for other 14 CBE Nb$_6$ cluster units.[10] The same holds for the Nb–Cl^i distances, ranging from 2.4261 Å (in **1**) to 2.4304 Å (in **4**), compared to e.g. 2.42 Å in [(CH$_3$)$_4$N]$_2$[Nb$_6$Cl$_{18}$].[12]

As expected, the Nb–Nb distances in **5**, which has one CBE more than **1–4**, are shorter than those in **1** to **4**, (2.9833 and 2.9877 Å) because of the metal–metal bonding character of the occupied a$_{2u}$ orbital. At the same time the Nb–Cl^i distances are slightly longer because of the Nb–Cl^i antibonding character.[4d,8a,8c]

An interesting issue of this series of cluster compounds in comparison to those with the same cluster anions, but non-protic organic cations, as reported by our group in 2016,[10] is the possible existence of hydrogen bonds and hydrogen-bonded networks with possible directional orientation preferences of units in the structures of the present investigation. In fact, all five cluster compounds contain H-bonded arrangements. In **1**, **2**, **4**, and **5** one acidic H atom exist at the N-base cation and in **3** two acidic H atoms. In three of these compounds **1**, **2**, and **5** hydrogen-bonded trimers of the composition [Base-H]$_2$[Nb$_6$Cl$_{18}$] exist, which are shown in Figure 1, Figure 2, and Figure 5 with the hydrogen bonds drawn as red dashed lines. The acidic H atoms bond to two of the six outer Cl atoms, which apparently are the most basic atoms in those compounds, and the used reaction systems, respectively. Different hydrogen bond situation are found for **3** and **4**. Compound **3** contains the [TMGu-H]$^+$ cation, which carries two acidic H atoms per cation and is thereby able to set up more than one hydrogen bond. In fact, the NH$_2$ group forms two hydrogen bonds, each one to one *outer* Cl atom of two neighboring clusters units. Because this Cl^a atom has a symmetry equivalent Cl atom (Wyckoff symmetry of the cluster: 2/m),

Table 1. Selected crystal, X-ray diffraction, and refinement parameters for **1–5**.

	1	2	3	4	5
Empirical formula	$C_8H_{14}Cl_{22}N_4Nb_6O_2S_2$	$C_{20}H_{48}Cl_{22}N_2Nb_6$	$C_{10}H_{28}Cl_{18}N_6Nb_6$	$C_{14}H_{24}Cl_{18}N_6Nb_6O_2$	$C_{36}H_{88}Cl_{19}N_4Nb_6$
M_r /g·mol^{-1}	1599.71	1653.96	1427.94	1503.95	1808.11
ρ /g·cm^{-3}	2.586	2.150	2.456	2.429	1.781
Crystal system	monoclinic	triclinic	monoclinic	triclinic	triclinic
Space group, Z	$P2_1/n$, 2	$P\bar{1}$, 1	$C2/m$, 2	$P\bar{1}$, 1	$P\bar{1}$, 2
a /Å	10.7189(4)	9.314(3)	9.4241(3)	9.0146(7)	13.1256(3)
b /Å	8.8023(3)	12.582(4)	23.4924(6)	11.1633(8)	13.1438(3)
c /Å	21.7946(9)	13.120(4)	8.7220(3)	11.275(1)	23.1410(6)
α /°	90	113.61(2)	90	101.058(3)	78.627(1)
β /°	92.395(2)	97.320(2)	89.980(2)	101.288(3)	75.351(1)
γ /°	90	108.47(1)	90	106.660(5)	61.207(1)
V /Å^3	2054.6(1)	1277.7(7)	1931.0(1)	1028.2(1)	3371.6(1)
T /K	173(2)	123(2)	173(2)	123(2)	173(2)
$2\Theta_{max}$	94.696	65.186	75.852	54.254	62.69
μ /mm^{-1}	3.13	2.44	2.95	2.779	1.746
Reflns. coll., ind.	72690 / 19024	57821 / 9268	14433 / 3980	50085 / 4559	80416 / 22047
Reflns. ind., $I > 2\sigma(I)$	10604	7211	2169	3760	14934
No. of parameters	202	253	100	210	611
R_1 / wR_2 (all data) [a]	0.1079 / 0.0818	0.0684 / 0.0884	0.0860 / 0.0443	0.0401 / 0.0399	0.0927 / 0.0993
R_1 / wR_2 [$F^2>2\sigma(F^2)$] [a]	0.0440 / 0.0658	0.0433 / 0.0804	0.0318 / 0.0365	0.0255 / 0.0373	0.0509 / 0.0814
Goof on F^2	0.954	1.037	0.617	1.062	1.064
A / B^a	0.0174 / 0	0.0221 / 4.1414	0 / 0	0.0087 / 0.9435	0.0219 / 5.5586
$\Delta\rho$(max/min) /e·Å^{-3}	1.06 / −1.29	1.93 / −1.58	0.95 / −1.08	0.528 / −0.505	1.394 / −1.075

a) $R1 = \sum |F_o| - |Fc||/\sum|F_o|$. b) $wR2 = (|\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]|)^{1/2}$; $w = 1/[\sigma2(F_o^2) + (AP)^2 + BP]$; $P = (F_o^2 + 2\,F_c^2)/3$.

cation-bridged cluster chains exist in the crystals of **3**. A short piece of such a cluster–cation chain is shown in Figure 6.

It is interesting to note, that those Nb–Cl^a distances which are involved in hydrogen bonds, are for all cluster compounds the longest within the ranges given in Table 2. The variation of the Nb–Cl^a distances and their ranges of standard deviations are shown in Figure 7.

For the synthesis of **4** the solvent THF was used, with an O atom, which apparently has a higher charge density (higher basicity) than the Cl^a atoms of the cluster units. Consequently, the strongest hydrogen bond in **4** is found between the acidic H atom of the [Tzn-H]$^+$ cation and the co-crystallized THF molecule, see Figure 4. Looking at the H-donor-acceptor distances, D–H···A, for the three structurally comparable cluster anion-N-base cation combinations in **1**, **2**, and **3**, it is interesting to note, that there seems to be an inverse correlation between the donor-acceptor distance of the hydrogen bond and the acidity of the cation. The length decreases with increase acidity strength, i.e. in **1** with the [MIm-H]$^+$ cation, which has a pKs value of 7.52[13] the shortest D–H···A distance of 3.157(2) Å is observed, followed by **2** with the [nPr$_3$N-H]$^+$ cation, pKs = 10.65,[14] D–H···A = 3.270(3) Å, and **3** pKs = 13.0,[15] and D–H···A = 3.487(3) Å.

ESI Mass Spectra

ESI mass spectra of [MIm-H]$_2$[Nb$_6$Cl$_{18}$]·2SOCl$_2$ (**1**) and [TMGu-H]$_2$[Nb$_6$Cl$_{18}$] (**3**) are shown in Figure 8. They were recorded under gentle conditions (U$_c$ = 20 V). Both spectra show the base peak centered at m/z = 596, attributed to the pseudo-molecular [Nb$_6$Cl$_{18}$]$^{2-}$ anion on the basis of the m/z

value and the anion's distinctive isotopic pattern. As in previous works, this pseudo-molecular peak appears accompanied by additional signals associated to chlorine atoms mass losses.[10] Spectra of **1** and **3** reveal one additional peak of similar intensity at 580 m/z, identified as the [Nb$_6$Cl$_{17}$□]$^{2-}$ anion (□: empty coordination site). An extra signal of smaller intensity is also observed in the spectrum of **3** at 562 m/z which corresponds to [Nb$_6$Cl$_{16}$□$_2$]$^{2-}$ anionic species. From a chemical point of view, this loss of chlorine atoms involves a simultaneous reduction of the cluster unit in order to preserve the charge. This redox behavior has been observed before for analogous [W$_6$Cl$_{18}$] and [W$_6$CCl$_{18}$] hexametallic cluster compounds and is assumed to take place in the mass spectrometer.[16] On the other hand, formation of "[Nb$_6$Cl$_{16}$]" species by losing chlorine atoms has been proposed to happen in heating processes of cluster precursors.[4b] Furthermore, the spectra of **1** and **3** reveal minor peaks centered at m/z = 1160, 1125, and 1087. They are identified as the monocharged [Nb$_6$Cl$_{17}$□]$^-$, [Nb$_6$Cl$_{16}$□$_2$]$^-$ and [Nb$_6$Cl$_{15}$□$_3$]$^-$, respectively, anions. Further peaks above m/z = 1200 (not shown in Figure 7) are assigned to cluster species containing impurity bromine atoms.

Further Characterization

The cluster compounds were further characterized by elemental analysis, IR, ^{1}H NMR, and ^{13}C NMR spectroscopy. Data is given in the Experimental Section. IR frequencies are as reference values if the respective compound is reproduced. They are not further discussed. The ^{1}H NMR spectroscopic data of **2** shows the signals of the protonated cations with the exception of the signal around 14.3 ppm. This together with
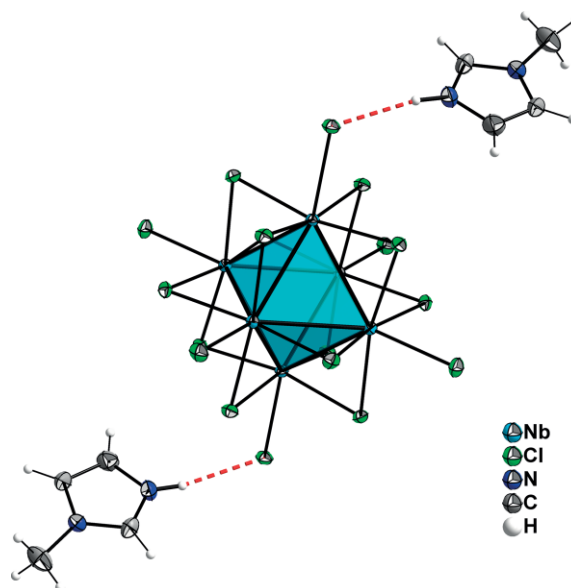
Table 2. Ranges and average values of selected atom distances /Å and shortest hydrogen bonds (donor–acceptor distance /Å) in **1** to **5**.

Compound / atom types	Range	Average
[MIm-H]$_2$[Nb$_6$Cl$_{18}$]·2SOCl$_2$ (**1**)		
Nb–Nb	3.0101(2) – 3.0369(2)	3.0242
Nb–Cl^i	2.4130(4) – 2.4431(5)	2.4261
Nb–Cl^a	2.4761(5) – 2.5313(5)	2.4981
Hydrogen bonds:		
N2–H2A···Cl1	3.157(2)	
[Pr$_3$N-H]$_2$[Nb$_6$Cl$_{18}$]·2CH$_2$Cl$_2$ (**2**)		
Nb–Nb	3.021(1) – 3.036(1)	3.028
Nb–Cl^i	2.419(1) – 2.436(1)	2.428
Nb–Cl^a	2.475(1) – 2.530(1)	2.495
Hydrogen bonds:		
N1–H1···Cl6	3.270(3)	
[TMGu-H]$_2$[Nb$_6$Cl$_{18}$] (**3**)		
Nb–Nb	3.0097(4) – 3.0355(4)	3.0270
Nb–Cl^i	2.4169(9) – 2.4403(7)	2.4273
Nb–Cl^a	2.4860(7) – 2.4938(9)	2.4886
Hydrogen bonds:		
N1–H1A···Cl2	3.452(3)	
N1–H1B···Cl6	3.3387(9)	
[Tzn-H]$_2$[Nb$_6$Cl$_{18}$]·2THF (**4**)		
Nb–Nb	3.0253(4) – 3.0360(4)	3.0303
Nb–Cl^i	2.4231(7) – 2.4382(7)	2.4304
Nb–Cl^a	2.4737(8) – 2.5068(7)	2.4883
Hydrogen bonds:		
N1–H1···O1	2.596(3)	
[Pr$_3$N-H]$_3$[Nb$_6$Cl$_{18}$]·[Pr$_3$N-H]Cl (**5**)		
Cluster 1:		
Nb–Nb	2.9740(5) – 2.9902(5)	2.9833
Nb–Cl^i	2.431(1) – 2.449(1)	2.439
Nb–Cl^a	2.490(1) – 2.562(1)	2.524
Cluster 2:		
Nb–Nb	2.9814(5) – 2.9951(5)	2.9877
Nb–Cl^i	2.434(1) – 2.450(1)	2.440
Nb–Cl^a	2.506(1) – 2.565(1)	2.529
Hydrogen bonds:		
N2–H2C···Cl19	3.133(5)	
N3–H3D···Cl19	3.138(4)	
N4–H4C···Cl18	3.184(4)	
N1–H1C···Cl3	3.205(4)	

Figure 1. View of the structure of the hydrogen bonded (red dashed lines) cation/anion trimer in [MIm-H]$_2$[Nb$_6$Cl$_{18}$]·2SOCl$_2$ (50 % probability thermal displacement parameters, co-crystallized SOCl$_2$ molecules are omitted).

Figure 2. Structure of the hydrogen-bonded cation/anion trimer in [Pr$_3$N-H]$_2$[Nb$_6$Cl$_{18}$]·2CH$_2$Cl$_2$ (50 % probability thermal displacement parameters; hydrogen bonds are shown as red dashed lines; of the disordered nPr chain only one orientation is shown, co-crystallized CH$_2$Cl$_2$ molecules are omitted).
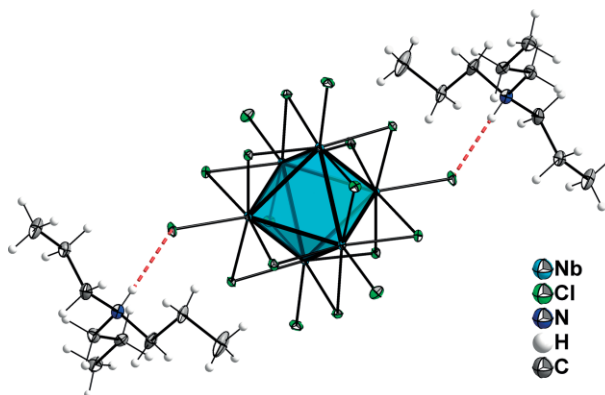
that around 9.2 ppm belongs to the acidic proton. Two signals exist because of protolytic equilibrium between the solvent DMSO and the cation, what has been proven by a dilution series. The integral of the two signals adds in all cases to two protons, what is in accordance with the structures. Powder X-ray diffraction patterns were recorded off the compounds to ensure structural identity and crystalline phase purity.

Conclusions

In this paper we have successfully applied the synthetic procedure for the preparation of new halide supported metal cluster compounds of electron poor transition metals, in which a cluster compound, which carries water ligands is dehydrated in the presence of sources for organic cations, to synthesis a series of hexanuclear niobium cluster compounds with protonated organic N-base cations. The acidic H atoms are prone to strong hydrogen bonding, what is in fact observed in the struc-

tures by the existence of cation-anion trimers and chains of cluster anions interconnected through hydrogen-bonded bridging cations. In the negative scan direction the ESI MS spectra show the expected isotope pattern of the cluster anions as well as patterns of species in which the original cluster unit has lost chlorine atoms. The cluster compounds investigated in this work offer the possibility to further develop this chemistry by applying acid-base reactions to members of this class of cluster compounds.

Experimental Section

Procedures and Materials: As before, [Nb$_6$Cl$_{14}$(H$_2$O)$_4$]·4H$_2$O was used as starting material.[10] It was prepared according to a published
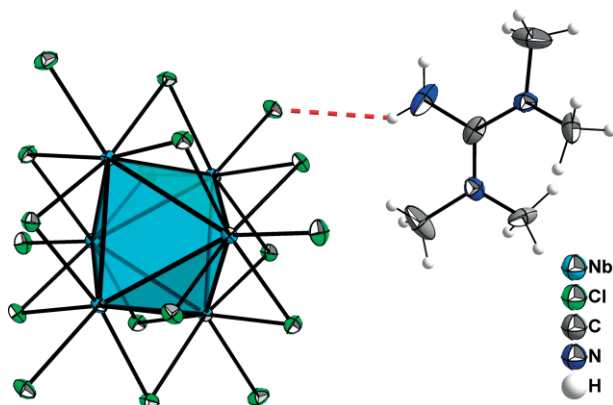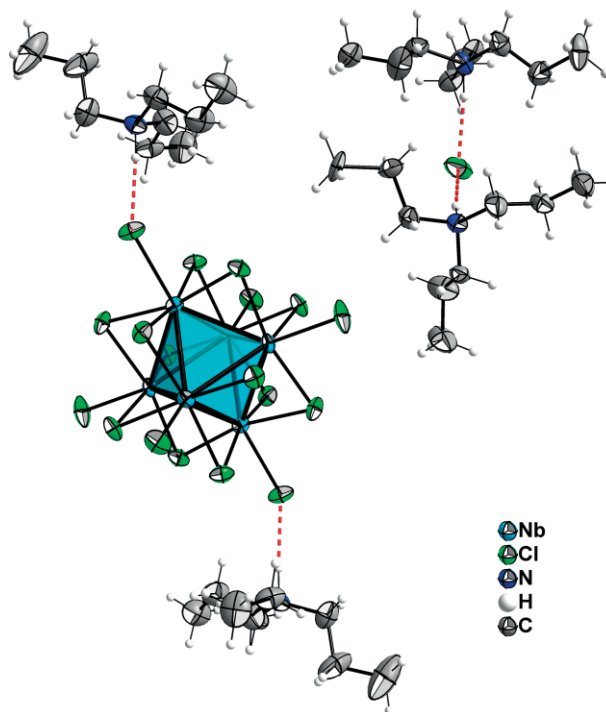
Figure 3. Structure of a hydrogen-bonded cluster anion-cation pair in [TMGu-H]$_2$[Nb$_6$Cl$_{18}$] (50 % probability thermal displacement parameters, hydrogen bonds are shown as red dashed line).
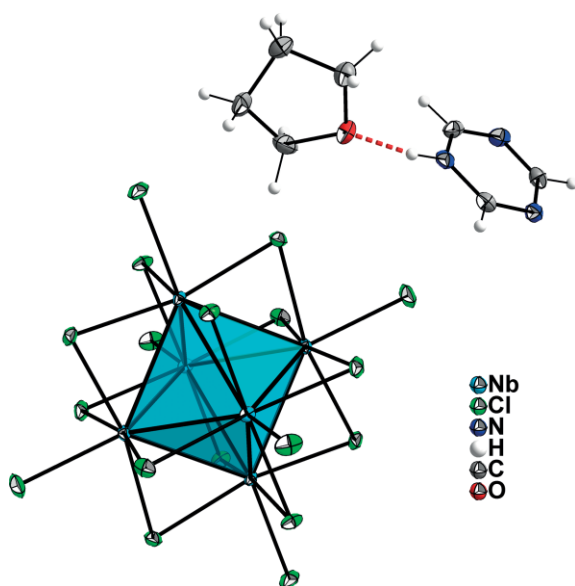

Figure 4. Structure of the cation/anion/THF unit in [Tzn-H]$_2$[Nb$_6$Cl$_{18}$]· 2 THF (50 % probability thermal displacement parameters, hydrogen bonds are shown as red dashed line).

Figure 5. Structure of the two cation/anion units in [Pr$_3$N-H]$_3$[Nb$_6$Cl$_{18}$]· [Pr$_3$N-H]Cl (50 % probability thermal displacement parameters; hydrogen bonds are shown as red dashed lines; of the disordered *n*Pr chain only one orientation is shown).
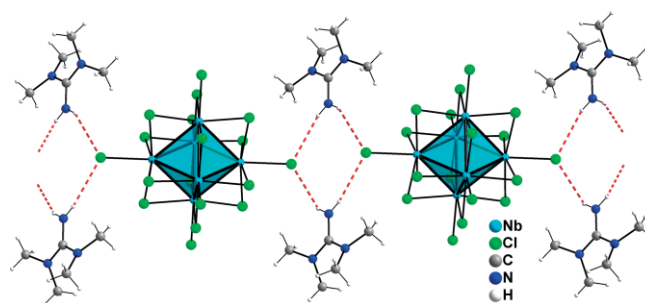
Figure 6. A short cut-out section of the [Nb$_6$Cl$_{18}$]$^{2-}$ cluster-[TMGu-H]$^+$ cation chain in crystals of **3**.

procedure.[17] For the synthesis of the compounds **1–4**, **2B**, and **3B** it was treated with thionyl chloride, SOCl$_2$, and for **5** with acetic acid anhydride, (Ac)$_2$O, in the presence of compounds from which the final counter cations originated. SOCl$_2$ was distilled prior to use. The compounds, which supply the counter cations and the other materials were used as received from commercial suppliers. Elemental analyses (C and H) were done using a Elementar vario MICRO cube device. ^{1}H and ^{13}C NMR spectra were obtained with a Bruker AVANCE 300 II spectrometer and calibrated with respect to the solvent signal of [D$_6$]DMSO. Infrared spectra in the range of 4000–500 cm^{-1} were obtained with a Nicolet 380 FT-IR spectrometer with a Smart Endurance ATR device and a Bruker ALPHA IR spectrometer with Platinum ATR unit.

Synthesis of [MIm-H]$_2$[Nb$_6$Cl$_{18}$]·2SOCl$_2$ (1): The following procedure was used to synthesize and to grow single-crystals of **1**. An amount of 30 mg (0.16 mmol) of trimethylsilyl methylimidazolium chloride (TMS-MImCl) was placed in a glass vial of 6 mm diameter, which had the opening tapered down to 1 mm. A small amount of

[Nb$_6$Cl$_{14}$(H$_2$O)$_4$]·4H$_2$O (10 mg, 0.008 mmol) was placed in a larger, 12 mL screwed glass. The prepared vial with the TMS-MImCl was placed in the screwed glass with the orifice pointing upwards. Thionyl chloride (SOCl$_2$) was added with a pipette until the orifice of the inner vial was covered and the inner vial was filled with the liquid. The outer vial was closed with a cap loosely, such that gaseous by-products could escape. Large black crystals of the title compound have been grown on diffusion within two weeks. After this time the liquid SOCl$_2$ phase was colorless to pale yellow. For analyses and X-ray diffraction the crystals were taken directly out of the liquid. **Yield**: (not optimized, visually expected) ca. 50 %. On recrystallization from CHCl$_3$ the co-crystallized SOCl$_2$ solvate molecules were exchanged by CHCl$_3$ with an amount of about one molecule CHCl$_3$ per cluster unit. [MIm-H]$_2$[Nb$_6$Cl$_{18}$]·0.92CHCl$_3$: calcd. C, 7.28; H, 1.02; N, 3.81 %, found: C, 7.46; H, 0.99; N, 3,80 %. **IR** (for [MIm-H]$_2$[Nb$_6$Cl$_{18}$]·2SOCl$_2$, ATR, room temperature): ṽ = 621 (vs); 662 (m); 737 (vs); 752 (s); 775 (s); 847 (m); 912 (m); 955 (m); 1012 (m); 1078 (s); 1099 (s); 1142 (m);
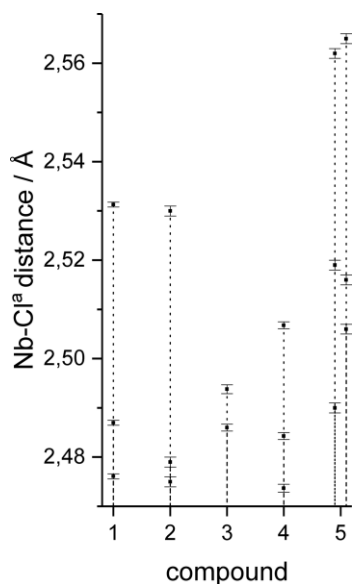
Figure 7. Variation of Nb–Cl^a distances in **1** to **5** within their standard deviations.
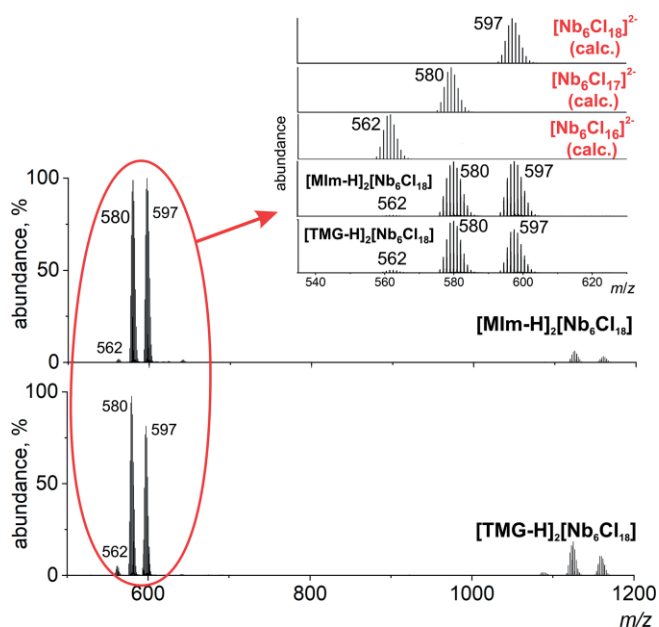
Figure 8. ESI-MS spectrum of **1** and **3** showing the patterns of $[Nb_6Cl_{18}]^{2-}$, $[Nb_6Cl_{17}\square]^{2-}$, $[Nb_6Cl_{16}\square_2]^{2-}$ and mono-anionic cluster species.

1167 (m); 1221 (s); 1277 (m); 1306 (s); 1329 (m); 1381 (m); 1437 (s); 1462 (m); 1547 (s); 1581 (s); 1711 (m); 2324 (m); 2353 (m); 2434 (m); 2611 (m); 2713 (m); 2750 (m); 2874 (m); 2978 (m); 3012 (m); 3068 (s); 3101 (m); 3138 (m) cm^{-1}. **^{1}HNMR** ([D$_6$]DMSO, room temperature, ppm): δ = 14.29 (br. s, 1.72 H), 9.20 (br. s, 0.24 H), 9.06 (br. s, 2 H), 8.30 (s, 0.92 H), 7.69 (br. s, 2 H), 7.66 (br., 2 H), 3.87 (s, 6 H). **^{13}C NMR** ([D$_6$]DMSO, room temperature, ppm): δ = 135.56 (s, 2 C), 123.33 (s, 2 C), 119.66 (s, 2 C), 78.88 (s, 2 C).

[nPr$_3$N-H]$_2$[Nb$_6$Cl$_{18}$]·2CH$_2$Cl$_2$ (2) and [nPr$_3$N-H]$_2$[Nb$_6$Cl$_{18}$] (2B): [Nb$_6$Cl$_{14}$(H$_2$O)$_4$]·4H$_2$O (50 mg, 0.04 mmol), [nPr$_3$N-H]Cl (30 mg, 0.16 mmol), dichloromethane (CH$_2$Cl$_2$) (4 mL), and SOCl$_2$ (0.3 mL)

were filled into a 50 mL Schlenk flask. The flask was sealed with a ground glass stopcock. The by-products HCl$_{(g)}$ and SO$_{2(g)}$ were released via the open tap of the Schlenk flask. The formation of black crystals of [nPr$_3$N-H]$_2$[Nb$_6$Cl$_{18}$]·2CH$_2$Cl$_2$ was observed after about 2 days. Crystals for analyses and X-ray diffraction experiments were taken out of the mother liquor. Further crystalline material was isolated by removal of the liquid using a syringe under argon. The crystals were washed with 1 mL CH$_2$Cl$_2$ twice and dried in vacuo. Thereby, the compound loses the co-crystallized solvate molecules and **2B** was obtained. Yield (for **2**): 51 mg (82 % for **2B**). [nPr$_3$N-H]$_2$[Nb$_6$Cl$_{18}$]: calcd. C, 14.57; H, 2,99; N, 1,89 %, found: C, 14.13; H, 2.90; N, 1,89 %. **IR** (for **2**, ATR, room temperature): $\tilde{\nu}$ = 589 (s), 666 (m), 750 (vs), 875 (s), 920 (s), 987 (s), 1043 (s), 1095 (m), 1171 (m), 1327 (m), 1381 (s), 1455 (vs), 1470 (vs), 1615 (m), 2686 (m), 2785 (m), 2877 (m), 2967 (s), 3039 (m), 3470 (s) cm^{-1}. **^{1}H NMR** (for **2**, [D$_6$]DMSO, room temperature, ppm): δ = 14.62 (br. s, 0.62 H), 9.21 (br. s, 1.42 H), 2.99 (t, J = 1.00 Hz, 12 H), 1.63 (m, 12 H), 0.92 (t, J = 6.99 Hz, 18 H) ppm. **^{13}C NMR** ([D$_6$]DMSO, room temperature): δ = 53.78 (s, 6 C), 16.83 (s, 6 C), 11.45 (s, 6 C) ppm.

[TMGu-H]$_2$[Nb$_6$Cl$_{18}$] (3) and [TMGu-H]$_2$[Nb$_6$Cl$_{18}$]·0.41CHCl$_3$ (3B): The preparation of crystals of **3** was done using the same procedure as described for **1**. Instead of TMS-MImCl, 30 mg (0.23 mmol) tetramethylguanidine hydrochloride (TMGu·HCl) were used. Dark red almost black crystals were obtained. For **3B** the following procedure was applied: An amount of 50 mg (0.04 mmol) [Nb$_6$Cl$_{14}$(H$_2$O)$_4$]·4H$_2$O and 240 mg polyethylene glycol (PEG 3000), dissolved in 1.5 mL SOCl$_2$, was transferred into a 12 mL screwed glass. 6 mL CHCl$_3$ were added. The chloroform was overlayered with TMGu·HCl (60 mg), dissolved in 0.3 mL CHCl$_3$. The screwed glass was closed loosely with the cap. The gaseous by-products should be able to be released. In the bottom area of the screwed glass a dark green to brown solution forms. Black needle-like crystals of **3B** grow as a result of diffusion within 2 weeks. The product was transferred into a Schlenk flask in an argon atmosphere. The liquid phase was removed. The crystals were washed twice with 4 mL CH$_3$Cl and dried for a few minutes in vacuo. Yield: 25 mg (41 % for **3B**). [TMGu-H]$_2$[Nb$_6$Cl$_{18}$]·0.41CHCl$_3$: calcd. C, 8.47; H, 1.94; N, 5.69 %, found: C, 8.46; H, 1.90; N, 5,69 %. **IR** (for **3**, ATR, room temperature): $\tilde{\nu}$ = 486 (vs); 526 (vs); 868 (m); 1037 (m); 1059 (m); 1070 (m); 1144 (m); 1191 (m); 1233 (m); 1323 (m); 1408 (vs); 1428 (m); 1449 (m); 1554 (s); 1602 (vs); 1626 (s); 2894 (m); 2935 (w); 2954 (w); 3368 (m); 3465 (m) cm^{-1}. **^{1}H NMR** ([D$_6$]DMSO, room temperature, ppm): δ = 14.49 (br. s, 0.83 H), 8.30 (s, 0.41 H), 7.80 (br. s, 3.17 H), 2.91 (s, 24 H) ppm. **^{13}C NMR** ([D$_6$]DMSO, room temperature): δ = 160.55 (s, 2 C), 78.94 (s, 0.41 C) ppm.

[Tzn-H]$_2$[Nb$_6$Cl$_{18}$]·2 THF (4): 50 mg (0.04 mmol) [Nb$_6$Cl$_{14}$(H$_2$O)$_4$]·4H$_2$O, 55 mg 1,3,5-triazine, 4 mL THF, and 1 mL SOCl$_2$ were placed in a 8 mL vial. As before, the vial was covered loosely with the cap. After about one hour the gas evolution stops and the color of the solution has turned into dark-brown. It was filtered and stored without any movement. After 3 days black crystals of **4** have formed. Crystals for analyses and X-ray diffraction experiments were taken directly out of the mother liquor. Figure 7 shows a view of such crystals through a light optical microscope. Bulk material was isolated by removal of the liquid with a pipette, washed 3 times with heptane and dried in vacuo. No reproducible elemental analysis data because of decomposition. Yield: 43 mg (63 %). **IR** (ATR, room temperature): $\tilde{\nu}$ = 534 (m), 556 (m), 598 (s), 624 (s), 676 (s), 727 (m), 802 (m), 878 (s), 1041 (vs), 1074 (s), 1270 (m), 1304 (s), 1331 (s), 1407 (s), 1445 (m), 1552 (m), 1624 (m), 1667 (s), 1679 (s), 1715 (s), 2887 (s), 2971 (s), 3153 (s). **^{1}H NMR** ([D$_6$]DMSO, room temperature, ppm) : 8.82 (m, 2 H), 9.32 (s, 1 H). **^{13}C NMR** ([D$_6$]DMSO, room temperature, ppm): 166.12 (s, 2 C), 157.31 (s, 1C).

[*n*Pr₃N-H]₃[Nb₆Cl₁₈]·[*n*Pr₃N-H]Cl (5): Amounts of 50 mg (0.04 mmol) [Nb₆Cl₁₄(H₂O)₄]·4H₂O, 170 mg (1.00 mmol) [*n*Pr₃N-H]Cl, 2 mL (0.02 mol) acetic anhydride and a small amount (4 drops) of tri-*n*-propylamine were placed in a 12 mL screwed glass vial. It was closed tight with a screw cap. The vial was heated at 60 °C for 24 hrs. A dark green-brown solution forms. Crystals of **5** were obtained by vapor diffusion of ethyl acetate into the cluster solution. The crystals were filtered off, washed two times with ethyl acetate and diethyl ether (3 mL each) and dried in vacuo. [*n*Pr₃N-H]₃[Nb₆Cl₁₈]·[*n*Pr₃N-H]Cl: calcd. C, 23.91; H, 4.91; N, 3.10 %, found: C, 23.82; H, 4.75; N, 2,41 %. Yield: 27 mg (36 %). **IR** (ATR, room temperature): ν̃ = 752 (vw); 874 (s); 913 (s); 987 (vw); 1045 (m); 1092 (s); 1169 (s); 1243 (s); 1329 (m); 1379 (m); 1449 (vw); 1470 (vw); 2523 (m); 2640 (m); 2708 (m); 2791 (m); 2830 (m); 2877 (m); 2937 (w); 2966 (vw). **¹H NMR** ([D₆]DMSO, room temperature, ppm): 9.36 (br. s, 4 H), 2.98 (br. s, 24 H), 1.64 (br. s, 24 H), 0.92. s, 36 H). **¹³C NMR** ([D₆]DMSO, room temperature, ppm): 53.70 (s, 12 C), 16.76 (s, 12 C), 11.43 (s, 12 C).

Single-Crystal X-ray Structure Analyses: Single-crystal X-ray diffraction measurements were carried out on crystals of compounds **1**–**5** with a Bruker-Nonius Apex-II diffractometer with graphite monochromated Mo-*K*ₐ radiation, λ = 0.71073 Å, an Oxford-Cryosystems 700-Series-Cryostream cooler, and a CCD detector. Intensity measurements, integration, correction, and scaling of the data was done using the Bruker Apex-II software.[18] Figure 9 shows a light microscopic picture of single crystals of **4**. The structures were solved by direct methods and refined on F² by full-matrix least-squares techniques with the SHELX suit of programs.[19] The non-hydrogen atoms were refined anisotropically. All hydrogen atoms of the title compounds were added on idealized positions and refined using riding models.

Figure 9. Light microscopic view of crystals of **4** with 20-times magnification.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1817421 (**1**), CCDC-1817513 (**2**), CCDC-1817503 (**3**), CCDC-1911033 (**4**),and CCDC-1835115 (**5**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

X-ray Powder Diffraction: X-ray powder diffraction measurements were carried out with a Stoe Stadi P powder diffractometer with Cu-*K*ₐ₁ radiation (λ = 1.5418 Å) using a linear PSD detector. Measurements were carried out in transmission / Debey-Scherrer setup. Handling and data collection was performed with the WinXPow software.[20]

ESI-Mass Spectrometry: ESI-mass spectra were recorded using a Premier quadrupole-hexapole Q-TOF mass spectrometer with an orthogonal Z-spray electrospray source (Waters, Manchester, UK). Samples of [MIm-H]₂[Nb₆Cl₁₈]·2SOCl₂ (**1**), dissolved in DMSO, and [TMGu-H]₂[Nb₆Cl₁₈] (**3**), dissolved in a mixture of DMSO and CH₃CN were used for the measurements. The temperature of the source block was set at 120 °C, and the desolvation temperature at 225 °C. A capillary voltage of 3.3 kV was used in the negative scan mode, and the cone voltage was set to Uc = 10 V for both compounds. Time-of-flight (TOF) mass spectra were acquired in the V-mode at a resolution of ca. 5000 [full width at half-maximum (FWHM)]. Sample solutions were injected with a syringe pump directly connected to the ESI source at a flow rate of 10 μL·min⁻¹. The observed isotopic pattern of each compound perfectly matched the theoretical isotope pattern calculated from their elemental composition by using the MassLynx 4.1 program.[21]

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