Journal of Solid State Chemistry 181 (2008) 2660–2665

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Synthesis and structures of new niobium cluster compounds with pyridinium cations: $(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$ (Pyr: pyridine, Et: ethyl) and the cubic modification of $(PyrH)_2[Nb_6Cl_{18}]$

Anke Flemming, Alessandra Hoppe, Martin Köckerling *

Institut für Chemie, Abteilung Anorganische Chemie/Festkörperchemie, Universität Rostock, Albert-Einstein-Str. 3a, Rostock D-18059, Germany

ARTICLE INFO

Article history:
Received 10 January 2008
Received in revised form
8 June 2008
Accepted 17 June 2008
Available online 20 June 2008

Keywords:
Niobium
Chlorides
Halide
Cluster
Crystal structure
Single crystal X-ray diffraction
Solid-state synthesis

ABSTRACT

Slow crystallization of $(PyrH)_2[Nb_6Cl_{18}]$ from hot ethanol solution affords triclinic $(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$. Treatment of $[Nb_6Cl_{14}(H_2O)_4]\cdot 4H_2O$ with pyridine in a methanol solution gives the second title compound, the cubic modification of $(PyrH)_2[Nb_6Cl_{18}]$. Both structures were determined by single crystal X-ray diffraction, $(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$: $P\bar{1}$, $a = 9.3475(3)$, $b = 9.3957(3)$, $c = 10.8600(3)$ Å, $\alpha = 82.582(1)^\circ$, $\beta = 78.608(1)^\circ$, and $\gamma = 78.085(1)^\circ$, $Z = 1$, $R_1(F)/wR_2(F^2) = 0.0254/0.0573$, *cub.*-$(PyrH)_2[Nb_6Cl_{18}]$: $Fd\bar{3}m$, $a = 19.935(2)$ Å, $Z = 8$, $R_1(F)/wR_2(F^2) = 0.0557/0.1796$. The cluster compounds contain isolated, molecular $[Nb_6Cl^i_{12}Cl^a_6]^{2-}$ cluster anions with an octahedron of metal atoms edge bridged by chlorido ligands with additional ones on all the six exo positions. These cluster anions are separated by the pyridinium cations and ethanol solvent molecules, respectively. For the cubic modification of $(PyrH)_2[Nb_6Cl_{18}]$, a structural comparison is given to the known rhombohedral modification using the group–subgroup relations as expressed by a *Bärnighausen* tree.

1. Introduction

The most common structural motif of reduced (metal-rich) niobium halide compounds is the cluster unit $[Nb_6X_{12}Y_6]^{n-}$ (X, Y = F, Cl, Br or I; $n = 2$, 3 or 4), which consists of an octahedron of niobium atoms with strong metal–metal bonding, surrounded by 12 edge bridging "inner" and 6 apical "outer" ligands [1,2]. The cluster units can exist isolated (e.g. in $K_4[Nb_6Cl_{18}]$, $K_4[Nb_6Br_{18}]$) [3,4] or linked by halides (e.g. in Nb_6Cl_{14}, Nb_6F_{15}, MNb_6Cl_{15}, M = alkali metal) [5–7]. In consequence, a wide variety of structures is available. Compounds with isolated cluster units represent the most interesting subgroup due to their solubility in polar organic solvents and in ionic liquids. This type of cluster anions exists with diverse counter cations. First to mention are the alkali or alkaline earth metal cations, e.g. K^+, Na^+, Rb^+, or Ba^{2+}, of which the cluster compounds can be easily obtained by solid-state synthesis techniques [3,8–11]. Not only alkali and alkaline earth metal but also rare earth metal [12], and transition metal cations [13], as well as Tl^+, and In^+ [14] can serve as counter cations for the $[Nb_6Cl_{18}]^{n-}$ anion. In addition, there are many examples of cluster anions crystallized with 2, 3, or 4 organic cations, e.g. $[(CH_3)_4N]^+$, dependent on the oxidation state of the cluster unit [15–18].

In this paper, we report on the synthesis and the crystal structure of the second modification of the well-known $(PyrH)_2[Nb_6Cl_{18}]$ [19–21], and of the new $(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$.

2. Experimental

2.1. Techniques and materials

Due to the air and moisture sensitivity of some of the reactants, the respective manipulations were carried out in a high-quality argon glovebox or under high vacuum. The use of Guinier X-ray diffraction procedures for the identification and rough purity estimation of substances has been described before [22].

2.2. Synthesis

The starting material $K_4[Nb_6Cl_{18}]$ was prepared by a high-temperature solid-state chemical technique according to Refs. [3,8–10]. KCl was vacuum sublimed prior to use, $NbCl_5$ and Nb (powder) were used as received without further purification. Pyridine, MeOH, and EtOH were routinely dried and freshly distilled prior to use.

---

* Corresponding author. Fax: +49 381 498 6382.
E-mail address: Martin.Koeckerling@uni-rostock.de (M. Köckerling).

0022-4596/$ - see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2008.06.038

2.2.1. *cub.-(PyrH)$_2$[Nb$_6$Cl$_{18}$]*

The compound [Nb$_6$Cl$_{14}$(H$_2$O)$_4$]$\cdot$4H$_2$O (usually written as [Nb$_6$Cl$_{14}$]$\cdot$8H$_2$O, see note [23]) was prepared according to Refs. [8,9] from K$_4$[Nb$_6$Cl$_{18}$]. In a typical experiment, 250 mg of [Nb$_6$Cl$_{14}$(H$_2$O)$_4$]$\cdot$4H$_2$O were dissolved in 12 ml pyridine. After several hours of stirring carried out in air a precipitate was obtained from this solution, which was dissolved in 22 ml methanol. Slow evaporation of the solvent yielded dark crystals of *cub.*-(PyrH)$_2$[Nb$_6$Cl$_{18}$]. The weighted amount of the material and the Guinier powder pattern indicated the yield to be in the order of 60% with respect to the used [Nb$_6$Cl$_{14}$(H$_2$O)$_4$]$\cdot$4H$_2$O.

Table 1
Selected data collection and refinement parameters for (PyrH)$_2$[Nb$_6$Cl$_{18}$]$\cdot$EtOH and *cub.*-(PyH)$_2$[Nb$_6$Cl$_{18}$]

Chemical formula	(PyrH)$_2$[Nb$_6$Cl$_{18}$]$\cdot$EtOH	*cub.*-(PyrH)$_2$[Nb$_6$Cl$_{18}$]
Density, ρ_{calc} (g cm^{-3})	2.555	2.273
Formula weight (g mol^{-1})	1401.84	1355.78
Crystal dimensions (mm^3)	ca. 0.19 × 0.17 × 0.12	0.36 × 0.29 × 0.22
Space group (Z)	P$\bar{1}$ (no. 2); 1	Fd$\bar{3}$m (no. 227); 8
Lattice parameters		
a (Å)	9.3475(3)	19.935(2)
b (Å)	9.3957(3)	
c (Å)	10.8600(3)	
α (°)	82.582(1)	
β (°)	78.608(1)	
γ (°)	78.085(1)	
V (Å^3)	910.97(5)	7921(4)
Temperature (K)	293(2)	
Range of data collection (°)	$6 \leqslant 2\theta \leqslant 65$	$4 \leqslant 2\theta \leqslant 52$
μ (Mo$K\alpha$, mm^{-1})	3.162	2.903
Measuring device	Bruker-Nonius Apex X8	Siemens P4
Radiation	Mo$K\alpha$ ($\lambda = 0.71073$ Å)	
No. measured reflections	21470	2345
No. of unique refl.; R_{int}	5772; 0.0303	417; 0.0838
Variables	200	21
$R_1(F)$[a]	0.0254	0.0557
w$R_2(F^2)$[b]	0.0573	0.1796
GOOF	1.022	1.007
Max. peak (e Å^{-3})	+0.743/−0.570	+1.152/−0.533

[a] $R_1 = ((\sum ||F_o| - |F_c||)/(\sum |F_o|))$ for 4593 ((PyrH)$_2$[Nb$_6$Cl$_{18}$]$\cdot$EtOH) and 238 (*cub.*-(PyrH)$_2$[Nb$_6$Cl$_{18}$]) reflections with $I_0 > 2\sigma(I_0)$.

[b] $\mathrm{w}R_2 = \sqrt{(\sum \mathrm{w}(|F_o^2| - |F_c^2|)^2)/(\sum \mathrm{w}(F_o^2)^2)}$ for all data, with $w = 1/[(\sigma^2(F_o^2)+(0.0274)^2]^2$ for (PyrH)$_2$[Nb$_6$Cl$_{18}$]$\cdot$EtOH and $w = 1/[(\sigma^2(F_o^2)+(0.0993)^2]^2$ for *cub.*-(PyrH)$_2$[Nb$_6$Cl$_{18}$].

2.2.2. *(PyrH)$_2$[Nb$_6$Cl$_{18}$]$\cdot$EtOH*

The new compound (PyrH)$_2$[Nb$_6$Cl$_{18}$]$\cdot$EtOH was obtained from the solvent-free rhombohedral (PyrH)$_2$[Nb$_6$Cl$_{18}$], which was prepared as described in Ref. [19]. According to Ref. [21], this product is soluble in hot ethanol. Single crystals of our title compound were obtained by slow evaporation of the solvent. The same material can be obtained by dissolving and heating [Nb$_6$Cl$_{14}$(MeOH)$_4$] [24] in a 1:1 mixture of ethanol and pyridine, and slow evaporation of the solvent. Yields are close to quantitative.

2.3. *Single crystal structure determinations*

2.3.1. *(PyrH)$_2$[Nb$_6$Cl$_{18}$]$\cdot$EtOH*

A dark-green single crystal with dimensions 0.19 × 0.17 × 0.12 mm^3 was fixed with previously dried grease inside a thin-walled glass capillary. X-ray diffraction data were collected on a Bruker–Nonius Apex X8 diffractometer, equipped with a CCD detector. Measurements were made using monochromatic Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Preliminary data of the unit cell were obtained from the reflex positions of 60 frames, measured in three different directions of the reciprocal space. After completing the data measurements, a total of 9692 reflections up to 62° (2θ) was used to establish the cell to be triclinic with $a = 9.3475(3)$, $b = 9.3957(3)$, $c = 10.8600(3)$ Å, $\alpha = 82.582(1)°$, $\beta = 78.608(1)°$, and $\gamma = 78.085(1)°$. Intensity data were measured for up to 65° in 2θ. The intensity statistics indicated the space group to be P$\bar{1}$ (no. 2). The structure was solved using direct methods and refined using F^2 data (Shelx97 program suite) [25]. Anisotropic refinement of all the atoms except H yielded $R_1(F) = 0.0254$ (4593 data with $I_0 > 2\sigma(I_0)$) and w$R_2(F^2) = 0.0573$ (all data). The structure contains one co-crystallized ethanol solvent molecule per cluster anion, disordered on two positions around an inversion center. Further disorder appears in the pyridinium cation, where the N atom is equally distributed on all the six ring positions. A summary of crystallographic data is given in Table 1.

2.3.2. *cub.-(PyrH)$_2$[Nb$_6$Cl$_{18}$]*

X-ray data of a dark-green crystal, protected as well against possible oxidation or hydrolysis through a thin-wall glass capillary, were collected at room temperature with a Siemens P4 diffractometer using graphite monochromatized Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). Initial parameters of the F-centered cubic unit cell were refined from the positions of 30 randomly found and

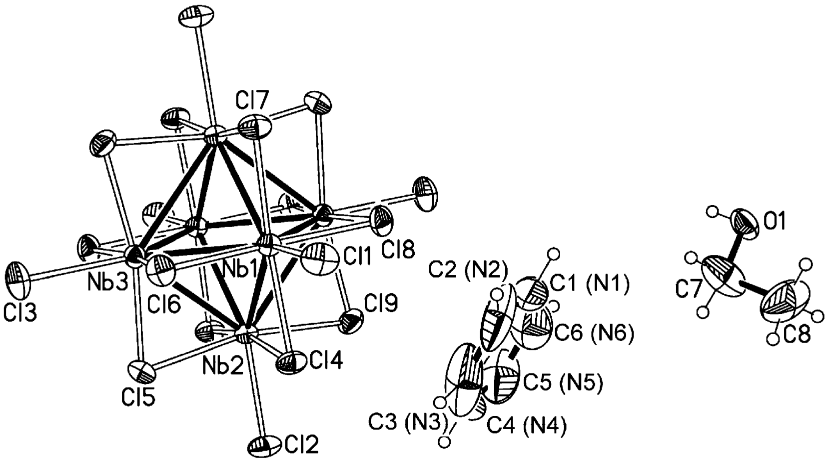


Fig. 1. Structure of the [Nb$_6$Cl$_{18}$]$^{2-}$ cluster anion (left), the pyridinum cation (middle), and the co-crystallized ethanol solvent molecule in crystals of (PyrH)$_2$[Nb$_6$Cl$_{18}$]$\cdot$EtOH (thermal ellipsoids with 50% probability; Nb–Nb bonds emphasized). The ethanol molecule is disordered on an inversion center of which only one orientation is shown.

Table 2
Selected interatomic distances (Å) for $(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$ and *cub.*-$(PyH)_2[Nb_6Cl_{18}]$

Atoms	Distance	Atoms	Distance
(PyrH)$_2$[Nb$_6$Cl$_{18}$]·EtOH			
Nb–Nb		*Nb–Cl^i*	
Nb1–Nb2	3.0245(3)	Nb1–Cl4	2.4204(5)
Nb1–Nb2	3.0252(3)	Nb1–Cl6	2.4239(5)
Nb1–Nb3	3.0288(3)	Nb1–Cl7	2.4331(5)
Nb1–Nb3	3.0294(3)	Nb1–Cl8	2.4207(6)
Nb2–Nb3	3.0168(3)	Nb2–Cl4	2.4195(5)
Nb2–Nb3	3.0385(3)	Nb2–Cl5	2.4170(6)
$\bar{d}$	3.0272	Nb2–Cl7	2.4314(6)
		Nb2–Cl9	2.4288(6)
Nb–Cl^a:		Nb3–Cl5	2.4187(5)
Nb1–Cl1	2.4997(6)	Nb3–Cl6	2.4253(6)
Nb2–Cl2	2.4982(6)	Nb3–Cl8	2.4255(6)
Nb3–Cl3	2.4849(6)	Nb3–Cl9	2.4243(5)
$\bar{d}$	2.4943	$\bar{d}$	2.4241
PyrH		*EtOH*	
C–C/C–N		*C–C*	
C1/N1–C2/N2	1.265(6)	C7A–C8A	1.46(1)
C2/N2–C3/N3	1.421(7)	*C–O*	
C3–C4	1.333(7)	C7A–O1A	1.49(3)
C4–C5	1.253(6)		
C5–C6	1.282(6)		
C1–C6	1.320(6)		
$\bar{d}$	1.312		
cub.-(PyH)$_2$[Nb$_6$Cl$_{18}$]			
Nb–Nb:		*Nb–Cl^a:*	
Nb1–Nb1	3.015(2)	Nb1–Cl1	2.501(5)
Nb–Cl^i:		*PyrH*	
Nb1–Cl2	2.424(3)	C–C/C–N	
		C1–C1/C1–N1	1.37(3)

indexed reflections in the range of 3.5–37.2° (in 2θ). This gave $a = 19.935(2)$ Å. The data collection was done up to 52° (2θ). The intensity data were corrected for Lorentz- and polarization effects as well as for absorption with the aid of 3Ψ scans. The structure was solved by Direct Methods [25] and the model was completed by using difference Fourier maps and refined by full-matrix least-squares methods on F^2 using the SHELX-97 program package [25]. As in the rhombohedral parent structure, and as in the ethanol-containing cluster compound (see above), the N-atom of the pyridinium cation is disordered equally on all the six ring atom positions. The final refinements on F^2 with all the heavy atoms treated anisotropically result in $R_1(F) = 0.0557$ and $wR_2(F^2) = 0.1796$. Crystallographic data for this compound are also summarized in Table 1.

3. Results and discussion

3.1. $(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$

The title compound is obtained by dissolving the solvent-free cluster material in hot ethanol and slow evaporation of the solvent. The structure of this new compound has been established by single crystal X-ray diffraction. It consists of a $[Nb_6Cl_{18}]^{2-}$ cluster anion, a pyridinium cation, and co-crystallized ethanol molecules. A thermal ellipsoid plot (at the 50% probability level) with atom numbering scheme is displayed in Fig. 1. Relevant crystallographic data are collected in Table 1, and selected interatomic distances in Table 2. The octahedral centrosymmetric Nb_6 unit with an average Nb–Nb distance of 3.0272 Å is surrounded by 12 chlorido ligands (average Nb–Cl^i distance: 2.4241 Å), capping all edges of the octahedron of niobium atoms. Six further chlorido ligands are bonded apical at the metal unit

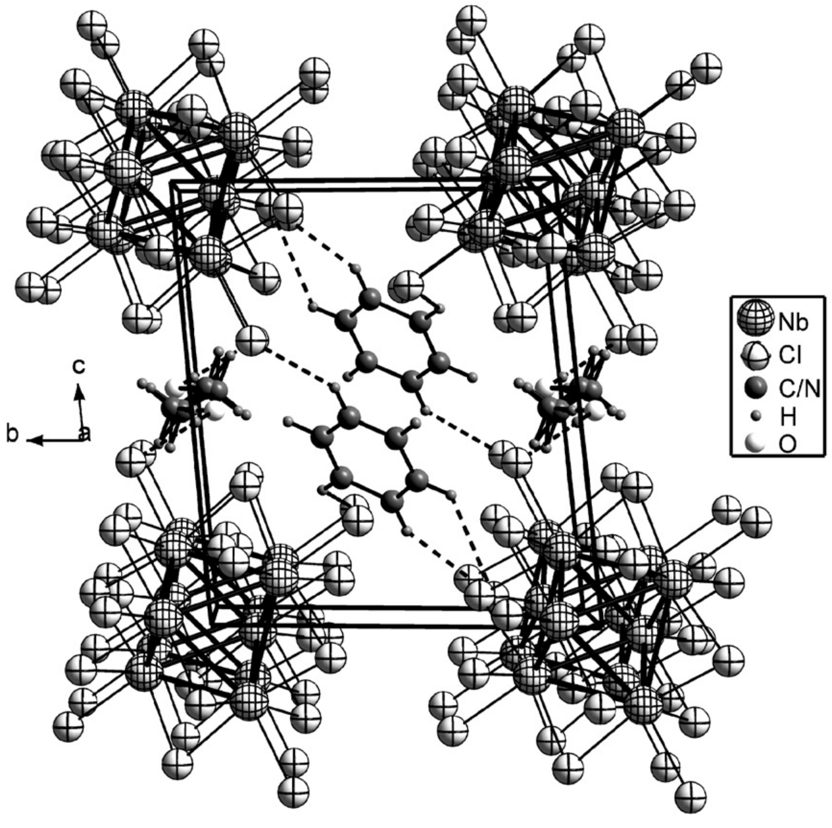


Fig. 2. View of the structure of $(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$; Nb–Nb bonds emphasized and Cl–H hydrogen bonds dashed.

corners with an average Nb–Cl^a distance of 2.4943 Å. These bond distances are in good agreement with other oxidized $[Nb_6Cl_{18}]^{2-}$ ions, for example in $[(CH_3)_4N]_2[Nb_6Cl_{18}]$ (Nb–Nb: 3.018 Å; Nb–Cl^i: 2.425 and 2.412 Å; Nb–Cl^a: 2.457 Å) [16], or rhombohedral-$(PyrH)_2[Nb_6Cl_{18}]$ (Nb–Nb: 3.045 Å; Nb–Cl^i: 2.433 Å; Nb–Cl^a: 2.475 Å) [19]. Within crystals of $(PyrH)_2[Nb_6Cl_{18}] \cdot EtOH$, the cluster units are isolated with shortest non-bonding distances of 3.4817(1) Å between Cl atoms of two neighboring cluster anions, as shown in Fig. 2.

The pyridinium cations and the ethanol molecules are located between the cluster anions. The unit cell hosts two pyridinium cations, which are parallel to each other and related through an inversion center. The distance between the rings amounts to 4.4437 Å. These double ring systems extend in the crystallographic *b*-direction (hexagonal setting) as rows, similar to the cluster anions. The N atom of the pyridinium cation is equally disordered on all six ring atom positions. The H atoms attached to N have distances (varying, dependent on the three symmetry-independent ring positions) to the Cl atoms of the neighboring cluster anions ranging from 2.728 to 2.973 Å, which might be considered as hydrogen bonds. These are depicted in Fig. 2 as dashed lines. The co-crystallized ethanol molecule is also located

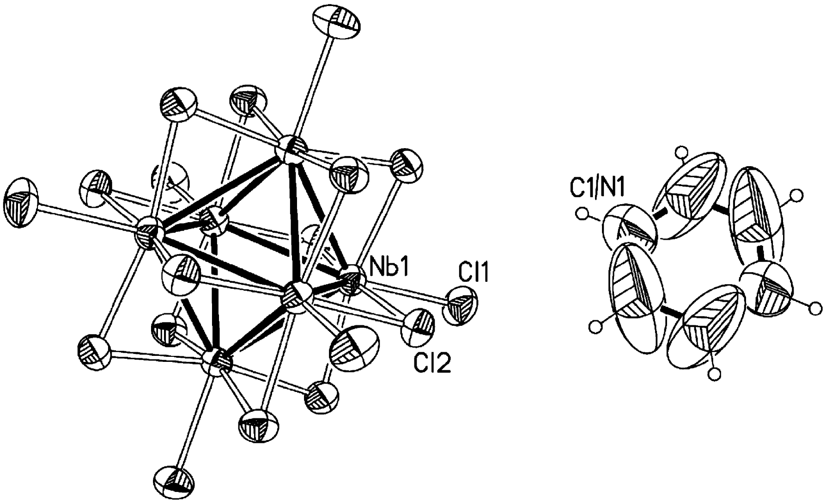


Fig. 3. Structure of the $[Nb_6Cl_{18}]^{2-}$ cluster anion (left) and the pyridinum cation (right) in crystals of *cub.*-$(PyrH)_2[Nb_6Cl_{18}]$ (thermal ellipsoids with 50% probability; Nb–Nb bonds are emphasized).

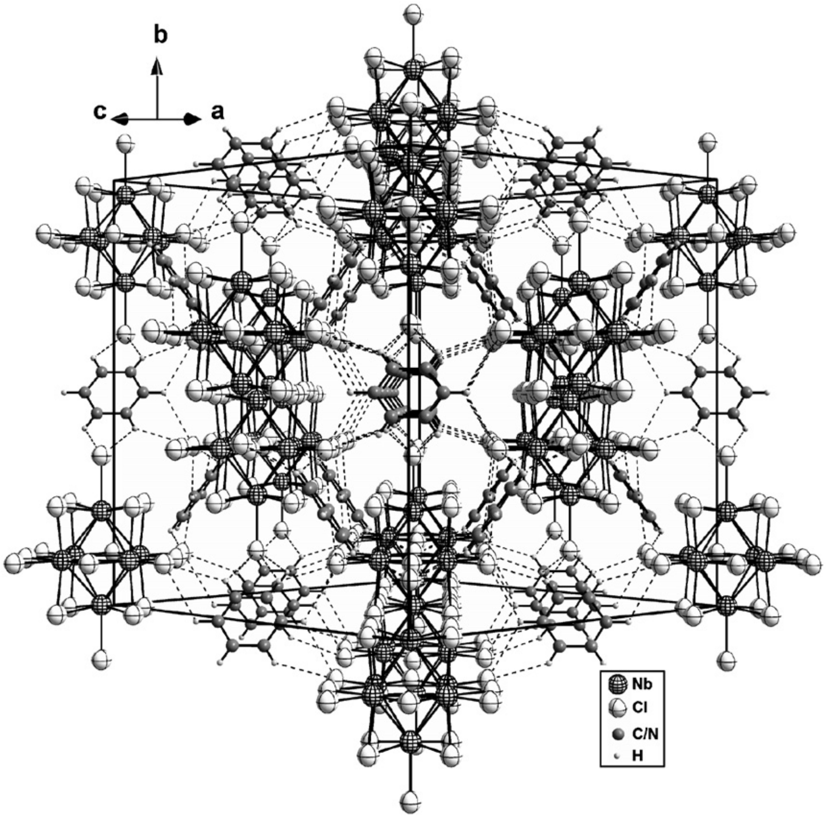


Fig. 4. View of the structure of the cubic modification of $(PyrH)_2[Nb_6Cl_{18}]$ along [110].

on an inversion center, and thereby disordered with two different orientations in a 1:1 ratio. Here we find also hydrogen bonds to neighboring chlorido ligands, with O–H···Cl distances ranging from 1.838 to 2.002 Å.

3.2. *cub.*-$(PyrH)_2[Nb_6Cl_{18}]$

The cubic modification of $(PyrH)_2[Nb_6Cl_{18}]$ is obtained from a solution of $[Nb_6Cl_{14}(H_2O)_4]\cdot 4H_2O$ in pyridine through an oxidation process with O_2 from the air, precipitation of the pyridinium salt and recrystallization from hot methanolic solutions. The use of methanol could be the reason for the formation of the cubic modification, since the rhombohedral modification is obtained from ethanolic solution, which was published already in 1971 [19]. The rhombohedral "parent" compound, $(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$, and the *cub.*-$(PyrH)_2[Nb_6Cl_{18}]$ contain an oxidized, isolated ("molecular") $[Nb_6Cl_{18}]^{2-}$ cluster anion and a pyridinium cation. The molecular structure of these ions is presented as thermal ellipsoid plot in Fig. 3. Structural data are given in Tables 1 and 2. Within the cubic unit cell the center of the cluster anion is located on the 8*a Wyckoff* site, resulting in a regular, undistorted octahedral cluster of O_h symmetry. The metal–metal distance between all neighboring Nb atoms is 3.015(3) Å, which closely resembles the ones found in the other compounds with the oxidized $[Nb_6Cl_{12}]^{4+}$ unit, as $(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$ (3.045 Å) or $[(CH_3)_4N]_2[Nb_6Cl_{18}]$ (3.018 Å) [16]. This is also essential for the Nb–Cl^i (2.424(3) Å), and the Nb–Cl^a distance (2.501(5) Å). In the rhombohedral "parent" structure, the cluster has only $\bar{3}m$ symmetry (see below). Thereby two symmetry non-related Nb–Nb distances exist, which, nevertheless, are the same within experimental error. The N atom of the pyridinium cation is disordered equally over the six ring positions, similar as in the structure of $(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$. The ring is centered on the 32*e Wyckoff* site with .3 m symmetry, resulting in a regular planar hexagon. The C–C bond distance (and C–N distance, respectively) amounts to 1.37(3) Å. Fig. 4 gives a view of the arrangement of the ions in crystals of *cub.*-$(PyrH)_2[Nb_6Cl_{18}]$ in a view down the [110] direction of the unit cell. Zig–zag chains of isolated cluster anions run along the body diagonals, forming channels along the same direction, which are occupied by the pyridinum cations. Fig. 4 shows the extensive network of N–H···Cl hydrogen bonds with an average H···Cl distance of 2.889 Å, indicated by dashed lines. A comparison of the cubic and the rhombohedral modification of $(PyrH)_2[Nb_6Cl_{18}]$ is given in Fig. 5, which clearly shows the differences in the three-dimensional arrangement of ions of both modifications. On the left side the structure of the cubic modification along the body diagonal of the unit cell is shown, whereas on the right side the structure of the rhombohedral modification, also in a view along [111] in the rhombohedral setting of the unit cell, is depicted. Comparing the two structures, cluster ions in the rhombohedral "parent" structure are stacked in rows along [111] which alternate with two parallel oriented pyridinium cations with the ring planes being arranged perpendicular to the [111] direction. In the cubic

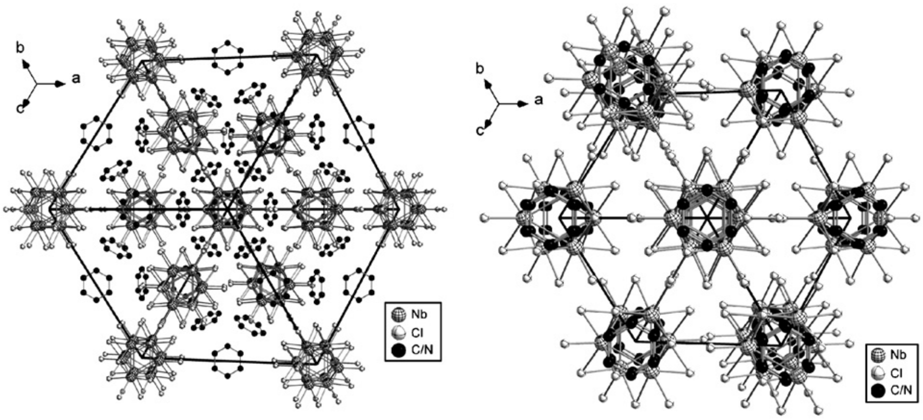
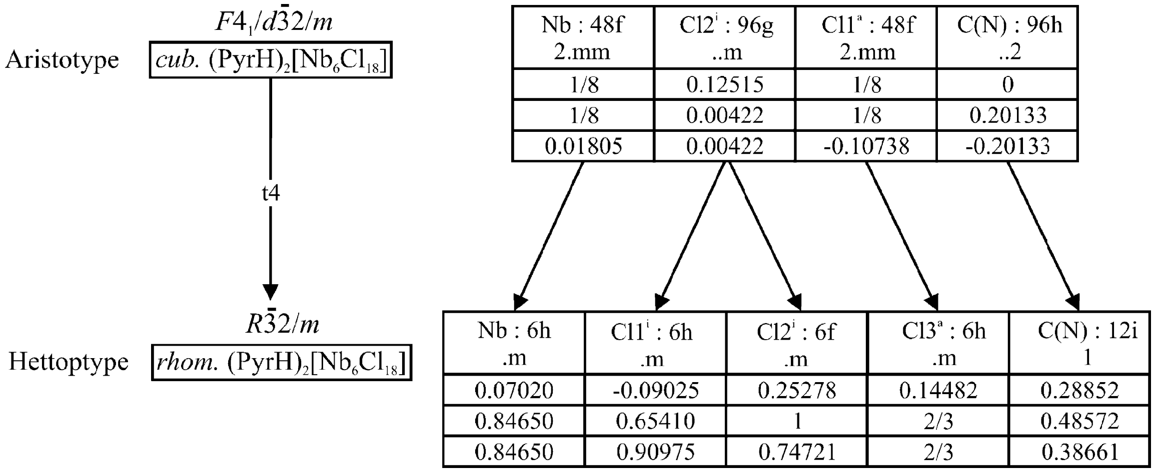


Fig. 5. Comparison of the structure of the cubic modification of $(PyrH)_2[Nb_6Cl_{18}]$ (left) with the rhombohedral one (right, rhombohedral setting). Both structures are shown in a view down the [111] direction.



Nb : 48f 2.mm	Cl2^i : 96g ..m	Cl1^a : 48f 2.mm	C(N) : 96h ..2
1/8	0.12515	1/8	0
1/8	0.00422	1/8	0.20133
0.01805	0.00422	-0.10738	-0.20133

Nb : 6h .m	Cl1^i : 6h .m	Cl2^i : 6f .m	Cl3^a : 6h .m	C(N) : 12i 1
0.07020	-0.09025	0.25278	0.14482	0.28852
0.84650	0.65410	1	2/3	0.48572
0.84650	0.90975	0.74721	2/3	0.38661

Fig. 6. Group–subgroup relationship (*Bärnighausen* tree) between the cubic and the rhombohedral modification of $(PyrH)_2[Nb_6Cl_{18}]$.

modification, two cluster anions alternate with one pyridinium cation along the same direction. The other cations are located between these cluster–cluster-ring rows and surround them. As might be expected observing Fig. 5, distances between the cluster anions are slightly larger in the cubic modification than in the rhombohedral, resulting in a lower density of 2.273 g/cm^3 compared to 2.705 g/cm^3.

The symmetry relation between the two modifications is presented in a *Bärnighausen* tree [26] in Fig. 6. The rhombohedral Hettotype with the space group $R\bar{3}m$ is a *translationsgleiche* subgroup of index 4 (*t*4) of the cubic Aristotype $Fd\bar{3}m$. Thereby the cluster symmetry reduces from $\bar{4}3m$ (cubic modification) to $\bar{3}m$. The position of the *inner* halides (96*g*) in the cubic modification splits up into the two *Wyckoff* sites 6*h* and 6*f* in the rhombohedral one.

Acknowledgments

This work was supported by the Deutsche Forschungsgemeinschaft (DFG). We are grateful to the state North Rhine Westphalia for the Benningsen Foerder award to M.K. and also to Prof. Dr. G. Henkel (University of Paderborn/Germany) for valuable discussions and their support. For all their experimental help we thank Dipl.-Chem. Janine Schwiertz, Simone Krüger, Luis Fernando Piedra Garza and we thank Jan Miller for language advice.

Appendix A. Supplementary material

CCDC ⟨654117 and 654118⟩ contain the supplementary crystallographic data for ⟨$(PyrH)_2[Nb_6Cl_{18}]\cdot EtOH$ and *cub.*-$(PyrH)_2[Nb_6Cl_{18}]$⟩. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] H. Schäfer, H.G. von Schnering, Angew. Chem. 20 (1964) 833–868.
[2] N. Prokopuk, D.F. Shriver, Advances in Inorganic Chemistry, vol. 46, Academic Press Inc., San Diego, 1999, pp. 1–49.
[3] A. Simon, H.G. von Schnering, H. Schäfer, Z. Anorg. Allg. Chem. 361 (1968) 235–248.
[4] F. Ueno, A. Simon, Acta Crystallogr. C 41 (1985) 308–310.
[5] A. Simon, H.G. von Schnering, H. Wörle, H. Schäfer, Z. Anorg. Allg. Chem. 339 (1965) 155–170.
[6] H. Schäfer, H.G. von Schnering, J.-J. Niehus, H.G. Nieder-Vahrenholz, J. Less-Common Met. 9 (1965) 95–104.
[7] (a) A. Simon, Angew. Chem. Int. Ed. Engl. 27 (1988) 159–183;
  (b) M.E. Sägebarth, A. Simon, H. Imoto, W. Weppner, G. Kliche, Z. Anorg. Allg. Chem. 621 (1995) 1589–1596;
  (c) A. Nägele, C. Day, A. Lachgar, H.-J. Meyer, Z. Naturforsch. 56B (2001) 1238–1240;
  (d) B. Baján, G. Balzer, H.-J. Meyer, Z. Anorg. Allg. Chem. 623 (1997) 1723–1728.
[8] F.W. Koknat, J.A. Parsons, A. Vongvush, Inorg. Chem. 13 (1974) 1699–1702.
[9] P.B. Fleming, L.A. Müller, R.E. McCarley, Inorg. Chem. 6 (1967) 1–4.
[10] A. Broll, D. Juza, H. Schäfer, Z. Anorg. Allg. Chem. 382 (1971) 69–79.
[11] A. Broll, H. Schäfer, J. Less-Common Met. 22 (1970) 367–368.
[12] (a) S. Ihmaïne, C. Perrin, O. Peña, M. Sergent, J. Less-Common Met. 137 (1988) 323–332;
  (b) O. Peña, S. Ihmaïne, C. Perrin, M. Sergent, Solid State Commun. 74 (1990) 285–290;
  (c) S. Ihmaïne, C. Perrin, O. Peña, M. Sergent, Physica B 163 (1990) 615–617;
  (d) C. Perrin, S. Cordier, S. Ihmaïne, M. Sergent, J. Alloys Comp. 229 (1995) 123–133;
  (e) S. Ihmaïne, C. Perrin, M. Sergent, Acta Crystallogr. C 43 (1987) 813–816;
  (f) S. Ihmaïne, C. Perrin, M. Sergent, Acta Crystallogr. C 45 (1989) 705–707.
[13] (a) T. Duraisamy, J.S. Qualls, A. Lachgar, J. Solid State Chem. 170 (2003) 227–231;
  (b) A. Nägele, E. Anokhina, J. Sitar, H.-J. Meyer, A. Lachgar, Z. Naturforsch. 55B (2000) 139–144.
[14] (a) B. Baján, H.-J. Meyer, Z. Naturforsch. 50B (1995) 1373–1376;
  (b) A. Lachgar, H.-J. Meyer, J. Solid State Chem. 110 (1994) 15–19.
[15] A. Pénicaud, P. Batail, P. Davidson, A.M. Levelut, C. Coulon, C. Perrin, Chem. Mater. 2 (1990) 117–123.
[16] F.W. Koknat, R.E. McCarley, Inorg. Chem. 11 (1972) 812–816.
[17] R.A. Field, D.L. Kepert, B.W. Robinson, A.H. White, J. Chem. Soc. Dalton Trans. (1973) 1858–1863.
[18] F.W. Koknat, R.E. McCarley, Inorg. Chem. 13 (1974) 295–299.
[19] B. Spreckelmeyer, H.G. von Schnering, Z. Anorg. Allg. Chem. 386 (1971) 27–37.
[20] B. Spreckelmeyer, C. Brendel, M. Dartmann, H. Schäfer, Z. Anorg. Allg. Chem. 386 (1971) 15–26.
[21] B. Spreckelmeyer, Z. Anorg. Allg. Chem. 368 (1969) 18–24.
[22] M. Köckerling, Z. Anorg. Allg. Chem. 625 (1999) 24–30.
[23] The structure of this compound, which is extensively used by several research groups as starting material, is not established thoroughly, so far. Due to the present established knowledge about this type of cluster materials a description as $[Nb_6Cl_{14}(H_2O)_4]\cdot 4H_2O$ seems more appropriate than $[Nb_6Cl_{14}]\cdot 8H_2O$.
[24] L.F. Piedra-Garza, M. Köckerling, Inorg. Chem. 45 (2006) 8829–8831.
[25] G.M. Sheldrick, SHELXS97 and SHELXL97. Programs for the Solution and Refinement of Crystal Structures, 1997.
[26] (a) H. Bärnighausen, MATCH, Commun. Math. Chem. 9 (1980) 139–175;
  (b) H. Wondratschek, U. Müller (Eds.), International Tables for Crystallography, vol. A1, Kluwer Academic Publisher, Dordrecht, The Netherlands, 2004.