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Synthesis, Crystal Structures and Properties of New Chloroniobium Cluster Hydroxides with Co-ordinated and Non-coordinated OH^- Groups. The Presence of $H_3O_2^-$ Intercluster Bridges

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The isostructural, trigonal clusters of the composition $[Nb_6Cl_{12}(H_2O)_6](OH)_2 \cdot 1/4CH_3OH \cdot 6H_2O$ **1** and $[Nb_6Cl_{12}(H_2O)_6](OH)_2 \cdot 6H_2O$ **2** have been isolated from alkaline solutions of $[Nb_6Cl_{12}]^{2+}$ cluster in alcohol/water (1:3) in the presence of NMe_4OH, while the presence of NEt_4OH yielded $NEt_4[Nb_6Cl_{12}(H_3O_2)_{6/2}] \cdot 3H_2O$ **3**. Compound **1** crystallizes in trigonal space group $R\bar{3}m$ with $a = 21.166(5)$ Å and $c = 23.812(4)$ Å, $\gamma = 120°$, $U = 9238.6(3)$ Å^3, $Z = 12$. Two crystallographically independent cluster octahedra (**I** and **II**) have been found in the unit cell of **1** in the ratio 3:1. The Nb–O distances of 2.211(11) Å and 2.217(16) Å for **I** and 2.238(19) Å for **II** indicate six co-ordinated water molecules. The cluster units of **I** are connected by hydrogen bonds of 2.49(1) Å into a two-dimensional framework. Compound **3** is monoclinic, space group $P2_1/n$, $a = 10.085(5)$ Å, $b = 11.446(4)$ Å, $c = 14.971(6)$ Å, $\beta = 102.95(6)°$, $U = 1684.2(1)$ Å^3, $Z = 2$. The short Nb–O distances at 2.167(6), 2.177(8) and 2.187(7) Å and considerable reduction of the Nb–O stretching frequency in the IR spectra support the presence of $H_3O_2^-$ (co-ordinated water molecule from one cluster unit and co-ordinated OH^- group from the neighbouring cluster unit) bridges. Each cluster unit is joined to the six neighbouring units by intermolecular hydrogen bonds of distances 2.540(11) Å and 2.594(10) Å in a three-dimensional network.

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INTRODUCTION

The behaviour of $[Nb_6Cl_{12}]^{2+}$ unit in an alkaline medium is completely different from the other members in the series $[M_6X_{12}]^{2+}$, M = Nb, Ta, X = Cl, Br.[1] Fast decomposition of bromo clusters is observed at pH > 7, while $[Ta_6Cl_{12}]^{2+}$ is slowly oxidized to $[Ta_6Cl_{12}]^{3+}$, and, finally to $[Ta_6Cl_{12}]^{4+}$ under the influence of air-oxygen. The $[Nb_6Cl_{12}]^{2+}$ is the only unchanged cluster in an alkaline medium, yet its stability at pH > 7 is a function of the amount of water present in the solution. In aliphatic alcohols, decomposition of $[Nb_6Cl_{12}]^{2+}$ units to $Nb(OH)_5 \cdot nH_2O$ is found. As indicated by the ^{1}H- and ^{35}Cl-NMR spectra and conductance data,[2] the stability of $[Nb_6Cl_{12}]^{2+}$ in aliphatic alcohol/water solutions might be related to the simultaneous competitive processes of Cl^-, H_2O and ROH (R = CH_3, C_2H_5) molecules as ligands for the six terminal octahedral co-ordination sites. Yet, a role for the cations present in the alkaline solutions and their influence on the formation of a particular crystallographic phase of chloroniobium cluster hydroxide has been found.[3] Here we report on the preparation, spectroscopic properties and crystallography of two new phases formed in the presence of alkylammonium cations.

EXPERIMENTAL

Materials

Methanol and reagent grade ethanol (Kemika or Mallinckrodt) were used as received. Alkylammonium hydroxides (25% water solutions) were purchased from Eastman Organic Chemicals. The cluster $[(Nb_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$ was prepared according to Koknat *et al.*[4]

Preparations of $[Nb_6Cl_{12}(H_2O)_6](OH)_2 \cdot 1/4CH_3OH \cdot 6H_2O$ **1**, $[Nb_6Cl_{12}(H_2O)_6](OH)_2 \cdot 6H_2O$ **2** *and* $NEt_4[Nb_6Cl_{12}(H_3O_2)_{6/2}] \cdot 3H_2O$ **3**.

Suspension of $[(Nb_6Cl_{12})Cl_2(H_2O)_4] \cdot 4H_2O$ (0.5 g; 0.417 mmol) in methanol (15 cm^3) was slightly heated over a heating plate in order to dissolve the cluster. After cooling to room temperature, water (45 cm^3) was added dropwise and the solution was usually left overnight. It was filtered through fine filter paper in order to remove the small amount of niobium(V) oxide usually formed. An aqueous solution of NMe_4OH, NEt_4OH or NPr_4OH (0.2 mol dm^{-3}) was added dropwise to the solution. At addition of 2 base equivalent per mol of cluster (pH = 6.6), the cluster hydroxides $[Nb_6Cl_{12}(H_2O)_6](OH)_2 \cdot 1/4CH_3OH \cdot 6H_2O$ **1**, $Nb_6Cl_{12}(H_2O)_{14}(OMe)_2$ (Ref. 3) and $[Nb_6Cl_{12}(OH)_2(H_2O)_4] \cdot 4H_2O$ **4** (Ref. 3) were precipitated quantitatively in the presence of NMe_4OH, NEt_4OH or NPr_4OH, respectively. With further addition of a base, the cluster was completely dissolved and at ≥6 equivalents the solution was completely clear (pH ~ 10.1). Addition of tetraalkylammonium hydroxides slightly changed the colour of the solution to dark olive-green, but the electronic spectra did not confirm any oxidation of the cluster to $[Nb_6Cl_{12}]^{3+}$ or $[Nb_6Cl_{12}]^{4+}$ units. The alkaline solutions were filtered again and left to crystallize in a closed Erlenmeyer flask at room temperature. From the solutions containing tetramethylammonium hydroxide black, cube-like crystals of the composition $[Nb_6Cl_{12}(H_2O)_6](OH)_2 \cdot 1/4CH_3OH \cdot 6H_2O$ were crystallized in a few days. A substance of the composition $NEt_4[Nb_6Cl_{12}(H_3O_2)_{6/2}] \cdot 3H_2O$ started to crystallize over night from solutions containing NEt_4OH. In the presence of NPr_4OH the cluster hydroxide $[Nb_6Cl_{12}(OH)_2(H_2O)_4] \cdot 4H_2O$ **4** was formed, *i.e.* the same substance as in the presence of lithium, sodium or potassium hydroxide.[3] The same procedure was used for the preparation of $[Nb_6Cl_{12}(H_2O)_6](OH)_2 \cdot 6H_2O$ **2** using ethanol/water (1:3) and NMe_4OH.

Anal. calcd. for $Nb_6Cl_{12}O_{14.25}C_{0.25}H_{27}$ **1**: Nb 44.90, Cl 34.30, C 0.25, H 2.20%; found: Nb 44.80, Cl 34.20, C 0.35, H 2.35. IR (ν_{max}/cm^{-1}): 3630m, 3400m (br), 1625sh, 1610m, 1480m, 1007m, 945w, 445w, 330vs, 295sh.

Anal. calcd. for $Nb_6Cl_{12}O_{14}H_{26}$ **2**: Nb 45.20, Cl 34.50%; found: Nb 44.95, Cl 34.40. IR (ν_{max}/cm^{-1}): 3630m, 3400m (br), 1625sh, 1610m, 1480m, 445w, 330vs, 295sh.

Anal. calcd. for $Nb_6Cl_{12}O_9C_8NH_{35}$ **3**: Nb 43.80, Cl 33.45, C 7.55, H 2.80, N 1.10%; found: Nb 43.70, Cl 33.25, C 7.45, H 2.90, N 1.05. IR (ν_{max}/cm^{-1}): 3630vw, 3562vw, 2980w, 2930w, 1628m, 1483m, 1450vw, 1438m, 1416vw, 1392w, 1363w, 1171w, 1051w, 1023m, 998m, 723m, 480sh, 371s, 327vs, 295sh.

Elemental Analysis

Niobium was determined in the form of Nb_2O_5 using the »H-tube« method[5] and also from the amount of Nb_2O_5 obtained as a residue after decomposition of the clusters on a thermobalance. Chlorides were determined by potentiometric titration with standard silver nitrate solution after decomposition of the clusters with KOH and H_2O_2. Carbon, hydrogen and nitrogen were determined by the Ruđer Bošković Institute Microanalytical Service.

Physical Measurements

IR spectra were recorded as KBr pellets or nujol mulls using a Perkin-Elmer 580B spectrometer. Thermogravimetric measurements were carried out on a Cahn RG microanalytical balance at a heating rate of 2 °C/min. The X-ray powder diffraction patterns were recorded on a Philips X-ray diffractometer using graphite-monochromatized Cu Kα radiation.

X-Ray Structure Determination

A summary of crystal data and refinement details for both compounds is presented in Table I. The crystals of these compounds were separated from the mother solution, coated with a viscous, high molecular weight hydrocarbon oil, and secured on a glass fiber by cooling to 173 K in a cold N_2 stream on the diffractometer. The intensities of three standard reflections were measured every hour of the X-ray exposure time during data collection. Lorentz-polarization and an empirical absorption correction from Ψ-scan data for several reflections were applied by the Enraf-Nonius SDP/VAX package.[6] The structure of **1** was solved by the Patterson method, and that of **3** by direct methods using the program SHELXS 86.[7] Both structures were refined on F values using SHELX 77.[8] Details of the procedure are given in Table I. Niobium scattering factors and anomalous dispersion values were taken from Ref. 9. For the other atoms, the scattering factors were those included in the SHELX 77 program.[8]

TABLE I

Crystal Data and Details of the Structure Determination for Compounds **1** and **3**

Crystal data	**1**	**3**
Molecular formula	$[Nb_6Cl_{12}(H_2O)_6](OH)_2 \cdot 1/4CH_3OH \cdot 6H_2O$	$NEt_4[Nb_6Cl_{12}(H_3O_2)_{6/2}] \cdot 3H_2O$
M_r	1241.08	1272.30
Crystal system	trigonal	monoclinic
Space group	$R\bar{3}m$	$P2_1/n$
a/Å	21.166(5)	10.085(5)
b/Å		11.446(4)
c/Å	23.812(4)	14.971(6)
β/°		102.95(6)
γ/°	120	
U/Å^3	9238.6(3)	1684.2(1)
D_c/g cm^{-3}	2.67	2.51
Z	12	2
μ(Mo Kα)/cm^{-1}	31.6	28.9
F(000)	7110	1224
Data collection on Enraf-Nonius CAD4 diffractometer with Mo Kα (λ = 0.71073 Å)		
T/K	173(2)	173(2)
No. of reflections used for cell parameters and θ range / °	23 7, 18	25 6, 20
θ range for intensity measurement	2, 25	2, 25
hkl range	0, 25; 0, 25; 0, 28	0, 12; 0, 13; –17, 17
scan	ω	$\omega/2\theta$
$\Delta\omega$	1.2 + 0.35 tanθ	0.8 + 0.35 tanθ
No. of measured reflections	2109	2731
Refinement		
No. of observed reflections	921[$I>3\sigma(I)$]	2177 [$I>4\sigma(I)$]
No. of variables	115	124
R	0.041	0.042
R_w, $w = k/[\sigma^2(F_o)+gF_o^2]$*	0.046; k=5.961, g=0.00017	0.047; k=1.855, g=0.00072
Final shift/error	–0.008(O7, z)	0.104 (Nb3, z)
Residual electron density $(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$/eÅ^3	1.34, –1.36	2.3, –1.51

* $R_w = \left[\sum w(|F_o| - |F_c|)^2 \; / \; \sum w \, |F_o|^2 \right]^{1/2}$

The crystal structure of **1** reveals the special positions at the mirror plane [18 *h* in $R\bar{3}m$] to be occupied by atoms Nb1, Nb3, Cl4, Cl6, O1, O3, O5, O6, O7 and C1. The special positions at the two-fold axis 18 *g* are populated by Cl2 and Cl5 atoms. The oxygen atom O8 is at 3*m*, site 6 *c*. The atoms of the solvent molecule, CH_3OH, are in special positions as well: C1 at $\bar{3}m$ [3 *a*] and O9 at the mirror plane [18 *h*] with occupancy 0.0833. The C1–O9 bond distance was adjusted to 1.40 Å during the refinement. These two atoms were refined isotropically whereas the other non-H atoms were treated anisotropically. The O–H distances of hydroxyl groups were adjusted to 0.983 Å. These H-atoms were included in the structure calculations, only. Molecular geometries were calculated by the EUCLID program[10] and plots of the molecular structure were drawn by ORTEP II.[11] Final atomic coordinates and equivalent isotropic thermal parameters are listed in Tables II and III.

TABLE II

Final atomic coordinates and equivalent isotropic thermal parameters $(\times 10^4)$ for compound **1** with estimated standard deviations (e.s.d.s.) in parentheses

	x	*y*	*z*	pp	U_{eq}/Å^2
Cluster unit **I**					
Nb1	0.43507(10)	0.21753(10)	0.13183(10)	0.5	189(6)
Nb2	0.30030(10)	0.0807(2)	0.1105	1	183(5)
Cl1	0.4153(2)	0.1278(4)	0.05810(10)	1	187(11)
Cl2	1/3	0.0035(2)	1/6	0.5	193(16)
Cl3	0.1729(2)	0.0049(4)	0.14260(10)	1	218(11)
Cl4	0.2550(3)	0.1275(4)	0.0348(2)	0.5	202(16)
O1	0.5464(7)	0.2732(11)	0.0954(6)	0.5	250(50)
O2	0.2679(5)	–0.0112(10)	0.0516(3)	1	240(30)
Cluster unit **II**					
Nb3	0.24150(10)	0.6208(2)	0.11640(10)	0.5	402(8)
Cl5	0.3370(3)	0.3370(3)	1/6	0.5	430(20)
Cl6	0.2785(2)	0.5569(3)	0.0490(2)	0.5	410(20)
O3	0.1449(9)	0.5724(13)	0.0589(6)	0.5	390(60)
O9*	0.038	0.076	0.0058	0.03	700(300)
C1*	0	0	0	0.083	330(150)
O4+	0.0377(12)	0.4319(6)	0.0514(4)	1	370(40)
O5+	0.0735(4)	0.1471(9)	0.2778(6)	0.5	360(50)
O6+	0.1432(5)	0.2864(10)	0.2200(7)	0.5	500(60)
O7#	0.1600(8)	0.3200(15)	0.0955(8)	0.5	1030(110)
O8#	0	0	0.1687(17)	0.166	820(140)

U_{eq} = 1/3 of the trace of orthogonalized $\boldsymbol{U}_{ij}$ tensor
* Methanol as solvent
# Hydroxyl groups
+ Crystalline water molecules

In the crystal structure of **3** the nitrogen atom N1 is located at an inversion centre [2 *a* position of $P2_1/n$]. The tetrahedral symmetry of NEt_4 is in disagreement with the crystallographic site 2 *a* of the space group $P2_1/n$. Therefore, a disorder of NEt_4 cation occurs; carbon atoms C1, C2, C3, and C4 are disordered in a general position with occupancy 0.5. The N–C and C–C bonds in tetraethylammonium ion were adjusted to the theoretical values of 1.48 and 1.53 Å, respectively. The population parameter of O5 is found to be 0.5. The non-coordinated oxygen atoms O4 and O5 as well as the nitrogen and carbon atoms of the cation were refined isotropically. Other atoms were refined with their anisotropic thermal parameters. The hydrogen atoms were located from a difference Fourier map; their O–H distances were normalized to the value 0.983 Å (obtained from literature, neutron diffraction data). The crystallographically independent unit is one-half of the cluster unit; by the inversion symmetry operation, the complete molecule is obtained.

TABLE III

Final atomic coordinates and equivalent isotropic thermal parameters (× 10^4) for compound **3** with e.s.d.s. in parentheses

	x	y	z	U_{eq}/Å^2
Nb1	0.0545(1)	0.8995(1)	0.6180(1)	198(3)
Nb2	−0.0696(1)	0.8519(1)	0.4255(1)	187(3)
Nb3	−0.1906(1)	1.0263(1)	0.5261(1)	199(3)
Cl1	0.1490(2)	1.0563(2)	0.7263(1)	216(7)
Cl2	0.2886(2)	0.8498(2)	0.6073(2)	241(8)
Cl3	−0.1605(2)	0.9143(2)	0.6705(2)	228(8)
Cl4	0.1425(2)	0.7937(2)	0.3807(2)	226(8)
Cl5	−0.3053(2)	0.8560(2)	0.4432(2)	213(7)
Cl6	−0.0206(3)	0.7076(2)	0.5510(2)	215(8)
O1	0.1146(8)	0.7956(7)	0.7423(5)	309(28)
O2	−0.1493(7)	0.6964(6)	0.3466(5)	281(23)
O3	−0.3932(6)	1.0500(7)	0.5497(5)	306(27)
				U/Å^2
O4 +	0.0834(13)	0.3468(12)	0.2133(9)	882(38)
O5 +	0.0481(25)	0.5300(22)	0.2777(16)	773(67)
N1	0.5000(0)	0.5000(0)	0.5000(0)	262(28)
C1	0.6229(0)	0.4286(0)	0.5356(0)	315(50)
C2	0.3966(0)	0.4636(0)	0.5507(0)	298(49)
C3	0.4269(0)	0.4905(0)	0.4029(0)	283(48)
C4	0.5084(0)	0.6281(0)	0.5138(0)	305(48)
C5	0.2600(0)	0.5277(0)	0.5289(0)	483(33)
C6	0.4100(0)	0.3602(0)	0.3803(0)	573(42)

Atoms from O4 to C6 are refined isotropically only.
U_{eq} = 1/3 of the trace of orthogonalized $\boldsymbol{U}_{ij}$ tensor
+ Crystalline water molecules

DISCUSSION

In the presence of NMe_4OH, the isostructural trigonal crystals of **1** and **2**, were crystallized out from alkaline methanol or ethanol/water (1:3) solutions of $[Nb_6Cl_{12}]^{2+}$, respectively. Monoclinic **3** and triclinic **4** compounds were prepared from alkaline aliphatic alcohol solutions in the presence of NEt_4OH or NPr_4OH, respectively. The triclinic compound **4** is also formed in the presence of lithium, sodium or potassium hydroxides.[3] These compounds are not soluble, either in water or aliphatic alcohols, and are soluble only in strong oxygen donors like dimethylsulfoxide or *N,N'*-dimethylformamide. The presence of lattice held methanol molecules in **1** could be avoided by performing the reaction in an ethanol/water (1:3) mixture yielding the compound **2**. The difference in the structure between these compounds is reflected in their spectroscopic properties. Two infrared spectral regions for **1**, **3** and **4** are shown in Figure 1. In the region of 3600 cm^{-1}, all compounds exhibit O–H stretching vibrations. The position of this absorption band is different in all three compounds, and is found at higher frequency for **1** and **3**. This might be related to the short hydrogen bonds of 2.49(1) Å and 2.54(11) Å found for **1** and **3,** respectively. For compound **4** the shortest hydrogen bond is 2.645(8) Å[3]. It is the region of 400 cm^{-1} where the Nb–O (oxygen from co-ordinated OH^-

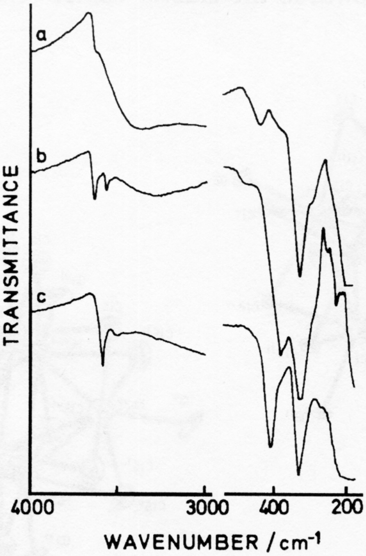

Figure 1. Infrared spectra (4000–3000 cm^{-1} and 550–200 cm^{-1})
a) $[Nb_6Cl_{12}(H_2O)_6](OH)_2\cdot 1/4CH_3OH\cdot 6H_2O$ (**1**)
b) $NEt_4[Nb_6Cl_{12}(H_3O_2)_{6/2}]\cdot 3H_2O$ (**3**)
c) $[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot 4H_2O$ (**4**, Ref. 3)

groups) vibrations are expected. In compound **1**, there is no Nb–O stretching vibration resolved. The non-appearance of this absorption band, together with the Nb–O interatomic distances of 2.211(11) Å and 2.217(16) Å, might be regarded to support that the OH^- groups are not co-ordinated to the niobium atoms in **1**. In the IR spectra of **3** and **4** there are strong absorption bands at 380 and 415 cm^{-1}, respectively. The reduction of the Nb–O stretching frequency in compound **3** in comparison with **4** might be a consequence of the presence of $H_3O_2^-$ bridges in compound **3**. Strong absorptions at 330 cm^{-1} (for **1** and **3**) and 332 cm^{-1} (for **4**) originate from Nb–Cl^i (i = inside)[12] vibrations.

Crystal Structures

There are two crystallographically independent octahedral clusters in the unit cell of **1** (Figure 2); the clusters are composed of Nb1, Nb2, Cl1, Cl2, Cl3, Cl4, O1, O2 (cluster **I**) and Nb3, Cl5, Cl6, O3, (cluster **II**) and symmetry related pairs of atoms for both units. Cluster **I** appears nine times and cluster **II** three times in the unit cell. Molecular geometries of cluster units (**I** and **II**) revealed no significant differences (Table IV). Distances Nb–Nb are in the range from 2.906(3) to 2.940(4) Å and bond lengths Nb–Cl from 2.459(5) to 2.473(5) Å. The Nb–O (co-ordinated water) distances range from 2.217(16) to 2.238(19) Å. Niobium atoms are shifted from the plane of four surrounding Cl atoms towards the cluster centre (0.360(12) to 0.398(12) Å).

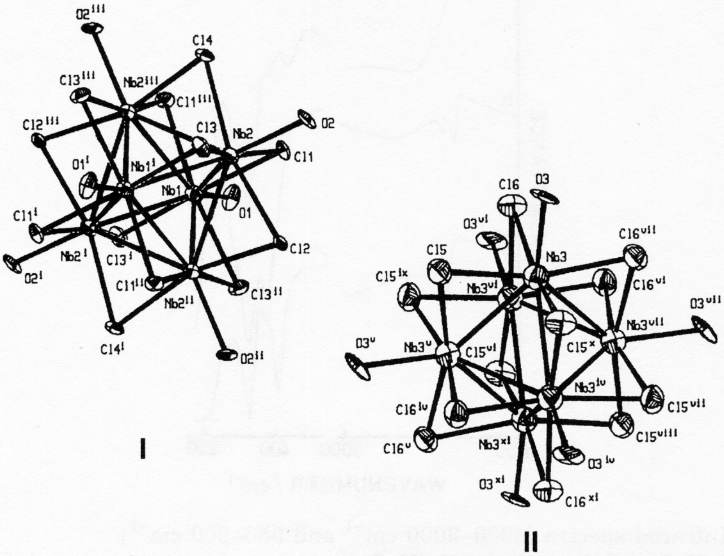

Figure 2. ORTEP drawing of two $[Nb_6Cl_{12}(H_2O)_6]^{2+}$ cluster units (**I** and **II**) in **1**. Symmetry operation code is given at the bottom of Table IV.

TABLE IV

Selected bond lengths/Å and angles/° for clusters **I** and **II** of compound **1** with e.s.d.s. in parentheses

Cluster **I**			
Nb1 - Nb2	2.919(3)	Nb2 - Nb1 - Nb2^{i}	91.02(9)
Nb1 - Nb2^{i}	2.906(3)	Nb2 - Nb1 - Nb2^{iii}	60.47(9)
Nb2 - Nb2^{iii}	2.940(4)	Nb2 - Nb1 - Nb2^{ii}	60.54(6)
Nb2 - Nb2^{ii}	2.936(2)	Nb2^{i} - Nb1 - Nb2^{ii}	60.79(8)
Nb1 - Cl1	2.464(5)	Nb1 - Nb2 - Nb1^{i}	88.98(8)
Nb1 - Cl3^{i}	2.470(5)	Nb2^{iii} - Nb2 - Nb1^{i}	59.61(7)
Nb1 - Cl3^{ii}	2.472(5)	Nb2^{ii} - Nb2 - Nb2^{iii}	90.00(8)
Nb2 - Cl1	2.459(5)	Nb1 - Nb2 - Nb2^{iii}	59.77(9)
Nb2 - Cl2	2.468(3)	Nb1 - Nb2 - Nb2^{ii}	59.50(8)
Nb2 - Cl3	2.471(6)	Nb1^{i} - Nb2 - Nb2^{ii}	59.96(7)
Nb2 - Cl4	2.470(6)	Nb2 - Nb1 - O1	135.3(4)
Nb1 - O1	2.217(16)	Nb2^{i} - Nb1 - O1	133.7(4)
Nb2 - O2	2.211(11)	Nb1 - Nb2 - O2	134.6(3)
		Nb1^{i} - Nb2 - O2	136.3(3)
		Cl1 - Nb1 - O1	81.8(4)
		Cl3^{ii} - Nb1 - O1	79.7(4)
		Cl1 - Nb2 - O2	81.0(3)
		Cl2 - Nb2 - O2	80.0(3)
		Cl3 - Nb2 - O2	82.4(3)
		Cl4 - Nb2 - O2	83.0(3)
		Nb1 - Cl1 - Nb2	72.7(1)
		Nb2 - Cl2 - Nb2^{ii}	73.0(1)
		Nb1^{i} - Cl3 - Nb2	72.0(2)
		Nb2 - Cl4 - Nb2^{iii}	73.1(2)
Cluster **II**			
Nb3 - Nb3^{vi}	2.916(4)	Nb3^{iv} - Nb3 - Nb3^{v}	59.76(9)
Nb3 - Nb3^{v}	2.926(4)	Nb3^{iv} - Nb3 - Nb3^{vi}	90.00(11)
Nb3 - Cl5	2.473(5)	Nb3^{v} - Nb3 - Nb3^{vi}	60.12(10)
Nb3 - Cl6	2.465(6)	Nb3^{vi} - Nb3 - Nb3^{vii}	60.00(10)
Nb3 - O3	2.238(19)	Nb3^{iv} - Nb3 - O3	136.7(5)
		Nb3^{vi} - Nb3 - O3	133.2(5)
		Cl5 - Nb3 - O3	83.0(5)
		Cl6 - Nb3 - O3	79.6(5)
		Nb3 - Cl5 - Nb3^{v}	72.6(2)
		Nb3 - Cl6 - Nb3^{vi}	72.6(2)

Symmetry operation codes: i) 2/3−*x*, 1/3−*y*, 1/3−*z*; ii) 2/3−*x*, 1/3−*x*+*y*, 1/3−*z*; iii) *x*, *x*−*y*, *z*; iv) −1+2/3+y, 1/3−x+y, 1/3−*z*; v) 2/3+*x*−*y*, 1/3+*x*, 1/3−*z*; vi) 1−*y*, 1+*x*−*y*, *z*; vii) −*x*+*y*, 1−*x*, *z*

The type **I** cluster units (Nb1–Nb2) are connected by hydrogen bonds into a two-dimensional framework (Figure 3a). Each cluster unit is connected to four others *via* four hydrogen bonds O2–H···O2, 2.49(1) Å. Oxygen atoms O1 from co-ordinated water molecules and two oxygen atoms O5 from crystalline water molecules form triangles (Figure 3b). They are involved in hydrogen bonds O1–H···O5, 2.66(2) Å. Oxygen atoms O8 from hydroxyl groups lie at the three-fold axis through the centres of these triangles (Figure 3b). Most probably, the proton attached to O8 is on the three-fold axes as well. Each O8 is involved in hydrogen bonds with three O1 atoms, O8–H···O1, 2.75(3) Å forming tri-furcated (four-centre) hydrogen bonds.[13] However, a disorder model with H81 out of $3m$ ($6c$) position is also possible. In that case hydrogen bond O8–H···O1 would appear with 1/3 of occurrence (Figure 3b).

Oxygen atoms O3 from co-ordinated water molecules of cluster **II** (Nb3–Nb3) are involved in hydrogen bonds with oxygen atoms O4 from crystalline water molecules. Each O3 atom is involved in two symmetrical hydrogen bonds with two O4 atoms, O3–H···O4, 2.70(3) Å; O3 acts twice as donor and O4 as acceptor. Oxygen atoms O3 are also included in a weak hydrogen bond with O5: O3–H···O5, 2.82(2) Å. The hydrogen bond network is completed with O4–H···O6, 2.82(3) Å and O4–H···O4, 2.81(2) Å contacts.

Oxygen O7 of the hydroxyl group which balances the charge of cluster unit **I** is not involved in any hydrogen bond. Examination of the neighbourhood around O7 (contact distance criterion of 3.50 Å) revealed oxygen atoms at distances of 3.01(3) and 3.03(3) Å which cannot be interpreted as hydrogen bonds.

The Nb-Nb distances (2.924(2) – 2.930(2) Å) and Nb–Cl distances (2.451(3) – 2.473(3) Å) in **3** are comparable with corresponding distances in other $[Nb_6Cl_{12}]^{2+}$ units.[14] The Nb atoms are displaced (0.364(7) to 0.373(7) Å) from the plane of four Cl atoms towards the cluster centre. Ethyl groups bonded to nitrogen appear in two orientations simulating an octahedral symmetry which is in agreement with the symmetry of site 2 *a* occupied by atom N1.

According to the X-ray structure analysis of **3** (Figure 4), two structural formulae should be considered: a) $NEt_4[Nb_6Cl_{12}(H_3O_2)_{6/2}]\cdot 3H_2O$ and b) $NEt_4[Nb_6Cl_{12}(OH)_2(H_2O)_4](OH)\cdot 2H_2O$. In both formulae, the co-ordinated water molecules and co-ordinated hydroxo groups are present at the terminal sites of the cluster unit, resulting in disorder. The oxygen co-ordination sites, generated by an inversion operation (Figure 3) of three crystallographically different sites, should allow recognition of the difference between bond distances Nb–OH and Nb–OH_2. However, a detailed analysis of the Nb–O bond distances, found in-between the distances of Nb–OH and Nb–OH_2 (2.167(6) to 2.187(7) Å) (Table V), gives preference to the formula with $H_3O_2^-$ groups. Ardon and Bino have observed exceptionally short inter-

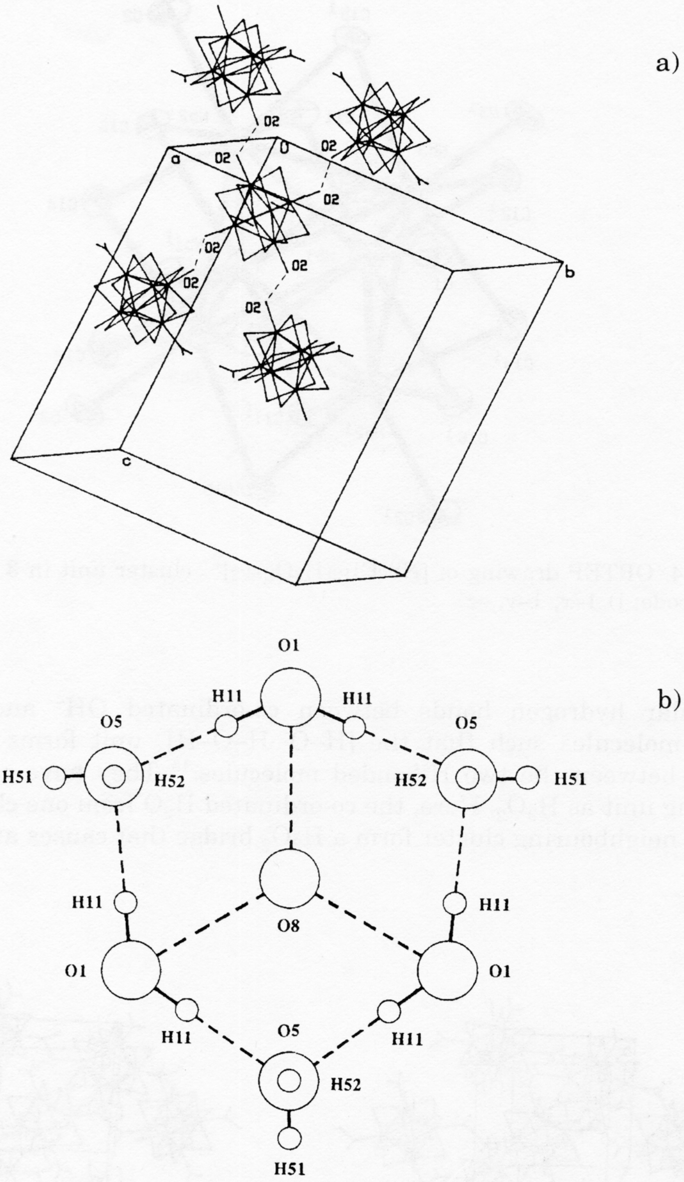

Figure 3. Details of molecular packing in **1**:
a) two-dimensional network of cluster octahedra in unit I
b) triangles formed by oxygen atoms O1 (co-ordinated water) and O5 (crystalline water). O8 from OH^- is at $3m$ (position 6 *c*), hydrogen bonds are marked by dashed lines. Two different types of O8–H...O1 are possible: three-furcated hydrogen bonds with H81 at $3m$ or disorder model with O8–H...O1 of 1/3 occurrence. (Atom H81 was not visible in a difference Fourier map).

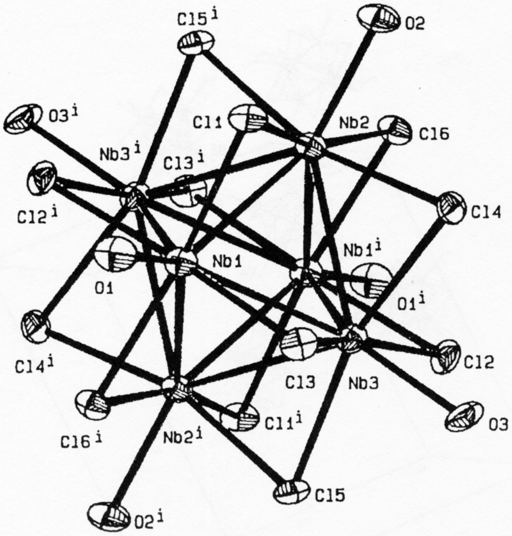

Figure 4. ORTEP drawing of $[Nb_6Cl_{12}(H_3O_2)_{6/2}]^{2+}$ cluster unit in **3**. Symmetry operation code: i) 1–*x*, 1–*y*, –*z*

molecular hydrogen bonds between co-ordinated OH^- and co-ordinated water molecules such that the $[H–O\cdots H–O–H]^-$ unit forms a very strong bridge between the two H-bonded molecules.[15] They have referred to this bridging unit as $H_3O_2^-$. Here, the co-ordinated H_2O from one cluster and OH^- from a neighbouring cluster form a $H_3O_2^-$ bridge that causes averaging of the

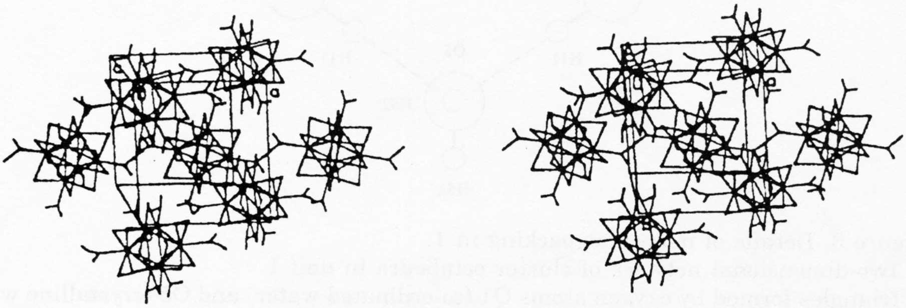

Figure 5. A stereoscopic view of three-dimensional cluster octahedra network in **3**. For simplicity the cation $[NEt_4]^+$ and OH^- groups are omitted.

TABLE V

Selected bond lengths/Å and angles/° with e.s.d.s. in parentheses for compound **3**

Nb1 - Nb2	2.9306(16)	Nb2 - Nb1 - Nb3	59.67(4)
Nb1 - Nb2^{i}	2.924(2)	Nb2 - Nb1 - Nb2^{i}	89.65(5)
Nb1 - Nb3	2.9300(17)	Nb2 - Nb1 - Nb3^{i}	59.92(4)
Nb1 - Nb3^{i}	2.9303(18)	Nb3 - Nb1 - Nb2^{i}	59.99(4)
Nb2 - Nb3	2.9159(16)	Nb3 - Nb1 - Nb3^{i}	89.76(5)
Nb2 - Nb3^{i}	2.9267(17)	Nb2^{i} - Nb1 - Nb3^{i}	59.74(4)
Nb1 - Cl1	2.463(2)	Nb1 - Nb2 - Nb3	60.15(4)
Nb1 - Cl2^{i}	2.468(2)	Nb1 - Nb2 - Nb1^{i}	90.35(5)
Nb1 Cl3	2.472(2)	Nb1 - Nb2 - Nb3^{i}	60.04(4)
Nb1 - Cl6^{i}	2.462(3)	Nb3 - Nb2 - Nb1^{i}	60.23(4)
Nb2 - Cl1	2.469(2)	Nb3 - Nb2 - Nb3^{i}	90.10(5)
Nb2 - Cl4	2.472(2)	Nb1^{i} - Nb2 Nb3^{i}	60.10(4)
Nb2 - Cl5^{i}	2.451(2)	Nb1 - Nb3 - Nb2	60.17(4)
Nb2 - Cl6	2.467(3)	Nb1 - Nb3 - Nb1^{i}	90.24(5)
Nb3 - Cl2	2.468(3)	Nb1 - Nb3 - Nb2^{i}	59.91(4)
Nb3 - Cl3	2.473(3)	Nb1^{i} - Nb3 - Nb2^{i}	60.05(4)
Nb3 - Cl4	2.475(3)	Nb2 - Nb3 - Nb1^{i}	60.03(4)
Nb3 - Cl5	2.457(3)	Nb2 - Nb3 - Nb2^{i}	89.90(4)
Nb1 - O1	2.177(8)	Cl1 - Nb1 - O1	81.0(2)
Nb2 - O2	2.187(7)	Cl2^{i} - Nb1 - O1	80.9(2)
Nb3 - O3	2.167(6)	Cl3 - Nb1 - O1	82.0(2)
		Cl6^{i} - Nb1 - O1	82.1(2)
		Cl1 - Nb2 - O2	81.1(2)
		Cl4 - Nb2 - O2	82.5(2)
		Cl5^{i} - Nb2 - O2	80.0(2)
		Cl6 - Nb2 - O2	81.6(2)
		Cl2 - Nb3 - O3	80.7(2)
		Cl3 - Nb3 - O3	81.8(2)
		Cl4 - Nb3 - O3	82.9(2)
		Cl5 - Nb3 - O3	80.1(2)
		Nb1 - Cl1 - Nb2	72.92(6)
		Nb3 - Cl2 - Nb1^{i}	72.82(8)
		Nb1 - Cl3 - Nb3	72.67(8)
		Nb2 - Cl4 - Nb3	72.24(8)
		Nb3 - Cl5 - Nb2^{i}	73.23(7)
		Nb2 - Cl6 - Nb1^{i}	72.77(8)

Symmetry operation code: i) 1-*x*, 1-*y*, -*z*

Nb–O distances, usually associated with separate entities. The shortest possible Nb–O bond distance of 2.21 Å for the co-ordinated water molecules averaged with 2.13 Å for Nb–OH leads to a weighted Nb–O distance of 2.17 Å, the same as the value 2.177(7) Å (Table V) observed in the structure of **3**.

The crystal packing is a three-dimensional network of cluster units connected by hydrogen bonds (Figure 5). Each cluster unit is joined to six surrounding cluster units by six intermolecular hydrogen bonds: O2–H···O1, 2.540(11) Å (four times) and O3–H···O3, 2.594(10) Å (two times).

Supplementary Materials. – Crystallographic data (excluding structure factors which are available from the authors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-109/68-861. Copies of the data can be obtained on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. (Fax: 44 (0) 1223-336033; E-mail: teched@chemcrys.cam.ac.uk).

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SAŽETAK

Sinteza, kristalna struktura i svojstva novih klusterskih kloroniobijevih hidroksida s koordiniranim i nekoordiniranim skupinama OH^-. Prisutnost interklusterskih mostova $H_3O_2^-$

Nevenka Brničević, Biserka Kojić-Prodić, Marija Luić, Aziz Kashta, Pavica Planinić i Robert E. McCarley

U prisutnosti NMe_4OH iz lužnatih otopina alkohol/voda (1 : 3) $[Nb_6Cl_{12}]^{2+}$ priređeni su izostrukturni, trigonski klusteri sastava $[Nb_6Cl_{12}(H_2O)_6](OH)_2 \cdot 1/4CH_3OH \cdot 6H_2O$ **1** i $[Nb_6Cl_{12}(H_2O)_6](OH)_2 \cdot 6H_2O$ **2**, dok je u istim uvjetima u prisutnosti NEt_4OH priređen $NEt_4[Nb_6Cl_{12}(H_3O_2)_{6/2}] \cdot 3H_2O$ **3**. Spoj **1** kristalizira u trigonskoj prostornoj grupi $R\bar{3}m$ s $a = 21.166(5)$ Å i $c = 23.812(4)$ Å, $\gamma = 120°$, $U = 9238.6(3)$ Å^3, $Z = 12$. Nađena su dva kristalografski neovisna oktaedarska klustera (**I** i **II**) u jediničnoj ćeliji spoja **1** u odnosu 3 : 1. Međuatomske udaljenosti Nb–O u iznosu 2.211(11) Å i 2.217(16) Å za **I** i 2.238(19) Å za **II** upućuju na šest koordiniranih molekula vode. Klusterske jedinice **I** povezane su vodikovim vezama duljine 2.49(1) Å u dvo-dimenzijsku mrežu.

Spoj **3** je monoklinski, prostorna grupa $P2_1/n$, $a = 10.085(5)$ Å, $b = 11.446(4)$ Å, $c = 14.971(6)$ Å, $\beta = 102.95(6)°$, $U = 1684.2(1)$ Å^3, $Z = 2$. Kratke udaljenosti veza Nb–O duljine 2.167(6), 2.177(8) i 2.187(7) Å, kao i znatno smanjenje frekvencije istezanja veze Nb–O u infracrvenim spektrima upućuju na prisutnost mostova $H_3O_2^-$ (koordinirana molekula vode iz jedne klusterske jedinice i koordinirana skupina OH^- iz susjedne klusterske jedinice). Svaka klusterska jedinica vezana je na šest susjednih jedinica intermolekulskim vodikovim vezama duljine 2.540(11) Å i 2.594(10) Å u tro-dimenzijsku mrežu.