Synthesis and Structural Characterization of Three New Compounds containing $[Nb_6Cl_{12}]^{2+}$ Units as Hydrated Hydroxides†

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Conditions have been established for the preparation of three different hydrated chloroniobium cluster hydroxide compounds from alkaline solutions: triclinic $[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot4H_2O$ **1** and two cubic compounds whose structures are uncertain with regard to the co-ordination of OH^- ions, $Nb_6Cl_{12}(OH)_2(H_2O)_{14}$ **2** and $Nb_6Cl_{12}(H_2O)_{14}(OMe)_2$ **3**. Based upon structural data **2** and **3** may contain either the cation $[Nb_6Cl_{12}(H_2O)_6]^{2+}$ or the neutral cluster $[Nb_6Cl_{12}(OH)_2(H_2O)_4]$ containing hydroxo ligands. In **1** distinct distances of 2.147(5) for Nb–OH, and 2.250(5) and 2.289(5) Å for Nb–OH_2 were found. In **2** and **3** only distances of 2.19(1) and 2.193(7) Å, respectively, were found for the Nb–O bonds of co-ordinated water (or hydroxide–water averaged). Compound **1** is triclinic, space group $P\bar{1}$, $a = 8.930(3)$, $b = 9.195(2)$, $c = 9.118(1)$ Å, $\alpha = 104.37(2)$, $\beta = 99.51(2)$ and $\gamma = 116.99(2)°$, $U = 611.9(3)$ Å^3, $Z = 1$, $R = 0.036$. Compound **2** is cubic, space group $Fm\bar{3}m$, $a = 14.59(2)$ Å, $U = 3105.7(1)$ Å^3, $Z = 4$, $R = 0.028$. Compound **3** is also cubic, space group $Fm\bar{3}m$, $a = 14.627(1)$ Å, $U = 3129.3(1)$ Å^3, $Z = 4$, $R = 0.031$. IR spectra of **1** show strong O–H and Nb–O stretching bands that reflect the presence of co-ordinated OH^- groups. In **2** and **3** the IR spectra are less definitive about possible co-ordination of hydroxide.

The niobium and tantalum chloride cluster compounds $[(M_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ are readily soluble in both methanol and ethanol. If the solutions in these solvents are titrated with alkali-metal hydroxides, the reversibility of the reaction in air is poor and occurs up to 3 mol OH^- per mol of cluster.[1] In alcohol–water mixtures the reversibility range is considerably increased. This is an indication of the stabilizing effect of water molecules on the $[M_6Cl_{12}]^{2+}$ cluster cation, and has also been confirmed by the ^1H NMR spectral studies.[2] Furthermore, there is a marked difference in the behaviour of $[Nb_6Cl_{12}]^{2+}$ and $[Ta_6Cl_{12}]^{2+}$ in an alkaline medium. If exposed to oxygen, the methanol–water alkaline solutions of $[Ta_6Cl_{12}]^{2+}$ slowly change from emerald-green to olive-green and finally to the dark red, indicating the oxidation[1,3,4] of the cluster units from $[Ta_6Cl_{12}]^{2+}$ to $[Ta_6Cl_{12}]^{3+}$ and finally to $[Ta_6Cl_{12}]^{4+}$. Under the same conditions, regardless of the methanol–water ratio at pH > 7, a similar oxidation of $[Nb_6Cl_{12}]^{2+}$ is not observed.

The cluster hydroxide of composition $[Nb_6Cl_{12}][OH]_2\cdot8H_2O$ is quantitatively precipitated from methanol–water mixtures at pH 7 (*i.e.* at 2 mol OH^- per cluster), as reported by several different authors,[5] who also took into consideration the available data on the preparation of $[Nb_6Cl_{12}][OH]_2\cdot6H_2O\cdot2MeOH$.[6] Following the described procedures, the preparation of crystals suitable for a structure determination has not been successful. So far the only available structural data for the $[Nb_6Cl_{12}]^{2+}$ unit are those for compounds with six chlorine atoms in terminal octahedral sites.[7]

Herein we report on a more extensive investigation of the influence of OH^- on $[Nb_6Cl_{12}]^{2+}$. Evidence for the presence of different hydrated chloro–hydroxo–niobium cluster species in crystals obtained from alkaline solutions is presented.

Experimental

Materials.—Reagent grade methanol and ethanol (Kemika or Malinckrodt) were used as received. The $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ cluster was prepared following the published procedure.[8]

Preparations.—$[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot4H_2O$ **1**. *Method* (*a*). The compound $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (0.5 g, 0.417 mmol) was dissolved in ethanol (20 cm^3) by magnetic stirring overnight. To the clear solution water (20 cm^3) was added dropwise, and the olive-green solution was filtered through fine filter paper in order to remove possible traces of hydrated niobium(V) oxide. To this solution was added dropwise an aqueous solution of lithium, sodium or potassium hydroxide (0.2 mol dm^{-3}). As soon as the first drops of alkali-metal hydroxide were added, a black precipitate of $[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot4H_2O$ appeared, and precipitation was quantitative upon addition of 2 mol OH^- per mol of cluster, leaving a colourless solution. With further addition of alkali-metal hydroxides the cluster hydroxide was dissolved, and at ⩾6 mol OH^- per mol of cluster the solution became completely clear (pH 10.3). With continued alkali-metal hydroxide addition, the solution changed slightly to dark olive-green, but the electronic spectra of these solutions did not indicate oxidation of the cluster units to the $[Nb_6Cl_{12}]^{3+}$ or $[Nb_6Cl_{12}]^{4+}$ species. The alkaline solution was again filtered and left to crystallize in a closed flask at room temperature. After a week, the plate-like crystals were separated, and then washed with water and air-dried.

Method (*b*). To a suspension of $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (0.5 g, 0.417 mmol) in water (30 cm^3) was added an aqueous solution of lithium, sodium or potassium hydroxide (0.2 mol dm^{-3}) until the cluster completely dissolved. The clear solution was filtered into an Erlenmeyer flask, closed and left to crystallize at room temperature.

Method (*c*). The compound $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Summary of data collection, structure solution and refinement

Compound	**1**	**2**	**3**
Molecular formula	$[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot 4H_2O$	$H_{30}Cl_{12}Nb_6O_{16}$	$C_2H_{34}Cl_{12}Nb_6O_{16}$
M_r	1161.00	1269.10	1297.13
Crystal system	Triclinic	Cubic	Cubic
Space group	$P\bar{1}$	$Fm\bar{3}m$	$Fm\bar{3}m$
a/Å	8.930(3)	14.59(2)	14.627(1)
b/Å	9.195(2)		
c/Å	9.118(1)		
α/°	104.37(2)		
β/°	99.51(2)		
γ/°	116.99(2)		
U/Å^3	611.9(3)	3105.7(1)	3129.3(1)
D_c/g cm^{-3}	3.15	2.71	2.77
Z	1	4	4
Crystal size/mm	0.14 × 0.10 × 0.11	0.2 × 0.2 × 0.25	0.17 × 0.17 × 0.22
Colour	Black	Black	Black
μ(Mo-Kα)/cm^{-1}	39.6	31.4	31.5
F(000)	548	2432	2696
T/K	100(3)	173(1)	100(3)
θ_{min}, θ_{max}/° for cell detection	6.9, 20.9	8, 18	2.1, 23
No. of reflections used for cell	25	25	25
θ Range	2.6–30.4	2–25	2.1–30.4
$\Delta\omega$ in ω–2θ scan/°	$1.14 + 0.72 \tan\theta$	$0.8 + 0.35 \tan\theta$	$0.74 + 0.5 \tan\theta$
hkl Limits	−12 to 12; 0–13; −13 to 13	0–12; 0–12; 0–17	−20 to 0; −20 to 0; −20 to 0
No. of measured reflections	3916	1616	1311
No. of symmetric independent reflections	2835 [$I > 2\sigma(I)$]	172 [$I > 3\sigma(I)$]	268 [$I > 2\sigma(I)$]
No. of variables	162	14	18
R, R'*	0.036, 0.036	0.028, 0.029	0.031, 0.042
$(\Delta/\sigma)_{max}$	0.06 [O(2), z]	0.043 [O(1), z]	0.013 [O(1), z]
Maximum, minimum residual electron density/e Å^{-3}	1.11, −1.48	0.52, −0.45	0.89, −1.41
g $\{w = k/[\sigma^2(F_o) + gF_o^2]\}$	0.000 563	0.029	0.002 489

* $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$.

(0.5 g, 0.417 mmol) was dissolved by stirring in methanol (20 cm^3) at room temperature. Upon dissolution water (40 cm^3) was slowly added to the solution, and subsequently 8 equivalents of aqueous lithium, sodium or potassium hydroxide (0.2 mol dm^{-3}) were added dropwise. The clear solution was filtered through fine filter paper and set aside to crystallize at room temperature. Occasionally, cubic crystals of **2** or more often of **3** also were found to cocrystallize in the procedure (Found: Cl, 36.50; Nb, 48.10. Calc. for $H_{18}Cl_{12}Nb_6O_{10}$: Cl, 35.65; Nb, 48.00%). IR (cm^{-1}): 3575s, 3000m (br), 1644m, 1600m, 1000w, 761w, 415s and 332s.

$[Nb_6Cl_{12}(H_2O)_6][OH]_2\cdot 8H_2O$ {or $[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot 10H_2O$} **2**. The compound $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (0.5 g, 0.417 mmol) was dissolved in methanol (20 cm^3) by stirring at room temperature. To the clear solution was added dropwise water (20 cm^3) and the solution was purified by using fine filter paper. An aqueous solution of rubidium hydroxide (0.2 mol dm^{-3}) was slowly added to the solution. After the addition of 2 mol RbOH per mol of cluster, a black precipitate quantitatively separated from the solution, in which some single crystals suitable for X-ray diffraction studies were found. It was not possible to dissolve this precipitate by any further addition of the rubidium hydroxide solution. Subsequently, the cluster hydroxide was filtered off, washed with water and dried in a desiccator over KOH (Found: Cl, 33.45; Nb, 43.70. Calc. for $H_{30}Cl_{12}Nb_6O_{16}$: Cl, 33.50; Nb, 43.90%). IR (cm^{-1}): 3570 (sh), 3390m, 3000m (br), 1625w, 950w, 410m (br) and 332s.

$[Nb_6Cl_{12}(H_2O)_6][OMe]_2\cdot 8H_2O$ {or $[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot 2MeOH\cdot 8H_2O$} **3**. The compound $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (0.5 g, 0.417 mmol) was dissolved in methanol (20 cm^3) by stirring at room temperature, after which the solution was filtered and an aqueous solution of lithium, sodium or potassium hydroxide (0.2 mol dm^{-3}) was added dropwise. Upon the addition of 2 mol OH$^-$ per mol of cluster, a black precipitate of composition $[Nb_6Cl_{12}(H_2O)_6][OMe]_2\cdot 8H_2O$ was quantitatively recovered. On further addition of alkali-metal hydroxides, this precipitate was progressively dissolved and at $\geqslant$6 mol OH$^-$ per mol of cluster it had dissolved completely (pH $\approx$ 10). The alkaline solution was then purified by filtration and set aside to crystallize in a closed flask at room temperature. Within a few days the octahedral crystals were separated, washed with a small amount of water, and due to their chemical and structural instability, quickly air-dried. The triclinic crystals of **1** were often found to cocrystallize in this procedure (Found: C, 1.80; H, 2.70; Cl, 32.75; Nb, 42.80. Calc. for $C_2H_{34}Cl_{12}Nb_6O_{16}$: C, 1.85; H, 2.65; Cl, 32.80; Nb, 42.95%). IR (cm^{-1}): 3525w, 3000m (br), 1620w, 1022m, 990m, 400m (br) and 332s.

Analysis.—The niobium was determined by the 'H-tube' method[9] and also from the amount of Nb_2O_5 left after thermal decomposition of the samples on the thermobalance, the chloride by potentiometric titration with standard silver nitrate solution after decomposition of the clusters with KOH and H_2O_2. Carbon and hydrogen analyses were performed by the Rudjer Bošković Institute Analytical Service.

Physical Measurements.—A Perkin-Elmer 580B spectrometer was used to record the infrared spectra, and thermogravimetric measurements were carried out on a Cahn RG microanalytical balance with a heating rate of 2 °C min^{-1}. X-Ray powder diffraction patterns were recorded on a Philips X-ray diffractometer using graphite-monochromatized Cu-Kα radiation.

Crystal Structure Determinations.—Table 1 summarizes the details of data collection, structure solution and refinement for compounds **1**–**3**. In order to minimize crystal decay the data were collected at low temperature (Table 1), on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated

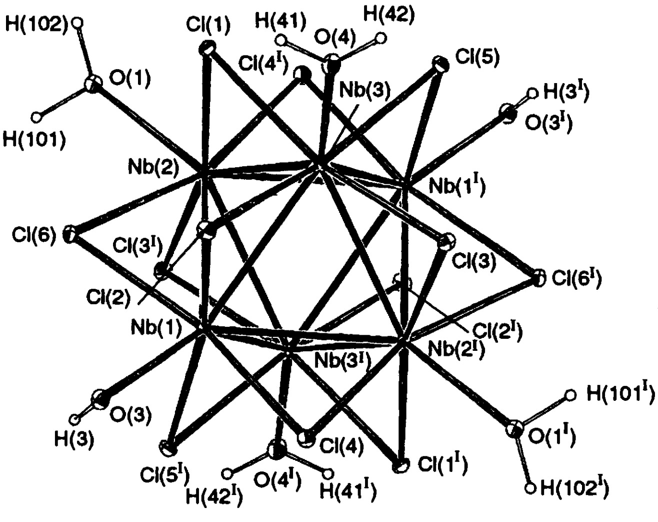

Fig. 1 An ORTEP drawing of $[Nb_6Cl_{12}(OH)_2(H_2O)_4]$ in **1**; symmetry operation: I $-x + 2, -y + 1, -z + 1$

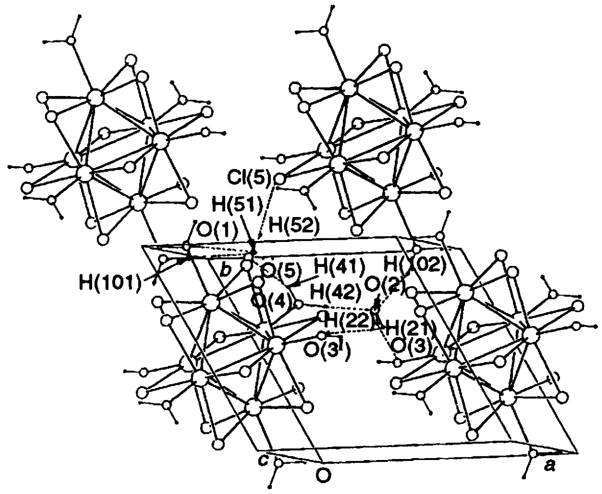

Fig. 2 Crystal packing of **1** with hydrogen bonds marked as dashed lines and symmetry operation as in Fig. 1

Mo-Kα radiation. During data collection decay of 3.2 for **1**, 1.8 for **2** and 1.9% for **3** was detected, and data were corrected for Lorentz, polarization, absorption (ψ-scan) and decay using the Enraf-Nonius SDP-VAX package.[10] Average transmissions were 0.915 (**1**), 0.957 (**2**) and 0.964 (**3**). The structures were solved by direct methods using SHELXS 86.[11] In the structure of **1** the asymmetric unit in the triclinic space group $P\bar{1}$ is one-half of the formula-unit; the other half is generated by an inversion operation, as the cluster unit of **1** is located on a centre of inversion (Fig. 1).

The structures of **2** and **3** are isotypic, and there is no difference of the unit cell parameters within the limits of statistical and experimental errors (Table 1). Both structures have the cubic space group $Fm\bar{3}m$ with the identical cluster units having internal $m\bar{3}m$ symmetry of a regular octahedron as shown in Fig. 2. The Nb and O(1) atoms are positioned at the $4mm$ [24(*e*) position] and the Cl is at mm site [48(*h*)]. The chemical difference between compounds **2** and **3** gives rise to different structural features. The oxygen atom O(2), which might be either a free hydroxide anion or a disordered water molecule, occupies the $\bar{4}3m$ site [8(*c*)] in **2**, whereas the O and C atoms of the methoxide groups or methanol molecules in **3** are at the $3m$ positions [32 (*f*)] with partly occupied sites (population parameter = 0.0417). The other crystalline water molecules in both **2** and **3** are located at the $3m$ sites [32(*f*)]. The crystal structures were refined anisotropically by full-matrix least squares minimizing $\Sigma w(|F_o| - |F_c|)^2$ with the SHELX 77[12] program using *F* values. The details of the refinement procedures are given in Table 1. The H atoms in **1** were located from Fourier-difference maps, whereas those in **2** and **3** were not observed. The niobium scattering factors and anomalous dispersion values were from ref. 13; for other atoms the scattering factors were those included in the SHELX 77 program.[12] The molecular geometry was calculated by the program package EUCLID,[14] and drawings were prepared by the PLUTON program incorporated in EUCLID[14] and ORTEP.[15] The final atomic coordinates are listed in Tables 2–4. The calculations were performed on Micro-VAX II and IRIS-4D25G computers of the X-ray laboratory, Rudjer Bošković Institute, Zagreb, Croatia. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates and anisotropic thermal parameters.

Table 2 Final atomic coordinates of the non-hydrogen atoms for compound **1** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Nb(1)	1.2223(1)	0.5245(1)	0.6446(1)
Nb(2)	0.9349(1)	0.2581(1)	0.3501(1)
Nb(3)	0.8531(1)	0.3833(1)	0.6320(1)
Cl(1)	0.7440(2)	0.0760(2)	0.4749(2)
Cl(2)	1.0864(2)	0.3930(2)	0.8260(2)
Cl(3)	0.8921(2)	0.6478(2)	0.8280(2)
Cl(4)	0.6632(2)	0.1825(2)	0.1520(2)
Cl(5)	0.5655(2)	0.3344(2)	0.4891(2)
Cl(6)	1.1734(2)	0.2358(2)	0.4947(2)
O(1)	0.8670(6)	−0.0057(6)	0.1743(5)
O(3)	1.4499(6)	0.5493(6)	0.7973(5)
O(4)	0.6989(6)	0.2516(6)	0.7789(5)
O(2)*	0.5582(6)	0.7125(6)	0.1191(5)
O(5)*	0.1984(7)	0.9904(7)	0.1539(6)

* Crystalline water molecules.

Table 3 Final atomic coordinates of the non-hydrogen atoms for compound **2** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Nb	0	0	0.1408(1)
Cl	0.1666	0	0.1666
O(1)	0	0	0.2908(6)
O(2)	0.25	0.25	0.25
O(3)	0.1238(6)	0.1238(6)	0.1238(6)

Table 4 Final atomic coordinates of the non-hydrogen atoms for compound **3** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Nb	0	0	0.140 5
Cl	0.166 3(1)	0	0.166 3(1)
O(1)	0	0	0.290 4(5)
O(2)	0.228 6	0.228 6	0.228 6
C(2)	0.284 70	0.284 70	0.284 70
O(3)	0.126 6(6)	0.126 6(6)	0.126 6(6)

Discussion

From alkali-metal hydroxide solutions in pure ethanol, water or water-dominated methanol–water mixtures two different types of hydrated chloroniobium cluster hydroxides are formed: triclinic $[Nb_6Cl_{12}(OH)_2(H_2O)_4]{\cdot}4H_2O$ **1** and cubic **2**. The former is formed in the presence of lithium, sodium or potassium hydroxide, while the latter is formed in the presence of rubidium hydroxide, showing the influence of the solution cation upon the formation of a particular cluster hydroxide type. This is further confirmed by the recent isolation of two

Table 5 Bond lengths (Å) and angles (°) with (e.s.d.s) in parentheses for compound **1**

Nb(1)–Nb(2)	2.926(1)	Nb(2)–Nb(3$^{\mathrm{I}}$)	2.909(1)	Nb(1)–Cl(2)	2.449(2)	Nb(2)–Cl(6)	2.433(2)
Nb(1)–Nb(3)	2.914(1)	Nb(1)–O(3)	2.147(5)	Nb(1)–Cl(6)	2.461(2)	Nb(2)–Cl(3$^{\mathrm{I}}$)	2.467(2)
Nb(1)–Nb(2$^{\mathrm{I}}$)	2.913(1)	Nb(2)–O(1)	2.289(5)	Nb(1)–Cl(4$^{\mathrm{I}}$)	2.478(2)	Nb(3)–Cl(1)	2.454(2)
Nb(1)–Nb(3$^{\mathrm{I}}$)	2.924(1)	Nb(3)–O(4)	2.250(5)	Nb(1)–Cl(5$^{\mathrm{I}}$)	2.466(2)	Nb(3)–Cl(2)	2.452(2)
Nb(2)–Nb(3)	2.895(1)			Nb(2)–Cl(1)	2.451(2)	Nb(3)–Cl(3)	2.470(2)
				Nb(2)–Cl(4)	2.456(2)	Nb(3)–Cl(5)	2.460(2)
Nb(2)–Nb(1)–Nb(3)	59.42(3)	Nb(2$^{\mathrm{I}}$)–Nb(1)–Nb(3$^{\mathrm{I}}$)	59.46(3)	Cl(5$^{\mathrm{I}}$)–Nb(1)–O(3)	82.9(2)	Nb(1$^{\mathrm{I}}$)–Nb(2)–Cl(4)	54.17(5)
Nb(2)–Nb(1)–Cl(2)	96.03(5)	Nb(2$^{\mathrm{I}}$)–Nb(1)–Cl(4$^{\mathrm{I}}$)	53.48(5)	Nb(3$^{\mathrm{I}}$)–Nb(2)–Cl(4)	96.64(5)	Cl(1)–Nb(3)–O(4)	80.1(1)
Nb(2)–Nb(1)–Cl(6)	52.83(5)	Nb(2$^{\mathrm{I}}$)–Nb(1)–Cl(5$^{\mathrm{I}}$)	95.79(6)	Cl(3$^{\mathrm{I}}$)–Nb(2)–Cl(4)	90.59(7)	Nb(1$^{\mathrm{I}}$)–Nb(3)–Cl(1)	95.17(5)
Nb(2)–Nb(1)–O(3)	135.8(1)	Nb(3$^{\mathrm{I}}$)–Nb(1)–Cl(4$^{\mathrm{I}}$)	95.74(5)	Cl(6)–Nb(2)–O(1)	81.9(1)	Nb(2$^{\mathrm{I}}$)–Nb(3)–Cl(1)	143.77(6)
Nb(2)–Nb(1)–Nb(2$^{\mathrm{I}}$)	89.32(4)	Nb(3$^{\mathrm{I}}$)–Nb(1)–Cl(5$^{\mathrm{I}}$)	53.50(5)	Nb(1$^{\mathrm{I}}$)–Nb(2)–Cl(6)	144.33(6)	Cl(2)–Nb(3)–Cl(3)	90.27(7)
Nb(2)–Nb(1)–Nb(3$^{\mathrm{I}}$)	59.63(3)	Cl(4$^{\mathrm{I}}$)–Nb(1)–Cl(5$^{\mathrm{I}}$)	89.03(7)	Nb(3$^{\mathrm{I}}$)–Nb(2)–Cl(6)	97.90(6)	Cl(2)–Nb(3)–Cl(5)	162.14(7)
Nb(2)–Nb(1)–Cl(4$^{\mathrm{I}}$)	142.79(6)	Nb(1)–Nb(2)–Nb(3)	60.09(3)	Cl(3$^{\mathrm{I}}$)–Nb(2)–Cl(6)	88.57(7)	Cl(2)–Nb(3)–O(4)	79.2(2)
Nb(2)–Nb(1)–Cl(5$^{\mathrm{I}}$)	95.66(5)	Nb(1)–Nb(2)–Cl(1)	97.10(5)	Nb(1$^{\mathrm{I}}$)–Nb(2)–O(1)	133.7(1)	Nb(1$^{\mathrm{I}}$)–Nb(3)–Cl(2)	144.16(6)
Nb(3)–Nb(1)–Cl(2)	53.56(5)	Nb(1)–Nb(2)–Cl(4)	144.86(6)	Nb(3$^{\mathrm{I}}$)–Nb(2)–O(1)	132.5(1)	Nb(2$^{\mathrm{I}}$)–Nb(3)–Cl(2)	95.80(5)
Nb(3)–Nb(1)–Cl(6)	93.56(6)	Nb(1)–Nb(2)–Cl(6)	53.73(5)	Cl(3$^{\mathrm{I}}$)–Nb(2)–O(1)	78.6(1)	Cl(3)–Nb(3)–Cl(5)	86.21(7)
Nb(3)–Nb(1)–O(3)	134.3(1)	Nb(1)–Nb(2)–O(1)	135.4(1)	Nb(1$^{\mathrm{I}}$)–Nb(2)–Nb(3$^{\mathrm{I}}$)	60.08(3)	Cl(3)–Nb(3)–O(4)	82.4(1)
Nb(3)–Nb(1)–Nb(2$^{\mathrm{I}}$)	59.89(3)	Nb(1)–Nb(2)–Nb(1$^{\mathrm{I}}$)	90.68(4)	Nb(1$^{\mathrm{I}}$)–Nb(2)–Cl(3$^{\mathrm{I}}$)	97.67(6)	Nb(1$^{\mathrm{I}}$)–Nb(3)–Cl(3)	94.62(5)
Nb(3)–Nb(1)–Nb(3$^{\mathrm{I}}$)	89.30(4)	Nb(1)–Nb(2)–Nb(3$^{\mathrm{I}}$)	60.15(3)	Nb(3$^{\mathrm{I}}$)–Nb(2)–Cl(3$^{\mathrm{I}}$)	53.94(5)	Nb(2$^{\mathrm{I}}$)–Nb(3)–Cl(3)	53.87(5)
Nb(3)–Nb(1)–Cl(4$^{\mathrm{I}}$)	96.00(6)	Nb(1)–Nb(2)–Cl(3$^{\mathrm{I}}$)	94.62(5)	Nb(1)–Nb(3)–Nb(2)	60.49(3)	Cl(5)–Nb(3)–O(4)	83.0(2)
Nb(3)–Nb(1)–Cl(5$^{\mathrm{I}}$)	142.80(6)	Nb(3)–Nb(2)–Cl(1)	53.88(5)	Nb(1)–Nb(3)–Cl(1)	97.34(6)	Nb(1$^{\mathrm{I}}$)–Nb(3)–Cl(5)	53.69(5)
Cl(2)–Nb(1)–Cl(6)	87.09(7)	Nb(3)–Nb(2)–Cl(4)	96.98(6)	Nb(1)–Nb(3)–Cl(2)	53.46(5)	Nb(2$^{\mathrm{I}}$)–Nb(3)–Cl(5)	96.23(5)
Cl(2)–Nb(1)–O(3)	80.7(2)	Nb(3)–Nb(2)–Cl(6)	94.66(5)	Nb(1)–Nb(3)–Cl(3)	97.58(6)	Nb(1$^{\mathrm{I}}$)–Nb(3)–O(4)	136.6(2)
Cl(2)–Nb(1)–Nb(2$^{\mathrm{I}}$)	95.76(6)	Nb(3)–Nb(2)–O(1)	137.5(1)	Nb(1)–Nb(3)–Cl(5)	144.38(6)	Nb(2$^{\mathrm{I}}$)–Nb(3)–O(4)	136.1(1)
Cl(2)–Nb(1)–Nb(3$^{\mathrm{I}}$)	142.86(6)	Nb(1$^{\mathrm{I}}$)–Nb(2)–Nb(3)	60.46(3)	Nb(1)–Nb(3)–O(4)	132.7(2)	Nb(1$^{\mathrm{I}}$)–Nb(3)–Nb(2$^{\mathrm{I}}$)	60.22(3)
Cl(2)–Nb(1)–Cl(4$^{\mathrm{I}}$)	88.56(6)	Nb(3)–Nb(2)–Nb(3$^{\mathrm{I}}$)	89.99(4)	Nb(1)–Nb(3)–Nb(1$^{\mathrm{I}}$)	90.70(4)	Nb(2)–Cl(1)–Nb(3)	72.33(6)
Cl(2)–Nb(1)–Cl(5$^{\mathrm{I}}$)	163.63(8)	Nb(3)–Nb(2)–Cl(3$^{\mathrm{I}}$)	143.83(6)	Nb(1)–Nb(3)–Nb(2$^{\mathrm{I}}$)	60.03(3)	Nb(1)–Cl(2)–Nb(3)	72.97(6)
Cl(6)–Nb(1)–O(3)	83.0(1)	Cl(1)–Nb(2)–Cl(4)	87.51(7)	Nb(2)–Nb(3)–Cl(1)	53.78(5)	Nb(2$^{\mathrm{I}}$)–Cl(3)–Nb(3)	72.19(6)
Cl(6)–Nb(1)–Nb(2$^{\mathrm{I}}$)	142.07(6)	Cl(1)–Nb(2)–Cl(6)	87.64(7)	Nb(2)–Nb(3)–Cl(2)	96.78(6)	Nb(1$^{\mathrm{I}}$)–Cl(4)–Nb(2)	72.35(6)
Cl(6)–Nb(1)–Nb(3$^{\mathrm{I}}$)	96.86(5)	Cl(1)–Nb(2)–O(1)	83.7(1)	Nb(2)–Nb(3)–Cl(3)	143.78(6)	Nb(1$^{\mathrm{I}}$)–Cl(5)–Nb(3)	72.81(6)
Cl(6)–Nb(1)–Cl(4$^{\mathrm{I}}$)	164.26(7)	Nb(1$^{\mathrm{I}}$)–Nb(2)–Cl(1)	95.52(6)	Nb(2)–Nb(3)–Cl(5)	96.38(5)	Nb(1)–Cl(6)–Nb(2)	73.44(6)
Cl(6)–Nb(1)–Cl(5$^{\mathrm{I}}$)	90.89(7)	Nb(3$^{\mathrm{I}}$)–Nb(2)–Cl(1)	143.84(6)	Nb(2)–Nb(3)–O(4)	133.8(1)	Cl(1)–Nb(3)–Cl(2)	90.58(7)
Nb(2$^{\mathrm{I}}$)–Nb(1)–O(3)	134.7(2)	Cl(1)–Nb(2)–Cl(3$^{\mathrm{I}}$)	162.21(7)	Nb(1$^{\mathrm{I}}$)–Nb(3)–Nb(2)	80.08(3)	Cl(1)–Nb(3)–Cl(3)	162.02(7)
Nb(3$^{\mathrm{I}}$)–Nb(1)–O(3)	136.4(1)	Cl(4)–Nb(2)–Cl(6)	161.34(7)	Nb(2)–Nb(3)–Nb(2$^{\mathrm{I}}$)	90.01(4)	Cl(1)–Nb(3)–Cl(5)	87.49(7)
Cl(4$^{\mathrm{I}}$)–Nb(1)–O(3)	81.4(1)	Cl(4)–Nb(2)–O(1)	79.6(1)				

new hydroxide forms with the $[Nb_6Cl_{12}]^{2+}$ unit in the presence of alkylammonium cations.[16] In the well defined triclinic form **1** two co-ordinated OH^- groups occupy two *trans* octahedral apical positions, while in the cubic form **2** these may be outwith the $[Nb_6Cl_{12}]^{2+}$ co-ordination sphere. To deduce the positions of the OH^- groups the spectroscopic properties of the two clusters were examined. In the IR spectra, apart from the vibrations due to the water molecules, the two strong sharp absorptions found in the triclinic form at 3575 and 415 cm^{-1} may be attributed to the O–H and Nb–O stretching vibrations of bound OH^-, respectively. However, in the cubic form these two absorptions are not so explicitly resolved (see Experimental section), with only a shoulder observed at 3570 cm^{-1}, and a broad, medium intensity band at 410 cm^{-1}. Interestingly, the position of the absorption band arising from Nb–Cl stretching (Cl bridging position) is not affected by the differences in symmetry of these compounds. In both cases the band occurs at *ca.* 332 cm^{-1}.

In methanol or mixtures with up to 50% water, the inclusion of methanol or methoxide takes place and the cubic compound **3** is formed. As previously described,[6] and confirmed here, this compound is precipitated as a fine powder by slow addition of 2 mol OH^- per mol of $[Nb_6Cl_{12}]^{2+}$ at pH 7. On further addition of OH^-, this precipitate is then dissolved. From this strongly alkaline solution octahedral single crystals of **3** were subsequently grown. The observed broad band of medium intensity at 400 cm^{-1} is comparable in its position and shape to that found for the cubic compound **2** but differs from the strong absorption band[4] observed for $[Na_2(MeOH)_9][Ta_6Cl_{12}(OMe)_6]\cdot 3MeOH$, where six methoxy groups are co-ordinated to the cluster unit.[17] This suggests that MeO^- is not co-ordinated in this compound. The splitting of the C–O absorption band observed at 1022 and 990 cm^{-1} is not understood. Owing to several vacant positions in the crystal structure of this cluster, it often crystallizes with one or two methanol molecule(s) (based on carbon and hydrogen analytical data), without any significant influence on the unit cell parameters. The X-ray powder diffraction patterns of the cubic forms **2** and **3** are almost identical, except for only a small difference in the diffraction line positions.

If this compound contains non-co-ordinated methoxy groups they may contribute to the structural instability of this cubic form; crystals of **3** (cubic symmetry) are very unstable at ambient conditions and if exposed to air they transform into the triclinic structure of **1**. This process was detected by the X-ray powder diffraction patterns. Thus, as a first step in the decomposition process, if methoxide ions are present protons from two co-ordinated water molecules may be transferred to non-co-ordinated MeO^- resulting in the formation of methanol. Subsequent release of these two methanol molecules and four water molecules would complete the transformation of **3** into **1**.

Crystal Structures.—The crystal structure of $[Nb_6Cl_{12}(OH)_2(H_2O)_4]\cdot 4H_2O$ exhibits an octahedral cluster unit with the symmetry $\bar{1}$ imposing three crystallographically independent Nb atoms (Table 2). Fig. 1 shows the cluster unit with the atom numbering scheme including the symmetry operation code. Table 5 lists the cluster geometry. The octahedron is slightly elongated in the direction of the *trans*-hydroxo groups O(3)–H and O(3$^{\mathrm{I}}$)–H (Fig. 1) with Nb(1)–O(3) 2.147(5) Å. The average Nb–Nb distance (2.918 Å) between the equatorial [Nb(2), Nb(3)] and apical [Nb(1), Nb(1$^{\mathrm{I}}$)] atoms is longer than the average Nb–Nb distance (2.902 Å) in the equatorial plane. With the inversion symmetry of an octahedron there are twelve Nb–Cl distances ranging from

Table 6 Hydrogen-bonds observed in the crystal structure of **1**

	D···A/Å	D–H/Å	H···A/Å	D–H···A/°	Symmetry operations on A
O(2)–H(21)···O(3)	2.713(6)	0.98(8)	1.73(8)	174(9)	$-1 + x, y, -1 + z$
O(2)–H(22)···O(3)	2.674(1)	1.02(9)	1.66(9)	173(9)	$2 - x, 1 - y, 1 - z$
O(1)–H(102)···O(2)	2.645(8)	0.98(9)	1.75(9)	149(9)	$x, -1 + y, z$
O(4)–H(42)···O(2)	2.736(8)	0.98(9)	1.77(9)	170(9)	$1 - x, 1 - y, 1 - z$
O(1)–H(101)···O(5)	3.011(9)	0.99(9)	2.09(9)	155(9)	$1 + x, -1 + y, z$
O(4)–H(41)···O(5)	2.917(8)	0.98(9)	1.99(9)	157(9)	$1 - x, 1 - y, 1 - z$
O(5)–H(51)···O(1)	3.004(7)	0.99(9)	2.04(9)	164(9)	$1 - x, 1 - y, -z$
O(5)–H(52)···Cl(5)	3.549(6)	0.98(9)	2.59(9)	167(9)	$x, 1 + y, z$

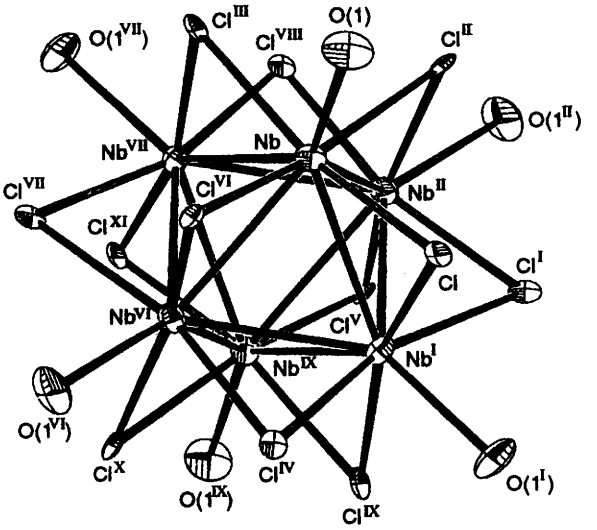

Fig. 3 An ORTEP drawing of the cluster unit in **2** and **3**. Symmetry operations: I z, x, y; II y, z, x; III $-x, -y, z$; IV $z, -x, -y$; V $-y, -z, -x$; VI $-y, -z, x$; VII $-z, -x, y$; VIII $-z, x, -y$; IX $x, -y, -z$; X $y, -z, -x$; XI $-x, y, -z$

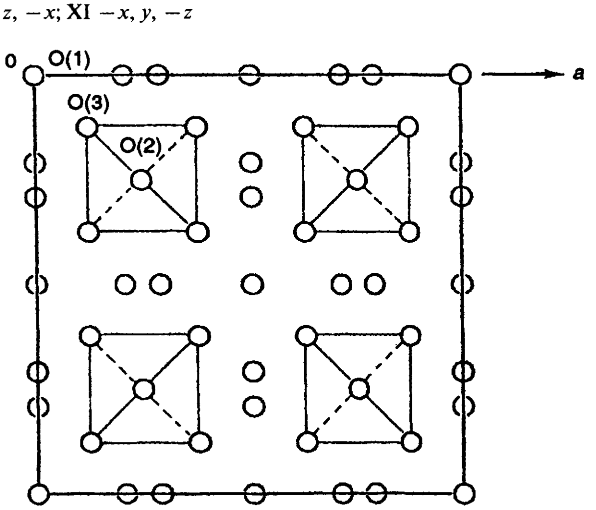

Fig. 4 The crystalline water molecules [O(3) at $3m$] in **2**. For simplicity, the cluster unit is omitted; only the co-ordinated water molecules (or water–hydroxide groups, averaged) [O(1) at $4mm$] are shown

2.433(2) to 2.478(2) Å. The co-ordinated water molecules with Nb–O distances of 2.289(5) and 2.250(5) Å are located at the terminal equatorial positions. The crystal packing is dominated by three-dimensional hydrogen bonds between cluster units {including both co-ordinated water molecules [O(1) and O(4)] and hydroxo groups [O(3)] and crystalline water molecules [O(2) and O(5)]} (Fig. 2, Table 6), as well as O–H···Cl interactions.

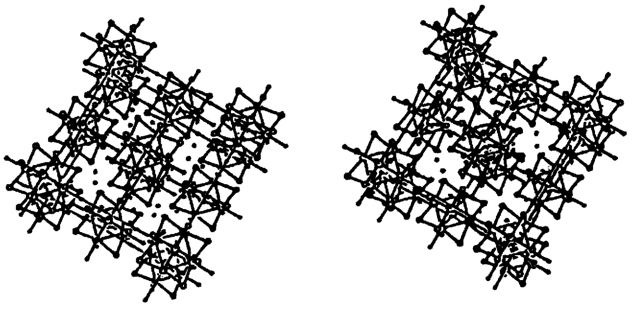

Fig. 5 A stereoscopic view of the unit cell of **2**

The crystal structures of **2** and **3** may be based on the hexanuclear cluster cation $[Nb_6Cl_{12}(H_2O)_6]^{2+}$ (Fig. 3), hydroxide anions in **2** or methoxide anions in **3**, together with crystalline water molecules [O(3)]. Since the hydrogen atoms of co-ordinated water molecules have not been determined, hypothetically in both cases the co-ordination sphere $[Nb_6Cl_{12}(OH)_2(H_2O)_4]$ should also be considered. In this case the co-ordinated O(1) would have to be considered to be disordered. This hypothesis is consistent with the Nb–O distances of 2.19(1) in **2** and 2.193(7) Å in **3**, which are a little shorter than the average Nb–O distance, 2.230(5) Å, in **1**. There is also evidence to support the formula having no co-ordinated OH^- ions, and no disorder in the O(2) (OH^-) atoms of **2** at the crystallographic $\bar{4}3m$ site ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$). This site is incompatible with the symmetry of a water molecule, whereas OH^- can align itself along the three-fold axis. Also, two independent crystallographic sites would both be occupied by water molecules, which is rather unusual for high symmetry space groups. The anisotropic thermal parameters of disordered atoms are generally higher than those of non-disordered atoms but there is no evidence that this is the case in these structures. In compound **3** the maximum value for the anisotropic thermal parameters of the co-ordinated O(1) atoms is of the same order of magnitude as for non-co-ordinated oxygen atoms [O(2) and O(3)] which are very closely packed in the crystal lattice as shown in Fig. 4.

The cluster units are regular octahedra implying $m\bar{3}m$ symmetry with the average Nb–Nb distance (for both structures) being 2.906(2) Å (Table 7). The Nb–Nb–Nb angles are those of a regular octahedron while average Nb–Cl–Nb and O–Nb–Cl angles are 72.39(6) and 81.20(5)°, respectively. The Nb–Cl distance of 2.460(2) Å (Table 7) is comparable with corresponding distances in other $[Nb_6Cl_{12}]^{2+}$ units.[7]

The crystalline water molecules, tetrahedrally arranged in groups of four, are situated in tunnels between the rows of cluster units (Figs. 4 and 5). Assuming no disorder (*i.e.* no co-ordinated OH^-) the hydroxide ions should be located within these tetrahedral interstices ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$). Based on the site symmetry $\bar{4}3m$ for O(2), it can be assumed that the H atom of OH^- would be located on the three-fold axis. The co-ordinated water molecules are involved in hydrogen bonding with

Table 7 Bond lengths (Å) and angles (°) with e.s.d.s in parentheses for **2** and **3***

	2	**3**
Nb–Nb$^{\mathrm{I}}$	2.905(2)	2.907(1)
Nb–Cl	2.460(2)	2.462(2)
Nb–O(1)	2.19(1)	2.193(7)
O(2)–C(2)		1.4213
Cl–Nb–O(1)	81.20(5)	81.18(3)
Nb$^{\mathrm{I}}$–Nb–Cl	53.80(4)	53.82(3)
Nb$^{\mathrm{II}}$–Nb–Cl	96.21(3)	96.22(2)
Cl–Nb–Cl$^{\mathrm{II}}$	88.66(1)	88.65(1)
Cl–Nb–Cl$^{\mathrm{III}}$	162.39(8)	162.36(5)
Nb$^{\mathrm{VII}}$–Nb–Cl	143.80(7)	143.82(3)
Nb$^{\mathrm{I}}$–Nb–O(1)	135.00(3)	135.00(1)
Nb–Cl–Nb$^{\mathrm{I}}$	72.39(6)	72.36(4)
Nb$^{\mathrm{I}}$–Nb–Nb$^{\mathrm{II}}$	60.00(3)	60.00(1)
Nb$^{\mathrm{I}}$–Nb–Nb$^{\mathrm{VII}}$	90.00(5)	90.00(1)

* For symmetry operations see caption to Fig. 3.

crystalline water molecules, O(1)–H $\cdots$ O(3) 2.84(1) Å. Each oxygen atom of the co-ordinated water is involved in four hydrogen bonds, twice as a donor and twice as an acceptor. Owing to the very high symmetry, the hydrogen-bond network is a very complicated one.

Acknowledgements

This work was supported by the U.S. Department of Energy through the Joint U.S.–Croatia Board for Scientific Cooperation under Contract JF-891, by the Ministry for Science and Technology of the Republic of Croatia under Projects 1–07–166, 1–07–179, and by the U.S. Department of Energy, Office of Basic Energy Sciences, through the Ames Laboratory, Iowa State University, under Contract No. W-7405-Eng-82.

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Received 25th *September* 1994; *Paper* 4/05837B