

# Cluster Salts $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6]A_n$ (with $\text{HIm} = 1H$ -imidazole and $A =$ Mineral Acid Anion, $n = 1$ or $2$ ) Made in and with Brønsted-basic Ionic Liquids and Liquid Mixtures

Eric Sperlich<sup>[a, b]</sup> and Martin Köckerling<sup>\*[a, c]</sup>

Four new hexanuclear niobium cluster compounds of the general formula  $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6](A)_n \cdot x(\text{solvent molecule})$  ( $\text{HIm} = 1H$ -imidazole,  $A =$  mineral acid anion,  $\text{Cl}^-$  ( $n = 2$ ) (1),  $(\text{SO}_4)^{2-}$  ( $n = 1$ ) (2),  $(\text{CrO}_4)^{2-}$  ( $n = 1$ ) (3), and  $(\text{HAsO}_4)^{2-}$  ( $n = 1$ ) (4)) were prepared. Their synthesis can be done in basic ionic liquids, which form on the addition of a mineral acid, which also delivers the counter anion for the final cluster compound, to an excess of the  $1H$ -imidazole. Some addition of an auxiliary

solvent, like methanol, improves the speed of crystallisation. The cluster unit comprises a hexanuclear  $\text{Nb}_6$  unit of octahedral shape with the edges bridged by Cl atoms and the exo sites being occupied by N-bonded  $1H$ -imidazole ligands. The cluster cation carries sixteen cluster-based electrons. Between the NH groups of the ligands of the cluster unit, the anions and the co-crystallised water (1), or  $1H$ -imidazole and methanol molecules (2, 3, and 4) a network of hydrogen bonds exists.

## 1. Introduction

The use of ionic liquids, salts with melting points below  $\sim 100^\circ\text{C}$ , as solvents and eventually also as reactants has enabled the preparation of unprecedented cluster materials and thereby has promoted immensely the cluster chemistry within about the last twenty years, see for example references [1]. Our research group focuses on hexanuclear cluster compounds of electron-poor transition metals  $M$ , which have octahedral  $M_6$  metal atom cores either edge- or face-bridged by inner halide or oxide ions  $X^i$ .<sup>[2]</sup> Each metal atom is further singly bonded to an exo-ligand  $X^e$ . The  $[M_6X^i_{12}]$  units of e.g. Zr, Hf, Nb and Ta are relatively robust and allow for extensive solution-based ligand exchange chemistry. The metal clusters exist with different oxidation states and depending on the number and type of  $X^e$  ligand (neutral or anionic), either cationic, neutral or anionic cluster units have been reported. Whereas for group VB, Nb and Ta, many cluster anions are known with  $X^e =$  halide or pseudohalide the number of structurally characterised com-

pounds comprising cluster cations is very limited. Examples include cluster units with  $X^e =$  neutral ligands like  $\text{H}_2\text{O}$ , alcohols, or N-bases and also double cluster salts.<sup>[1k,3]</sup> Because of solubility problems in common mostly non-polar organic solvents this solution chemistry (soft chemistry, *Chimie douce*) is somehow limited. Because of the great opportunities which are offered by ionic liquids as solvents and also as reactants, they were put on the agenda.

Here, we report about the ionothermal synthesis and X-ray structures of four new niobium cluster compounds of the composition  $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6]A_{(1 \text{ or } 2)} \cdot \text{solv.}$  ( $A$ : anion of a mineral acid, solv.: co-crystallised  $\text{H}_2\text{O}$  or  $\text{HIm} +$  methanol molecules):

- (1)  $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6]\text{Cl}_2 \cdot \text{H}_2\text{O}$ ,
- (2)  $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6](\text{SO}_4) \cdot 2\text{HIm} \cdot \text{CH}_3\text{OH}$ ,
- (3)  $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6](\text{CrO}_4) \cdot 2\text{HIm} \cdot 2\text{CH}_3\text{OH}$ , and
- (4)  $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6](\text{HAsO}_4) \cdot 2\text{HIm} \cdot 3\text{CH}_3\text{OH}$ .

## 2. Results and Discussion


### 2.1. Synthesis


The synthesis of the four title compounds is easily achieved by treating the cluster precursor compound  $[\text{Nb}_6\text{Cl}_{14}(\text{H}_2\text{O})_4] \cdot 4\text{H}_2\text{O}$ <sup>[2g]</sup> with a large excess of  $1H$ -imidazole in the presence of a mineral acid and eventually water (1) or methanol (2, 3 and 4). In the case of 1,  $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6]\text{Cl}_2 \cdot \text{H}_2\text{O}$ , no HCl or other chloride source needs to be added. All the outer ligands at the cluster precursor are substituted by  $1H$ -imidazole, thereby releasing four water molecules and two chloride ions per cluster unit. In all cases it is assumed that the released water molecules are deprotonated with the formation of  $1H$ -imidazolium ions and therefore an ionic liquid forms. In

[a] Dr. E. Sperlich, Prof. Dr. M. Köckerling  
Universität Rostock  
Institut für Chemie  
Anorganische Festkörperchemie  
Albert-Einstein-Str. 3a  
18059 Rostock (Germany)  
E-mail: Martin.Koeckerling@uni-rostock.de

[b] Dr. E. Sperlich  
Present address: Universität Potsdam, Institut für Chemie, Karl-Liebknecht-Str. 24–25, 14476 Potsdam (Germany)

[c] Prof. Dr. M. Köckerling  
Universität Rostock, Department Life, Light and Matter, 18051 Rostock (Germany)

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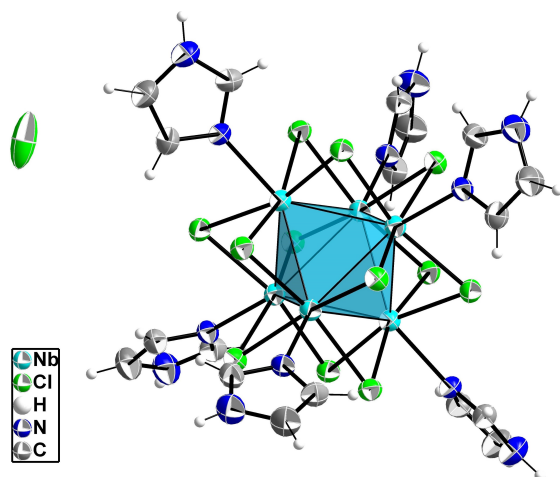
the first reaction attempts, mineral acids in a four-fold excess with respect to the cluster precursor are added as source for the cluster mineral acid counter anion for **2**, **3**, and **4**. They form in-situ ionic liquids. As turned out later the counter anions need not to be added as acids, but salts of the anions work as well. Apparently, both versions ensure a good ionic strength and solubility of the solution, such that large crystals form, see pictures in the Experimental Section.

It is worth to mention, that this is a simple method to produce hexanuclear cluster compounds of niobium, which contains cationic cluster units. The starting materials are simply mixed together and allowed to react for a few days at room temperature or at the slightly elevated temperature of 40 °C without any inert gas or moisture-free requirements. The addition of the auxiliary solvent methanol seems to speed up the crystallisation process.

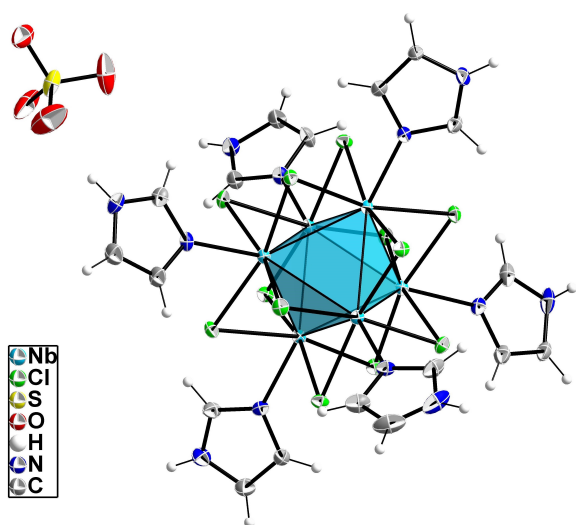
## 2.2. Single-Crystal Structures

The title compounds crystallise in the space groups  $Fd\bar{3}m$  (**1**, cubic),  $P2_1$  (**2**, monoclinic), and  $Pnma$  (**3** and **4**, orthorhombic). The unit cells consist of discrete niobium cluster dications  $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6]^{2+}$ , the respective mineral acid anion and co-crystallised water or 1*H*-imidazole and methanol molecules. Figures 1 to 4 show the structures of the cluster cations and the corresponding anions. Information about the crystals and the crystal structure determinations is collected in Table 1 and selected atom distances are compiled in Table 2.

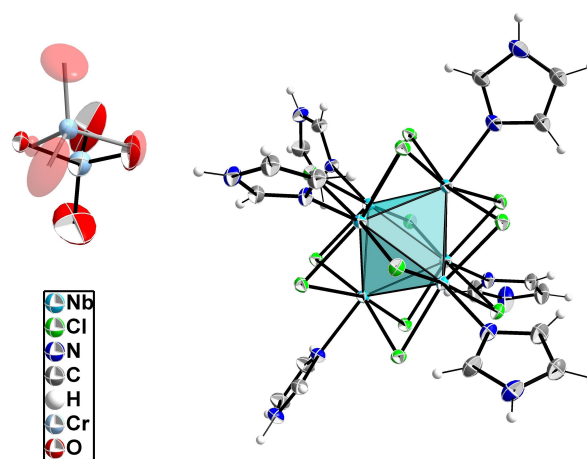
All four compounds contain nearly identical  $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6]^{2+}$  cluster cations, in which the exo sites of the metal atom octahedra are N-bonded to 1*H*-imidazole ligands. The Nb–Nb and Nb–Cl<sup>i</sup> distances indicate clearly the existence of 16 cluster-based electrons, i.e. the existence of non-oxidised cluster units. Such a cluster unit with very similar atom distances is present in  $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6](\text{OAc})_2 \cdot 3\text{CH}_3\text{OH}$ .<sup>[3e]</sup> In



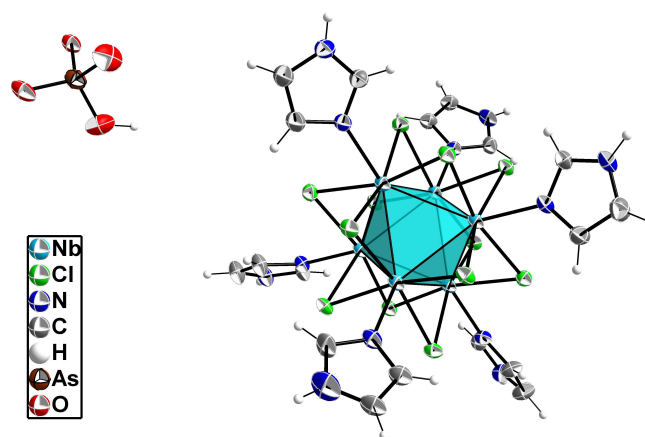
**Figure 1.** Structure of the cluster cation and the  $\text{Cl}^-$  anion in crystals of **1**. Displacement ellipsoids are shown at the 50% probability level.



**Figure 2.** Structure of the cluster cation and the  $(\text{SO}_4)^{2-}$  anion in crystals of **2**. Displacement ellipsoids are shown at the 50% probability level.



**Figure 3.** Structure of cluster cation and  $(\text{CrO}_4)^{2-}$  anion in crystals of **3**. The anion is disordered and has been refined on split positions. One of the orientations is shown in faded colours for clarity. Displacement ellipsoids are shown at the 50% probability level.



**Figure 4.** Structure of cluster cation and the  $(\text{HAsO}_4)^{2-}$  anion in crystals of **4**. The anion is disordered and has been refined on split positions. Only one of the orientations is shown for clarity. Displacement ellipsoids are shown at the 50% probability level.

**Table 1.** Crystal data and numbers pertinent to data collection and structure refinement for the four title compounds.

Compound	1	2	3	4
Formula	C <sub>18</sub> H <sub>26</sub> N <sub>12</sub> OCl <sub>14</sub> Nb <sub>6</sub>	C <sub>25</sub> H <sub>36</sub> N <sub>16</sub> O <sub>5</sub> SCl <sub>12</sub> Nb <sub>6</sub>	C <sub>26</sub> H <sub>40</sub> N <sub>16</sub> O <sub>6</sub> Cl <sub>12</sub> CrNb <sub>6</sub>	C <sub>27</sub> H <sub>45</sub> N <sub>16</sub> O <sub>7</sub> Cl <sub>12</sub> AsNb <sub>6</sub>
<i>M<sub>r</sub></i>	1480.27	1655.62	1707.60	1763.57
Cryst. size, mm <sup>3</sup>	0.16 × 0.14 × 0.13	0.60 × 0.15 × 0.15	0.10 × 0.10 × 0.10	0.10 × 0.10 × 0.10
<i>T</i> , K	123	123	123	123
Crystal system	cubic	monoclinic	orthorhombic	orthorhombic
Space group, <i>Z</i>	<i>Fd</i> $\bar{3}m$ , 8	<i>P2</i> <sub>1</sub> , 2	<i>Pnma</i> , 4	<i>Pnma</i> , 4
<i>a</i> , Å	20.6803(7)	8.7619(2)	19.420(1)	19.4387(7)
<i>b</i> , Å	20.6803(7)	26.7297(9)	14.738(1)	14.5635(5)
<i>c</i> , Å	20.6803(7)	11.4012(4)	19.049(1)	19.2312(7)
$\alpha$ , deg	90	90	90	90
$\beta$ , deg	90	109.332(2)	90	90
$\gamma$ , deg	90	90	90	90
<i>V</i> , Å <sup>3</sup>	8844.4(9)	2519.6(1)	5452.4(6)	5444.3(3)
<i>D</i> <sub>calcd</sub> , g cm <sup>-3</sup>	2.223	2.182	2.080	2.152
$\mu$ (MoK $\alpha$ ), cm <sup>-1</sup>	23.6	20.3	20.3	24.4
2 $\theta$ <sub>max</sub> , deg	64.8	72.38	64.98	55.11
Refl. measured	1334	78069	113051	32140
Refl. unique/ <i>R</i> <sub>int</sub>	800/0.065	23419/0.063	10167/0.019	6499/0.043
Param. refined	30	588	359	340
<i>R</i> ( <i>F</i> ) <sup>a</sup> / <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>b</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0578/0.1996	0.0457/0.0647	0.0394/0.0871	0.0413/0.0898
<i>R</i> ( <i>F</i> ) <sup>a</sup> / <i>wR</i> ( <i>F</i> <sup>2</sup> ) <sup>b</sup> (all refl.)	0.1024/0.2293	0.0780/0.0749	0.0480/0.0956	0.0710/0.1060
GoF ( <i>F</i> <sup>2</sup> ) <sup>c</sup>	1.195	1.037	1.158	1.052
$\Delta\rho$ <sub>fin</sub> (max/min), e Å <sup>-3</sup>	1.88/−0.66	1.51/−1.22	1.62/−1.39	1.41/−1.15

a,b

$$R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}; wR2 = \sqrt{\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2}}$$
**Table 2.** Selected atom distances (Å) of the title compounds 1–4.

	range	average
[Nb <sub>6</sub> Cl <sub>12</sub> (HIm) <sub>6</sub> ]Cl <sub>2</sub> ·H <sub>2</sub> O (1)		
Nb–Nb	2.923(1)–2.923(1)	2.923
Nb–Cl <sup>I</sup>	2.461(2)–2.461(2)	2.461
Nb–N	2.300(8)–2.300(8)	2.300
[Nb <sub>6</sub> Cl <sub>12</sub> (HIm) <sub>6</sub> ](SO <sub>4</sub> )·2HIm·CH <sub>3</sub> OH (2)		
Nb–Nb	2.9167(7)–2.9348(7)	2.924
Nb–Cl <sup>I</sup>	2.449(1)–2.475(1)	2.458
Nb–N	2.277(5)–2.310(5)	2.295
S–O	1.437(6)–1.465(7)	1.457
[Nb <sub>6</sub> Cl <sub>12</sub> (HIm) <sub>6</sub> ](CrO <sub>4</sub> )·2HIm·2CH <sub>3</sub> OH (3)		
Nb–Nb	2.9182(4)–2.9285(5)	2.922
Nb–Cl <sup>I</sup>	2.4534(7)–2.4668(7)	2.460
Nb–N	2.281(3)–2.286(4)	2.283
Cr–O	1.570(8)–1.725(6) (disordered)	1.660
[Nb <sub>6</sub> Cl <sub>12</sub> (HIm) <sub>6</sub> ](HAsO <sub>4</sub> )·2HIm·3CH <sub>3</sub> OH (4)		
Nb–Nb	2.9192(7)–2.9262(9)	2.923
Nb–Cl <sup>I</sup>	2.455(1)–2.467(1)	2.467
Nb–N	2.272(6)–2.291(6)	2.282
As–O	1.670(6)–1.678(5)	1.678

crystals of compound 1 the Nb<sub>6</sub> octahedron is located of the 8a Wyckoff site of the space group *Fd* $\bar{3}m$  with *O<sub>h</sub>* ( $\bar{4}3m$ ) symmetry. This has the consequence that a mirror plane cuts perpendicular through the imidazole ligand, what means that the non-Nb-bonded N2 atom (and the C2 atom, vice versa) is statistically located either on one or the other side of the mirror plane (50% occupation of this site with N and C). The H atoms of N2 and C2 form six equivalent hydrogen bonds to the counter Cl<sup>−</sup>

ion. This is located on the 16d Wyckoff site with also *O<sub>h</sub>* symmetry. Figure 5 shows this chloride environment. The Cl<sup>−</sup>...C/N distances measure 3.24 Å, a value in the range of non-classical hydrogen bonds according to Steiner.<sup>[4]</sup>

This high-symmetry interconnection of the cluster cations and the anions furthermore leads to pores in the structure, which are located around the 8b sites and defined by six imidazole ligands of six different cluster units and four tetrahedrally arranged chloride ions. This void accommodates the co-crystallised water molecule. Figure 6 shows the structure of this void.

The other three title compounds consist of the respective cluster cation and the doubly charged mineral acid anions (SO<sub>4</sub>)<sup>2−</sup> (2), (CrO<sub>4</sub>)<sup>2−</sup> (3), or (HAsO<sub>4</sub>)<sup>2−</sup> (4). In addition, they all contain co-crystallised 1*H*-imidazole and methanol molecules, which all are involved in hydrogen bonding. Exemplarily, Figure 7 shows the hydrogen-bonded environment of the cluster unit in the cluster sulfate, 2.

As a further example of the hydrogen bonding the environment around the mineral acid anion (HAsO<sub>4</sub>)<sup>2−</sup> in crystals of 4 is shown in Figure 8.

In the three structures of 2, 3 and 4 some of the co-crystallised imidazole and methanol molecules show a certain degree of disorder. The compounds 3 and 4 crystallise with very similar structures and with the same space group, *Pnma*. One site with mirror symmetry is half occupied with an imidazole molecule and half with a methanol molecule, arranged such that chains of hydrogen bond connected chains of imidazole-methanol dimers exist.

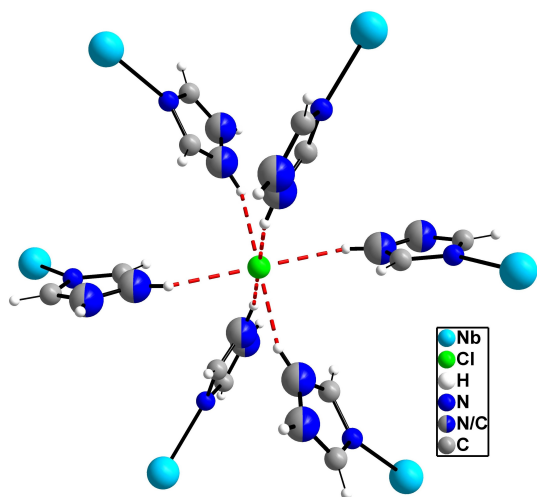


Figure 5. View of the octahedral environment with hydrogen bonding (red dashed lines) of the cluster charge balancing chloride ion in crystals of 1.

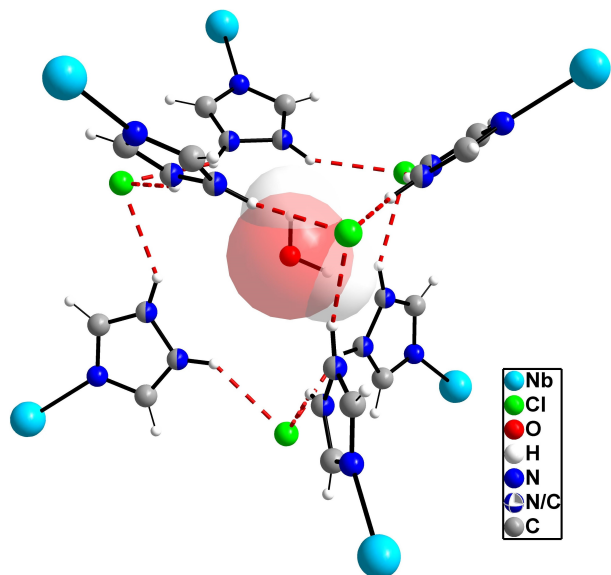


Figure 6. View of the environment of the voids in crystals of 1, which are filled with water molecules. Hydrogen bonds are drawn as red dotted lines.

### 3. Conclusions

In this paper we present the ionothermal preparation and crystal structures of four new member of the group of hexanuclear niobium cluster chlorides with octahedral Nb<sub>6</sub> core. The coordination environment of the cluster cation is completed by a 1*H*-imidazole ligand attached to each Nb atom. The charge of +2 on the cluster units is compensated by that of mineral acid anions. An extensive network of hydrogen bonds exist in crystals of the title compounds between the cluster units, the anions and co-crystallised solvents molecules. Using the Brønsted-basic (1*H*-imidazolium rich) ionic liquids and a co-solvent (like methanol) a high yield of well crystalline cluster compounds is accessible within a short time of a few days.

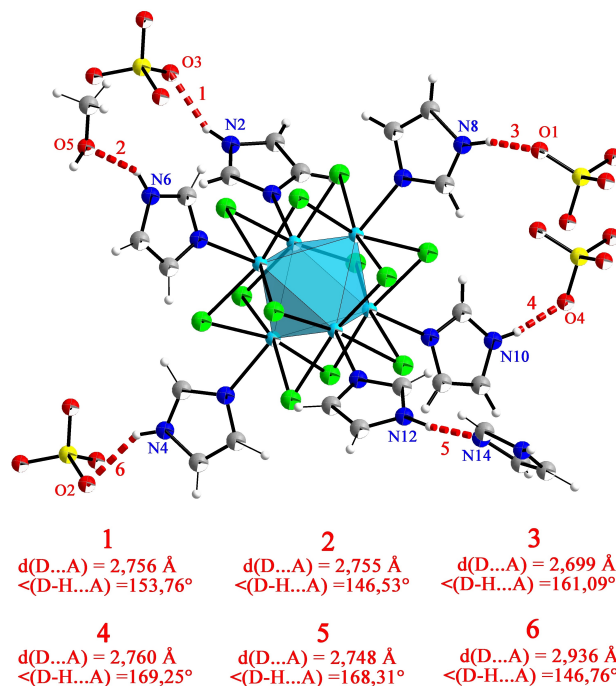


Figure 7. Hydrogen bonds between the NH-groups of the cluster bonded imidazole ligands and the surrounding groups in crystals of 2. The hydrogen bond values are numbered and given in the lower part of the figure.

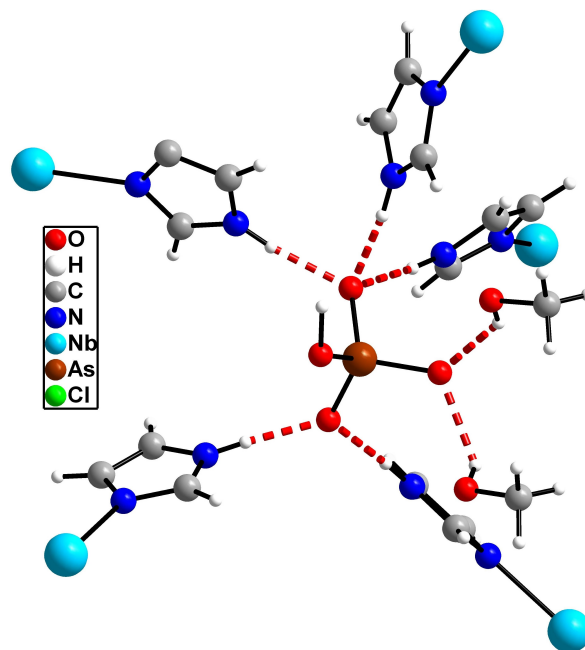


Figure 8. Hydrogen bonds (red dashed lines) between the NH-groups of the cluster bonded imidazole ligands and the hydrogenarsenate anion in crystals of 4.

## Experimental Section

### General

All chemicals were purchased from commercial suppliers and used without further purification. The cluster precursor compound



$[\text{Nb}_6\text{Cl}_{14}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  was synthesised by cluster excision of  $\text{K}_4[\text{Nb}_6\text{Cl}_{18}]$ , which in turn was prepared in a high-temperature reaction.<sup>[29,5]</sup> The excision is done in bi-distilled water and precipitation with concentrated hydrochloric acid. With the exception of the synthesis of  $\text{K}_4[\text{Nb}_6\text{Cl}_{18}]$  all reactions and manipulations were done in air. During the first exploratory reactions, the ionic liquids  $(\text{H}_2\text{Im})\text{Cl}$  and  $(\text{H}_2\text{Im})_2\text{SO}_4$  were prepared and used as reactants and together with methanol as solvent.  $(\text{H}_2\text{Im})\text{Cl}$  turned out to be a RTIL with a melting point below  $0^\circ\text{C}$ , whereas preliminary measurements give the melting point of  $(\text{H}_2\text{Im})_2\text{SO}_4$  at about  $45^\circ\text{C}$ .<sup>[6]</sup> Later it turned out, that adding a salt of the respective acid to the mixture of 1*H*-imidazole and methanol serves the purpose of preparing and crystallising the desired new cluster compounds even better, avoiding one preparative step. Furthermore this modification allows for the preparation of cluster compounds with acid anions, of which the pure acid does not exist, like e.g.  $\text{H}_2\text{CrO}_4$ .

### Single-Crystal X-Ray Diffraction

Single-crystals were selected using a light microscope with polarization filter. X-ray diffraction data were obtained with a Bruker-Apex D8 Quest diffractometer with a fine focus X-ray tube, an Apex Smart detector, and a Kryoflex cooling system. Graphite monochromated Mo- $\text{K}\alpha$ -radiation,  $\lambda = 0.71073 \text{ \AA}$  was used. The structures were solved by Direct Methods and refined against  $F^2$  on all data by full-matrix least-squares using the SHELX suite of programs.<sup>[7]</sup> All non-hydrogen atoms were refined anisotropically; all hydrogen atoms bound to C atoms were placed on calculated positions and refined using a riding model. Crystallographic data 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 number CCDC-2027121 for **1**, CCDC-2027082 for **2**, CCDC-2023298 for **3**, and CCDC-2022419 for **4**; Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>. In the structures of **3** and **4** the co-crystallised 1*H*-imidazole and methanol molecules are disordered on different sites. The disorder was treated by split sites with the sum of the occupancies of the sites being fixed to unity. The structure of **2** is described in the enantiomorphic space group  $P2_1$ . The structure refinement reveals a Flack parameter of 0.44(4) what might indicate centrosymmetry. Any attempts to refine the structure in a centrosymmetric space group failed. Also, the diffraction data were checked for multiple crystals, what was not approved, also. Because the calculated powder pattern agrees well with the experimental one of the bulk sample, we describe the structure with the space group  $P2_1$ .

### Elemental Analysis

Elemental analyses (C, H, N) were done using a Thermo Quest Flash EA 1112 analyser.

### NMR Spectroscopy

$^1\text{H}$  NMR spectra were obtained with a Bruker AVANCE 250 or a Bruker AVANCE 300 device and calibrated with respect to the solvent signal of carefully dried  $[\text{D}_6]\text{DMSO}$ .

### Infrared Spectroscopy

Infrared spectra in the range of  $4000\text{--}500 \text{ cm}^{-1}$  were obtained with a Nicolet 380 FT-IR or a Bruker Alpha FT-IR spectrometer. Both are equipped with ATR devices.

### Powder X-Ray Diffraction

Powder X-ray diffraction was carried out with a Stoe Stadi P powder diffractometer with Cu- $\text{K}\alpha_1$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) using a linear PSD detector. Measurements were carried out in transmission setup. Data collection and handling was performed with the WinXPow program.

### Synthesis of the Cluster compounds

#### $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6]\text{Cl}_2\cdot\text{H}_2\text{O}$ (**1**)

An amount of 20 mg (16.70  $\mu\text{mol}$ )  $[\text{Nb}_6\text{Cl}_{14}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  are filled in a 4 ml sample vial and 0.5 g (7.34 mmol) 1*H*-imidazole dissolved in 2 ml methanol are added. The vial is held at a temperature of  $40^\circ\text{C}$  for 5 days and then allowed to cool to RT. After 4 further days most of the cluster materials is crystallised in form of black crystals of octahedral shape, see Figure 9.

Yield: 18.78 mg (76%); IR: ( $25^\circ\text{C}$ , ATR, 32 scans,  $\text{cm}^{-1}$ ): 486 (m), 612 (s), 653 (vs), 742 (s), 771 (s), 826 (m), 841 (m), 917 (m), 938 (m), 1061 (vs), 1088 (m), 1119 (m), 1162 (m), 1228 (w), 1253 (m), 1319 (s), 1337 (m), 1372 (m), 1490 (m), 1504 (w), 1531 (w), 2341 (w), 2359 (w), 2850 (w), 2949 (w), 3077 (w), 3138 (m), 3161 (w).

The same cluster product is obtained using different cluster precursor compounds, like  $[\text{Nb}_6\text{Cl}_{14}(\text{CH}_3\text{OH})_4]\cdot 4\text{CH}_3\text{OH}$  or  $[\text{Nb}_6\text{Cl}_{14}(\text{CH}_3\text{OH})_4](\text{CH}_3\text{O})_2\cdot \text{DABCO}\cdot 0.66\text{CH}_2\text{Cl}_2$ , as shown by powder diffraction.

#### $[\text{Nb}_6\text{Cl}_{12}(\text{HIm})_6](\text{SO}_4)\cdot 2\text{HIm}\cdot \text{CH}_3\text{OH}$ (**2**)

A 4 ml sample vial is filled with 20 mg (16.70  $\mu\text{mol}$ )  $[\text{Nb}_6\text{Cl}_{14}(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$ , 1 g (14.69 mmol) 1*H*-imidazole, and 9.45 mg (66.79  $\mu\text{mol}$ ) anhydrous  $\text{Na}_2\text{SO}_4$ , and 2 ml methanol. The vial is heated at  $40^\circ\text{C}$  for 2 days and then allowed to cool to room temperature. After a few days the formation of black, strongly adhered crystals starts. This process stops when the solution is almost de-colourised, indicating that almost all cluster material is precipitated. A view of such crystals is given in Figure 10.

Yield: 25.71 mg (93%); IR: ( $25^\circ\text{C}$ , ATR, 32 scans,  $\text{cm}^{-1}$ ): 600 (vs), 618 (s), 657 (s), 703 (m), 729 (s), 756 (s), 826 (s), 884 (m), 907 (m), 942 (m), 969 (m), 1061 (vs), 1086 (s), 1193 (w), 1261 (m), 1325 (w), 1496 (m), 1539 (w), 1591 (w), 2361 (m), 2636 (m), 2837 (m), 2932 (m), 3031 (m), 3118 (w).

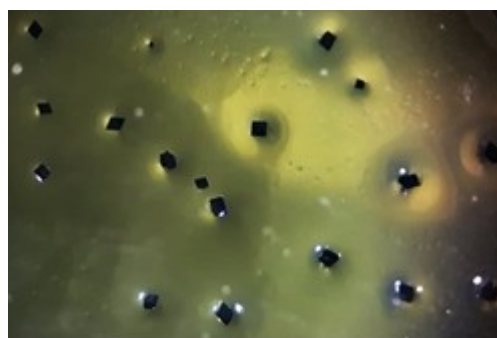


Figure 9. Light-microscopic picture of crystals of **1** (20-fold magnification).

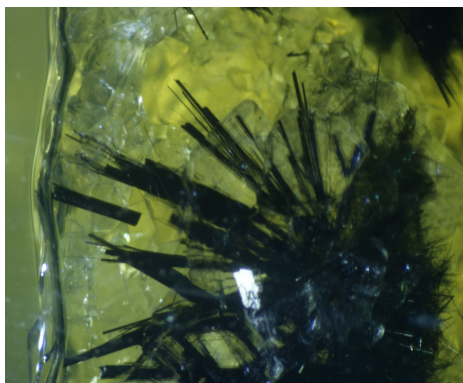


Figure 10. Light-microscopic picture of crystals of **2** (20-fold magnification).

**[Nb<sub>6</sub>Cl<sub>12</sub>(HIm)<sub>6</sub>](CrO<sub>4</sub>)·2HIm·2CH<sub>3</sub>OH (**3**)**

Within a few weeks at room temperature large single-crystals of **3** grow in a 4 ml sample vial, which was filled with 20 mg (16.70 μmol) [Nb<sub>6</sub>Cl<sub>14</sub>(H<sub>2</sub>O)<sub>4</sub>]·4H<sub>2</sub>O, 1 g (14.69 mmol) 1*H*-imidazole, 10.36 mg (66.79 μmol) potassium chromate, K<sub>2</sub>CrO<sub>4</sub>, and a mixture of 2 ml methanol with 0.5 ml water. During the reaction a larger amount of a yellow amorphous solid precipitates. The crystals of **3** are separated manually and washed with ethanol and dichloromethane. A microscopic view of such crystals is given in Figure 11.

Yield: (moderate, 5.42 mg (19%); IR: (25 °C, ATR, 32 scans, cm<sup>-1</sup>): 542 (w), 616 (s), 653 (vs), 765 (s), 822 (vs), 857 (s), 919 (m), 946 (w), 1072 (vs), 1105 (w), 1140 (w), 1175 (w), 1261 (m), 1323 (m), 1436 (m),



Figure 11. Light-microscopic picture of crystals of **3** (20-fold magnification).



Figure 12. Light-microscopic picture of crystals of **4** (20-fold magnification).

1496 (m), 1545 (w), 2341 (w), 2359 (m), 2611 (w), 2796 (m), 2914 (w), 3009 (w), 3126 (w).

**[Nb<sub>6</sub>Cl<sub>12</sub>(HIm)<sub>6</sub>](HAsO<sub>4</sub>)·2HIm·3CH<sub>3</sub>OH (**4**)**

Compound **4** is obtained in the form of crystals by a similar procedure as used for **2**. Again, 20 mg (16.70 μmol) [Nb<sub>6</sub>Cl<sub>14</sub>(H<sub>2</sub>O)<sub>4</sub>]·4H<sub>2</sub>O and 1 g (14.69 mmol) 1*H*-imidazole are used. An amount of 10.95 mg (66.79 μmol) of sodium dihydrogenarsenate, (NaH<sub>2</sub>AsO<sub>4</sub>) and 2 ml methanol are added. The vial is heated at 40 °C for one day and then allowed to stand untouched for several days. Black crystals grow and the solution shows some discolouration. The crystals (Figure 12) are filtered off and washed with ethanol and dichloromethane.

Yield: 21.50 mg (73%); IR: (25 °C, ATR, 32 scans, cm<sup>-1</sup>): 414 (w), 618 (s), 655 (vs), 740 (vs), 824 (s), 946 (m), 1026 (m), 1072 (vs), 1107 (m), 1142 (m), 1205 (w), 1261 (m), 1325 (m), 1453 (m), 1502 (m), 1548 (w), 1591 (w), 1702 (w), 2361 (m), 2695 (m), 2790 (m), 2930 (w), 3025 (w), 3132 (w).

Elemental Analysis: calcd. (%) for C<sub>18</sub>H<sub>25</sub>AsCl<sub>12</sub>N<sub>12</sub>Nb<sub>6</sub>O<sub>4</sub>, *M* = 1531.24 g·mol<sup>-1</sup>: C 14.15, N 10.98, H 1.65; found: C 15.57, N 11.25, H 2.25.

<sup>1</sup>H NMR ([D<sub>6</sub>]DMSO, ppm, RT): δ = 7.64 (s, 1H; NH), 7.01 (d, 2H; CH).

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### Conflict of Interest

The authors declare no conflict of interest.

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