Universität Rostock Traditio et Innovatio

New Niobium Alcoholate Cluster Compounds: Current State of Research

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Introduction:

Transition metal cluster compounds with polyhedral metal cores (strong metal-metal bonds) are well known for decades.[1,2] Ligand stabilized clusters contain often halide, chalcogenide, or organic ligand spheres. Metal-metal bridging ligands are commonly named „inner“ ligands (X^i) and apical ligands „outer“ (Y^a). Octahedral Nb_6-cluster units occur as $[Nb_6X_8]$ (X = I; μ_3 bridged) or $[Nb_6X_{12}]$ (X = Cl,Br,F; μ_2 bridged), see figure 1.[3]

Solution chemical methods are used for the synthesis of cluster compounds with organic ligands, which are not accessible by solid state reactions.[4] Because the inner ligands are more strongly bound to the metal cluster core than the inner ones, the outer ligands are primarily replaced. The exchange of inner ligands is rarely observed.

Previous studies [5,6] have shown that the exchange of the ligands of the inner coordination sphere starting from the cluster $K_4[Nb_6Cl_{18}]$ [7] ($[Nb_6X_{12}]$ type) with methanolato ligands is possible. Furthermore, it was possible starting from $[Nb_6I_{11}]$ [8,9] ($[Nb_6X_8]$ type) to achieve an exchange of the inner ligands by binding chelate ligands at the Nb_6-core.[6] The primary goal of this investigation is to extend the field of Nb_6 cluster compounds with iodido ligands and exchange reactions with alcoholato ligands.

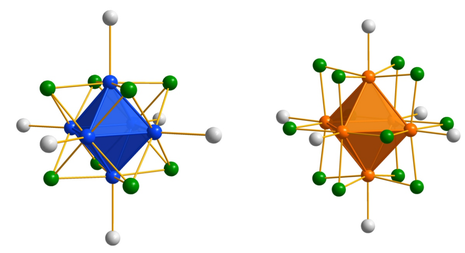
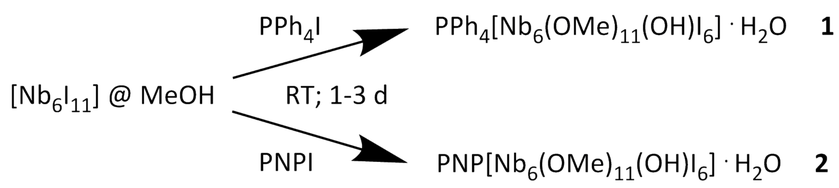


Figure 1. Ligand distribution on Nb_6 clusters $[Nb_6X_8]$ (left) and $[Nb_6X_{12}]$ (right)

Synthesis:

All reactions were carried out under argon, using Schlenk techniques and a dry box. The high temperature synthesis of $[Nb_6I_{11}]$ was done according to reference [9]. The starting material $[Nb_6I_{11}]$ was grinded with a ball mill and dissolved in methanol at 80 °C. After filtration and adding of PPh_4I (tetraphenylphosphonium iodide) or PNPI (bis(triphenylphosphine)iminium iodide) dark solutions were obtained after several days, from which red crystals of $(A^I)[Nb_6(OMe)_{11}(OH)I_6]\ H_2O$ (A^I = PPh_4 (**1**) or PNP (**2**), see scheme 1) were separated, suitable for single-crystal determination.



Scheme 1. Synthesis route of compounds **1** and **2**

Results:

Compounds **1** and **2** each consist of an Nb_6 octahedron whose inner positions are occupied by eleven OMe^- and one OH^- groups. The OH^- group is exactly located on one of the twelve inner ligand sites, and not mixed occupied over all sites. Via hydrogen bonding, a co-crystalline water molecule is attached to the OH^- group. The six outer ligand positions are occupied by iodido ligands.

From the single crystal structure it is apparent that one cation (PPh_4^+ or PNP^+) is present per cluster unit. Accordingly, thirteen CBE (cluster based electrons) in both cluster units are present.

The bond lengths and bond angles of compounds **1** and **2** are shown in table 1. The three-dimensional arrangement of the cluster units and cations, as well as the co-crystalline water molecules are shown in figure 3.

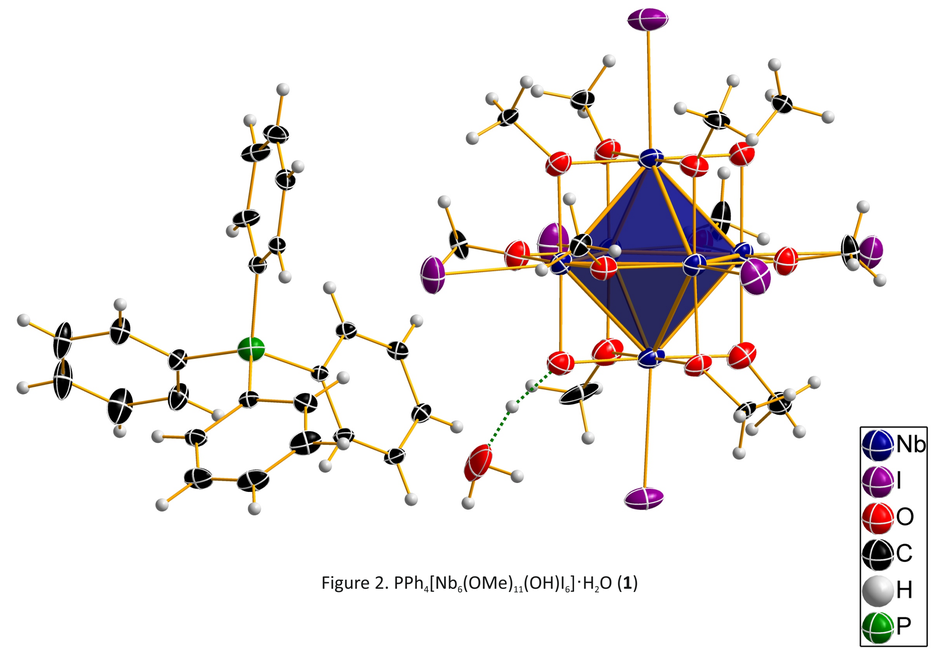


Figure 2. $PPh_4[Nb_6(OMe)_{11}(OH)I_6]\cdot H_2O$ (**1**)

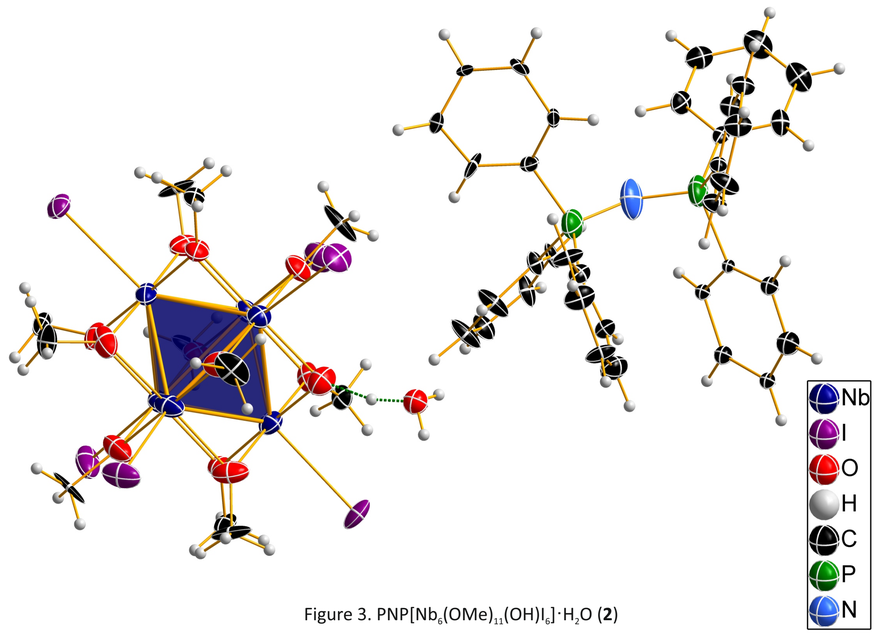


Figure 3. $PNP[Nb_6(OMe)_{11}(OH)I_6]\cdot H_2O$ (**2**)

It is particularly noticeable that in the course of the reaction the $[Nb_6X_8]$ type has changed into a $[Nb_6X_{12}]$ type. The three-dimensional linkage in the starting material $[Nb_6I_{11}]$ was disrupted and isolated cluster units were formed.

Table 1. Bond length and bond angles

		1	2
Ø bond length [Å]	Nb-Nb	2.892	2.879
	Nb-I	2.869	2.889
	Nb-O(Me)	2.066	2.061
	Nb-O(H)	2.047	2.049
	O-H-O	2.657	3.123
Ø bong angle [°]	Nb-Nb-Nb	90.05	90.01
	Nb-O(H)-Nb	88.47	88.67
	Nb-O(Me)-Nb	88.98	88.93
	Nb-Nb-I	176.01	175.62

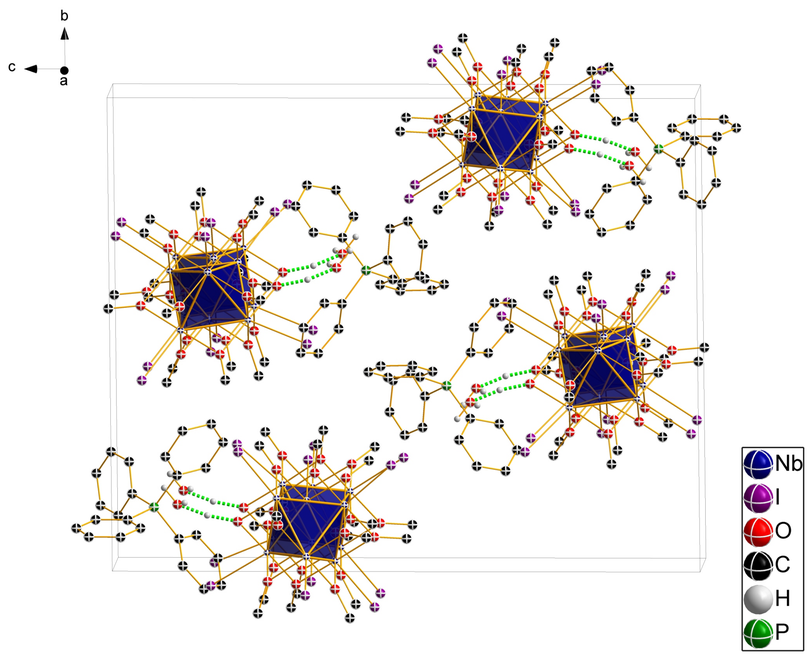


Figure 4. View of the unit cell of **1** without H-atoms

Literature:

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We gratefully acknowledge the financial support of the DFG (SPP 1708).

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