

Utilizing BMIm[PF₆] as Crystallization Agent in Niobium Cluster Chemistry: Room Temperature Synthesis of Extended Solid State Networks

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Abstract

We report about a novel synthetic method for the crystallization of three-dimensional frameworks through diffusion in the room temperature ionic liquid 1-Butyl-3-methylimidazolium hexafluorophosphate, BMIm[PF₆]. This technique allows the ambient temperature synthesis of several new compounds, of which two are presented here. The cluster frameworks BMIm₃[Nb₆Cl₁₂(NCS)₆{Ag₂(μ₂-NCS)}] (**1**) and BMIm₂[Nb₆Cl₁₂(NCS)₆{Ag₂(μ₂-Cl)}] · 2 CH₃CN (**2**) show very interesting structural arrangements in the solid state. Furthermore **2** can be emphasized as first chelate-ligated octahedral niobium cluster compound.

Synthesis

The synthesis of the starting materials is depicted in Scheme 1. High temperature synthesis of K₄[Nb₆Cl₁₈] was done according to literature^[1]. The crystallization of **1** and **2** in BMIm[PF₆] was performed in thin glass tubes using AgO₂CCF₃ · 0.5 C₆H₆ as solid Ag⁺ source. After layering with the ionic liquid, the cluster containing acetonitrile solution (see scheme 1) was layered above the pure BMIm[PF₆]. The reaction container was allowed to stand undisturbed for several days. Black gem-like crystals suitable for a structure determination formed on the glass wall in moderate yield (~50%).

Table 1: Crystallographic information

	1	2
SG	<i>P</i> $\bar{1}$	<i>I</i> 4 ₁ <i>cd</i>
Z	8	8
a [Å]	25.681(2)	17.463(1)
b [Å]	25.892(2)	
c [Å]	25.669(1)	38.108(2)
α [°]	90.669(1)	
β [°]	119.122(1)	
γ [°]	119.258(1)	
V [Å ³]	12415.8(7)	11621.5(5)

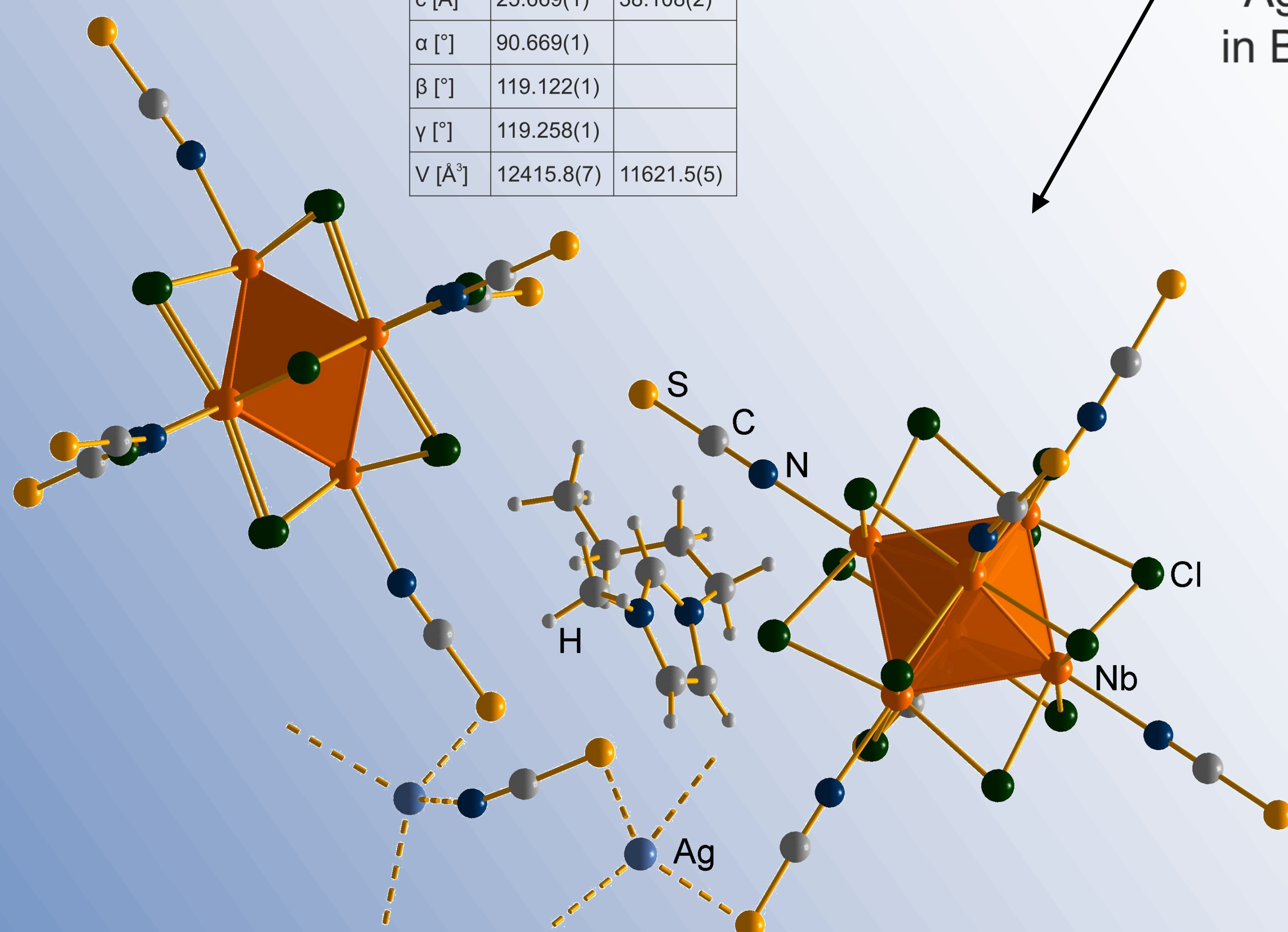


Figure 1: Part of the cluster unit of **1** (connectivity to next clusters implied by dashed bonds)

Results and Discussion

The use of the highly viscous ionic liquid BMIm[PF₆] as mediating agent for crystallization leads to three-dimensional extended frameworks built of [Nb₆Cl₁₂(NCS)₆]^{x-} subunits^[3,4] and the complex cations {Ag₂(μ₂-NCS)}⁺ (**1**, x = 4) and {Ag₂(μ₂-Cl)}⁺ (**2**, x = 3). In both compounds a tetrahedral coordination around the Ag⁺ cation is observed, whereas in **2** a novel and highly interesting 'intra-octahedral' connectivity mode is found (emphasized in Figure 2 with red bonds). The minimum distance between the inner chloride and the chelate ligand can be given with the sum of the vdW radii for the chloride atoms, respectively 3.5 Å. The crystallization products **1** and **2** are obtained from a mixture of BMIm[PF₆] and CH₃CN_{abs.} (volume 1:1) presumably due to the high excess of the imidazolium cation as well as the resulting polarity of the mixture.

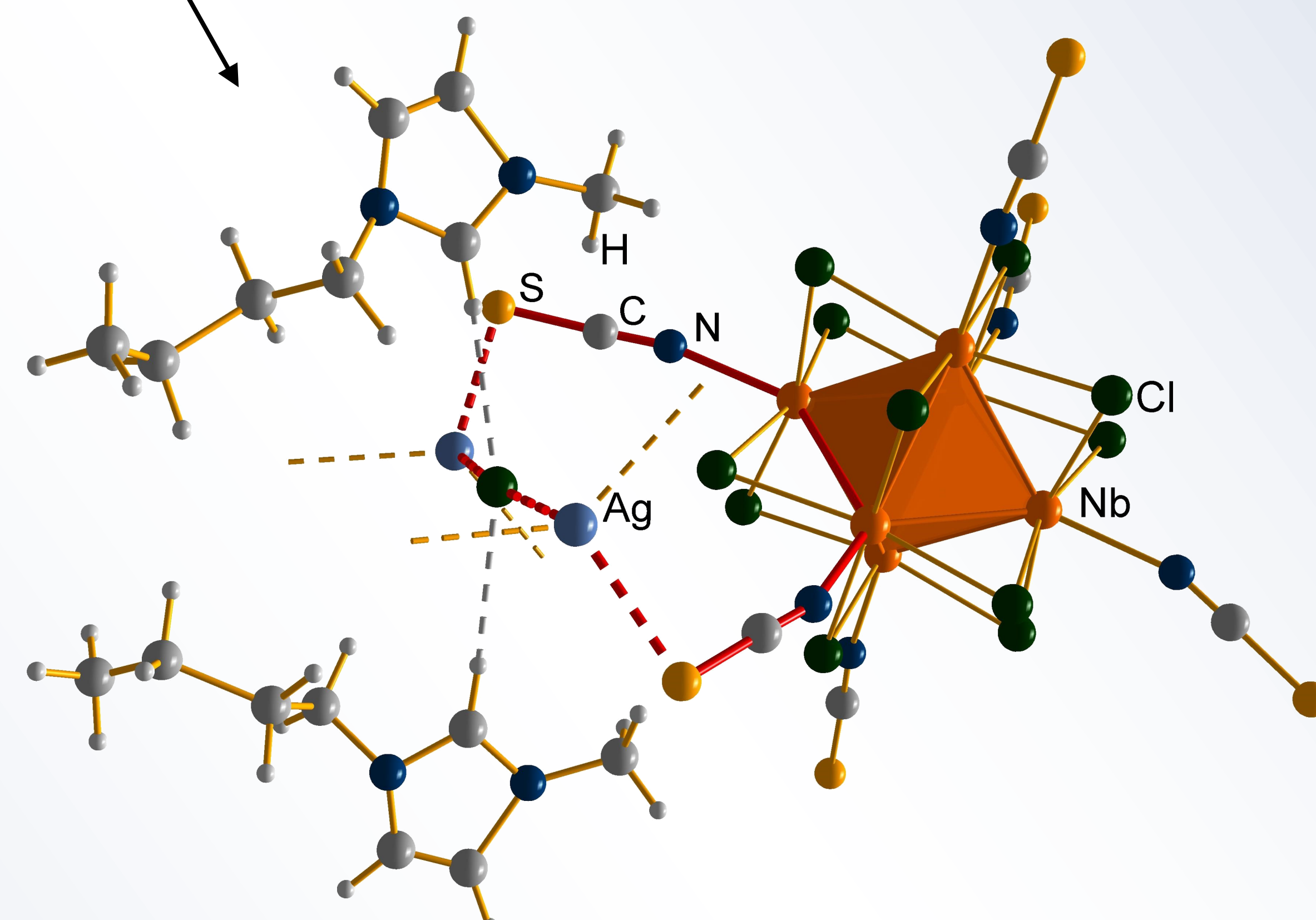


Figure 2: Symmetry independent unit of **2** (red bonds illustrate eleven-membered chelate ring)

Summary and Outlook

We synthesized and structurally characterized two new framework compounds with the aid of the room temperature ionic liquid BMIm[PF₆]. Title compound **2** is the first example of a chelate-ligated niobium cluster compound giving information about the minimum distance between the

inner halide and the chelate ligand. This is of high importance for designing organic chelate ligands that are able to coordinate niobium respectively tantalum cluster cores.

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