

Abstract

The objective of this work was to synthesize and characterize new molybdenum cluster complexes. The main focus was the structural characterization of inorganic-organic hybrid salts with alkyl-methylimidazolium cations ($C_n\text{mim}$, iso- $C_3\text{mim}$, CNCH_2mim , $\text{OH}(\text{CH}_2)_2\text{mim}$, bzmim ; $n = 3-5$, $\text{mim} = 3\text{-methylimidazolium}$) and the anionic cluster complexes $[\{\square\text{Mo}_6\}\text{X}_8^i\text{Y}_6^a]^{2-}$ ($\text{X}^i = \text{Cl, Br, I}$ and $\text{Y}^a = \text{Cl, Br, I, NCS}$).

In this area 16 new compounds could be synthesized. Each crystal structure shows alternating anionic and cationic layers, in which the packing of cluster complex anions and alkyl-methylimidazolium cations is of the ratio 1:2.

The comparison of Mo-Mo bond distances enables to show the correlation between the packing of the cationic sub-lattice and the metal-metal bond distances.

In the context of luminescence-measurements interesting results regarding the correlation of the ligands (axial and bridging) to the luminescent characteristics of the compounds were found. It has been established that the change of $\text{Cl}^i \rightarrow \text{I}^i$ causes a blue shift of emission and a red shift of excitation. When the axial halide ligand becomes heavier, a red shift of the emission is observed. In opposition to the change of the capping halide there is no influence of the axial halides on the maximum of the excitation.

Another aim of this work was to synthesize new crown ether stabilized cations with the cluster anions $[\{\square\text{Mo}_6\}\text{Cl}_8^i\text{Cl}_6^a]^{2-}$ and $[\{\square\text{Mo}_6\}\text{I}_8^i\text{I}_6^a]^{2-}$. Five new compounds could be synthesized. The crown ethers used were benzo-15-crown-5 and dibenzo-18-crown-6. In the case of $[\{\square\text{Mo}_6\}\text{I}_8^i\text{I}_6^a][(\text{K}(\text{B15K5})_2)_2]$, the synthesis of the first compound with the anionic cluster $[\{\square\text{Mo}_6\}\text{I}_8^i\text{I}_6^a]^{2-}$ and a crownether stabilized cation was obtained. In addition the first synthesis of a $[\{\square\text{Mo}_6\}\text{Cl}_8^i\text{Cl}_6^a]^{2-}$ anion with a transition metal which shows two coordination spheres, was successful $[\{\square\text{Mo}_6\}\text{Cl}_8^i\text{Cl}_6^a][(\text{Co}(\text{H}_2\text{O})_4(\text{MeCN})_2)(\text{Db18K6})_3](\text{MeCN})_2$. In the first coordination sphere octahedral coordination of the cobalt ion by four aqua-ligands and two molecules of acetonitrile is observed. The second coordination sphere consists of three molecules of dibenzo-18-crown-6.