CLUSTER IODIDES OF EARLY TRANSITION METALS

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Chemically robust octahedral cluster halide complexes of early transition metals, $[\{M_6(\mu_3\text{-}X)_8\}L_6]$ and $[\{M_6(\mu_3\text{-}X)_{12}\}L_6]$ (M = Nb, Ta, Mo, W; X = Cl, Br or I; L = neutral or anionic ligands) are stable, chemically robust and easily available. The iodide clusters of Mo and W exhibit superior emission lifetime and quantum yield values. We are carrying out systematic studies on the influence of terminal ligands L on the properties of the $[\{M_6I_8\}L_6]$ clusters, in order to achieve predictable tuning of their potentially useful characteristics such as the redox, spectroscopic and photophysical behaviour, that is intrinsically due to the presence of the $\{M_6I_8\}^{4+}$ cluster core, by the choice of an appropriate L. Coordination chemistry, photocatalytic activities on the water reduction reaction and other possible applications of the $[\{M_6I_8\}L_6]$ clusters will be discussed.

Coordination chemistry of Nb and Ta iodide clusters is virtually non-existent. Nevertheless, these iodides merit attention owing to unique combination of properties, offered by the cluster iodides of tantalum: the $[\{Ta_6(\mu_3\text{-}I)_{12}\}L_6]$ clusters will have 18 heavy (i.e., strongly X-ray absorbing) atoms per molecule. This makes them good candidates for new X-ray contrast agents. Additionally, their redox and optical properties makes them a good candidates for hydrogen generation from water using sunlight. In this work we will report preparation, photocatalytic and reactivity studies of some key $[\{Ta_6(\mu_3\text{-}I)_{12}\}L_6]$ clusters.

Nb and Re cluster iodides will be also covered.

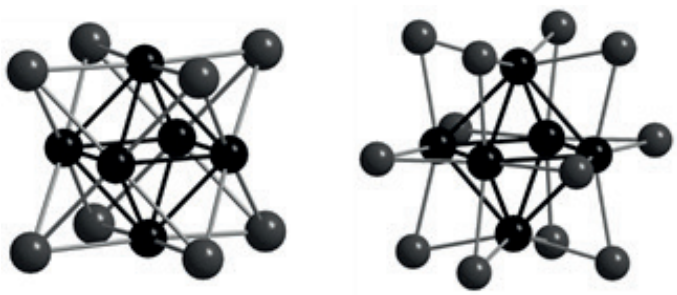

Figure 1. Octahedral cluster cores: $\{M_6I_8\}$ (left), $\{M_6I_{12}\}$ (right)

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References
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