Preparation, Characterization, and Redox Behavior of Molybdenum and Tungsten Complexes with Terminal Sulfide Groups

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It is important to successfully add terminal sulfide groups to a single molybdenum and tungsten ion centers, since $[MS]^{2+/3+}$ and $[M(O)S]^{2+}$ (M = W and Mo) units play a key role in the active sites of the molybdenum and tungsten cofactors such as xanthine oxidase family and aldehyde ferredoxin oxidoreductase. Although a number of sulfur containing these metal complexes have been presented, mononuclear complexes including $[MS]^{2+/3+}$ and $[M(O)S]^{2+}$ (M = W and Mo) units have been limited. Here, we report preparation and characterization of some molybdenum and tungsten complexes containing [MS] and $[MO(S_n)]$ cores (M = Mo and W) supported by thiolate ligands.

A mononuclear five coordinate monosulfide molybdenum(IV) complex, $[Mo^{IV}S(L1)_m]^{n-}$ (L1 = thiolate), (**1**) was obtained and characterized by IR, UV-vis spectroscopic methods, and X-ray crystallography. In contrast to other mononuclear five coordinate monosulfide molybdenum complexes, (**1**) changed to the corresponding mononuclear molybdenum(V) complex (**2**) by oxidation with the ferrocenium cation, which was identified by ESI-MS, IR, ESR, and UV-vis spectroscopic methods. Furthermore, the dimerization from (**2**) to $[Mo_2(\mu\text{-}S)_2(L1)_2]$ (**3**) was monitored by UV-vis spectroscopy and analyzed by second-order kinetics. As a tungsten complex, seven coordinate persulfide tungsten(VI) complex, $[W^{VI}(O)(S_2)(L2)_m]^{n-}$ (L2 = thiolate), (**4**) was obtained and characterized by similar methods applied to (**1**). Comparing the W=O and W-S(S_2) distances, and the ν(W=O) stretching band of (**4**) with those of other complexes containing $[W(O)(S_2)]^{2+}$ core, the employed thiolate ligand was suggested to weaken the W=O and the W-S bonds. Abstraction of the sulfur atom of persulfide by treatment with phosphines and the redox behavior will be discussed.