

## Chapter 1. General Introduction

Compounds of group 6 metals (chromium, molybdenum, and tungsten) are highly interested as substances suited for the appearance of multifunction combined photochemistry, electromagnetic property, and so on.<sup>1-9)</sup> For example, a large number of mononuclear and polynuclear chromium complexes have been investigated for photochemical and photophysical properties.<sup>1)</sup> Especially, polynuclear chromium complexes, in which metal-containing fragments are connected covalently via cyano- or isocyano-bridging ligands, exhibit an efficient energy transfer. Both molybdenum and tungsten complexes have a wide variety of stereochemistries in addition to a variety of oxidation states, and their chemistries are among the most complicated of the transition elements. Molybdenum and tungsten, in their highest oxidation state, tend to form large polynuclear cluster compounds.<sup>2)</sup> These large polymolybdate and polytungstate cluster have been interested in the relationship to metal oxide-type catalysis and widely investigated. Moreover, these metals, in divalent state, can form metal-metal quadruple bonds.<sup>3)</sup> Molybdenum is the most prolific form of quadruple bonds among all metals.

It has been known that chromium and molybdenum in the group 6 metals, which are essential trace metal elements, contribute to redox reactions in organisms.<sup>4-7)</sup> The functional importance of chromium ion is redox interaction with thiol-containing molecules<sup>4)</sup> or metabolism of sugar.<sup>5)</sup> Chromium(VI) ion is reduced to chromium(III) ion by sulfur-containing amino acid such as glutathione *in vivo*.<sup>4)</sup> The reaction mechanism of chromium(III) adenosin 5'-triphosphate as well as chromium(III) amino acidato complexes were studied as a model for glucose tolerance factors (GTFs).<sup>5)</sup> Molybdenum ion acts as active sites in a number of metallo-enzymes. Undoubtedly, some molybdenum enzymes in organisms have been known (Figure 1-1).<sup>6,7)</sup> The oxotransferase such as xanthine oxidase effectively catalyzes the addition or removal reactions of one oxygen atom from substrate X or XO. These enzymes have been shown to contain a

dissociable molybdenum cofactor (Mo-co).<sup>6)</sup> The most principally known molybdenum enzyme is nitrogenase. The iron-molybdenum cofactor (FeMo-co) of nitrogenase is recognized as the site where an inert nitrogen gas is activated and reduced to ammonia.<sup>7)</sup> Thus, some polynuclear structure containing the group 6 metals and sulfur atoms were observed in organisms, and the metals are noted in the importance of vital reactivity, especially interaction with sulfur atoms. Although the polynuclear complexes of chromium and molybdenum involving sulfur coordination are interested in their stereochemistry and reactivity, it has been little fundamental investigation combined them so far. It seems attributed to synthetic difficulty because of relatively weak metal-sulfur bonds. From these viewpoints, incorporation of group 6 metals into S-bridged polynuclear structures will be considered.

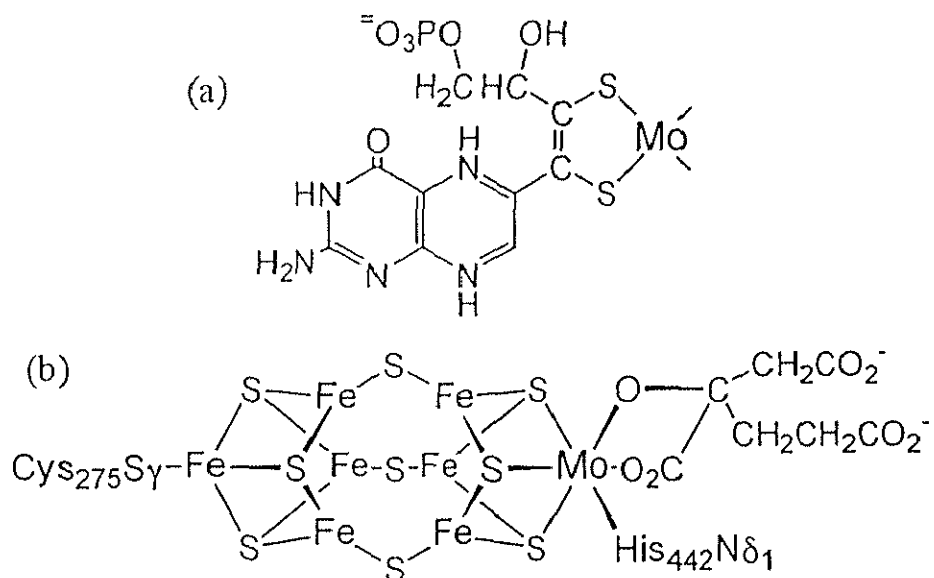
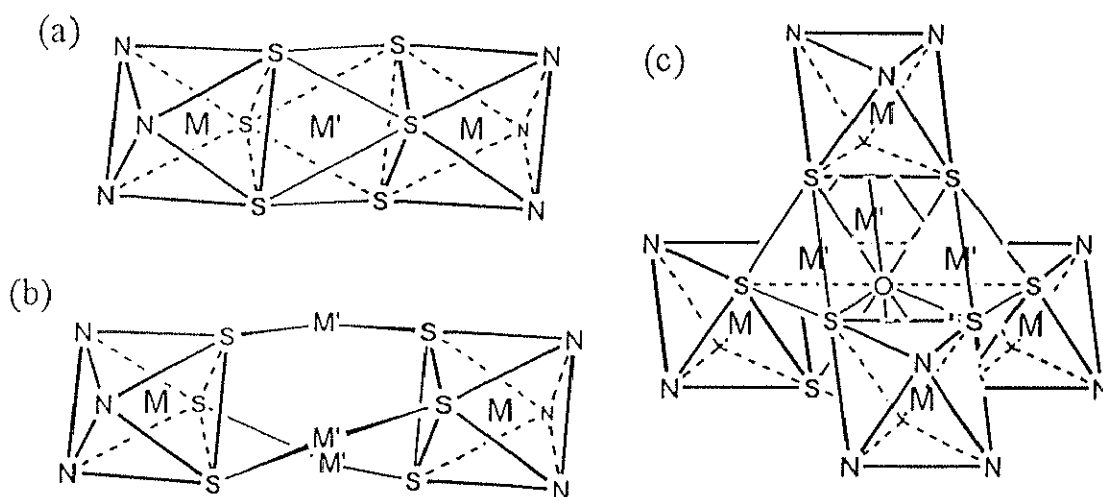


Figure 1-1. Proposed structures of (a) Mo cofactor of oxotransferase and (b) FeMo cofactor of nitrogenase.

Generally, some coordinated thiolato sulfur atoms in mononuclear complexes can bind with other metal ions from their strong nucleophilic property. The mononuclear complexes can be regarded as building blocks for contraction of polynuclear complexes to form a variety of S-bridged

polynuclear structure.<sup>10-13)</sup> It has been recognized that the mononuclear complexes of group 9 metals, *fac(S)*-[M(aet)<sub>3</sub>] (M = Co<sup>III</sup>, Rh<sup>III</sup>, and Ir<sup>III</sup>) reacts with a variety of metal ions to form S-bridged polynuclear complexes with retaining their *fac(S)* structure. The formation of the S-bridged polynuclear structures is highly dependent on the coordination geometry of the reacting metal ions. A number of S-bridged trinuclear [M'<sub>2</sub>{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>n+</sup> (M' = Fe<sup>III</sup>, Co<sup>III</sup>, and Ni<sup>II</sup>),<sup>10)</sup> pentanuclear [M'<sub>3</sub>{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>n+</sup> (M' = Ag<sup>I</sup> and Hg<sup>I</sup>),<sup>11)</sup> and octanuclear [M'<sub>4</sub>O{M(aet)<sub>3</sub>}<sub>4</sub>]<sup>6+</sup> (M' = Co<sup>II</sup>, Zn<sup>II</sup>, and Cd<sup>II</sup>) complexes,<sup>12)</sup> in which *fac(S)*-[M(aet)<sub>3</sub>] units are linked by metal ions with an octahedral-, linear-, or tetrahedral-type coordination geometry (Figure 1-2), have been selectively prepared and stereochemical properties have been clarified.



**Figure 1-2.** S-Bridged polynuclear structures; (a) [M'<sub>2</sub>{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>n+</sup>, (b) [M'<sub>3</sub>{M(aet)<sub>3</sub>}<sub>2</sub>]<sup>n+</sup>, and (c) [M'<sub>4</sub>O{M(aet)<sub>3</sub>}<sub>4</sub>]<sup>n+</sup>.

Nevertheless the thiolate chemistry of the late transition metal complexes has been widely investigated, that of the early transition metal complexes are little known. Recently, I preliminary reported a mononuclear *fac(S)*-[Cr<sup>III</sup>(aet)<sub>3</sub>] complex as a building block.<sup>14)</sup> The nickel(II) and zinc(II) ion was allowed to react with the thiolato sulfur atoms in *fac(S)*-[Cr<sup>III</sup>(aet)<sub>3</sub>], which gave the S-bridged trinuclear [Ni<sup>II</sup>{Cr<sup>III</sup>(aet)<sub>3</sub>}<sub>2</sub>]<sup>3+</sup> and octanuclear [Zn<sup>II</sup><sub>4</sub>O{Cr<sup>III</sup>(aet)<sub>3</sub>}<sub>4</sub>]<sup>6+</sup> complexes.<sup>14)</sup> However, it has never reported that early transition metal ion is incorporated in the building blocks such as *fac(S)*-

[M(aet)<sub>3</sub>]. The previously reported S-bridged polynuclear systems have been studied about mainly stereochemical viewpoint because of relatively strong affinity of late transition metal ions and thiolato sulfur atoms. Appearance of various interesting properties will be expected from fundamental investigation for reactivity of early transition metal ions with thiolato sulfur atoms and electromagnetic interaction in the polynuclear structures. Stereochemistry around the metal ions in the coordination sphere and some basic data about trace metal ions in organisms will be given by the polynuclear complexes involving group 6 metal ions and sulfur atoms. In addition, the synthesis and reactivity of group 6 and group 9 heterometallic clusters have been interested in their catalytic properties.<sup>9)</sup> Accordingly, it is worth to attempt the formation of polynuclear complexes by reaction of chromium or molybdenum ion with the mononuclear complexes. It is also expected that some novel polynuclear structures are formed owing to relatively weak metal-sulfur bonds.

In this thesis, I will describe that stereochemistry and reactivity of S-bridged polynuclear structures involving group 6 metal ions, especially chromium and molybdenum.<sup>15,16)</sup> This work is the first attempt to incorporate the early transition metal ions into S-bridged polynuclear structures by using the building blocks, *fac(S)*-[M(aet)<sub>3</sub>] (M = Co<sup>III</sup>, Rh<sup>III</sup>, and Ir<sup>III</sup>). I noted especially trivalent chromium and molybdenum ions, and attempted to incorporate these metal ions into S-bridged polynuclear structures in aqueous solution. Various S-bridged polynuclear complexes, which incorporate chromium or molybdenum ions, were newly prepared by the reaction with the thiolato sulfur atoms in mononuclear complexes, *fac(S)*-[M(aet)<sub>3</sub>] (M = Co<sup>III</sup>, Rh<sup>III</sup>, and Ir<sup>III</sup>). Almost all structures of the obtained complexes were determined by X-ray diffraction method and these complexes were characterized on the basis of their spectroscopic property and compared to related complexes. The electrochemistry and the stability of the S-bridged polynuclear complexes are also discussed. In connection with the chromium-sulfur bond strengths, the novel dinuclear iridium complex, which does not involve chromium(III) ion, was also obtained by similar reaction to above polynuclear complexes.<sup>15)</sup> The oxidation reaction of *fac(S)*-[M(aet)<sub>3</sub>]

was investigated in order to understand more clearly the reactivity of chromium(III) ion.<sup>17)</sup> Novel dinuclear rhodium complex as well as the iridium complex were prepared and characterized in relation to a coordinated disulfide bond. The redox property of the dinuclear complexes was investigated. Reactivity of the present mononuclear and polynuclear complexes depending upon building blocks is discussed and their structural changes are also explored.

### **Purpose of This Work**

This work was undertaken for the following purposes:

- (a) To prepare the S-bridged polynuclear complexes, which incorporate chromium or molybdenum ions.
- (b) To explore the formation of the new dinuclear complexes, which have a coordinated disulfide bond.
- (c) To determine the molecular structures and their absolute configurations of the newly isolated complexes by X-ray diffraction method.
- (d) To characterize the obtained complexes on the basis of their electronic absorption, diffuse reflectance, circular dichroism (CD), carbon-13 nuclear magnetic resonance (<sup>13</sup>C NMR), infrared and Raman spectroscopy, and compare to the related complexes.
- (e) To study the electrochemistry of the complexes by the cyclic voltammetry experiments.
- (f) To monitor the reactivity including the structural change relating to stability of the mono- and polynuclear complexes.
- (g) To investigate the redox property of thiolato and disulfide moieties in the complexes.
- (h) To reveal the differences in stereochemistry and electrochemical property of the complexes depending upon building blocks.
- (i) To elucidate the relationship between the spectroscopic property and metal-metal interaction in polynuclear structures.

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