

Chapter 5. Concluding Remarks

In this thesis, I described the reactions of chromium(III) ion (chapter 2) and molybdenum(III) ion (chapter 4) with *fac(S)*-[M(aet)₃] (M = Co^{III}, Rh^{III}, and Ir^{III}), as the first attempt to incorporate the early transition metal into S-bridged polynuclear structures in aqueous solution. In chapter 3, I described the oxidation reaction of *fac(S)*-[M(aet)₃], in order to understand more clearly the reactivity of chromium(III) ion with the thiolato sulfur atoms of *fac(S)*-[M(aet)₃]. As a result, the polynuclear complexes, [Cr^{III}{M(aet)₃}₂]³⁺, (M = Ir^{III} (1), Rh^{III} (2)), [M₂(aet)₄(cysta)]²⁺ (M = Ir^{III} (3), Rh^{III} (4)), [Mo^{IV}{Ir(aet)₃}₂]⁴⁺ (5), [Mo^{III}{Rh(aet)₃}₂]³⁺ (6), [Mo^V₂O₃{Rh(aet)₃}₃]⁴⁺ (7), and [Mo^V₂O₄{Co(aet)₃}₂]²⁺ (8) were newly prepared.

The present polynuclear complexes can be possible to take many isomers, but they are selectively formed as follows: the linear-type S-bridged trinuclear MCr^{III}M complexes 1 and 2 were separated and optically resolved into the $\Delta\Delta$ ((-)₆₀₀^{CD}-1b and (-)₆₀₀^{CD}-2b), $\Lambda\Lambda$ ((+)₆₀₀^{CD}-1b and (+)₆₀₀^{CD}-2b), and $\Delta\Lambda$ (1a and 2a) isomers, respectively. Both dinuclear disulfide complexes 3 and 4 were obtained as only meso ($\Delta_R\Lambda_S$) isomer, probably because of the structural stability. The linear-type S-bridged trinuclear Ir^{III}Mo^{IV}Ir^{III} complex 5 and Rh^{III}Mo^{III}Rh^{III} complex 6 were obtained as only meso ($\Delta\Delta$) and racemic ($\Delta\Delta/\Lambda\Lambda$) isomer, respectively, probably because of the relative solubility. The novel pentanuclear Rh^{III}₃Mo^V₂ complex 7 and the tetranuclear Co^{III}₂Mo^V₂ complex 8 were also obtained as only one isomer.

The crystal structures of 1a and 2a, which are representative $\Delta\Delta$ isomers of 1 and 2, respectively, were determined by X-ray diffraction method. Similarly, the crystal structures of the other obtained complexes except 8 were determined. The crystal structures of the linear-type S-bridged trinuclear complexes, [M'^{III}{Rh(aet)₃}₂]³⁺ (M' = Fe^{III} (9), Co^{III} (10)), were also determined for a structural comparison. Each of the trinuclear MM'M complexes 1a, 2a, 5, 6, 9, and 10 consists of two *fac(S)*-[M(aet)₃] subunits and a central metal atom, in which three metals is aligned to be linear. The central metal atom is situated in an octahedral environment with an M'S₆ chromophore, which is

formed by the coordination of two terminal *fac(S)*-[M(aet)₃] units. In the structurally characterized trinuclear MM'M complexes, 5, 6, and 9 have short M'-M distances (< 2.9 Å), while the others have long M'-M distances (> 2.9 Å). In the structures of the dinuclear disulfide complexes, [M₂(aet)₄(cysta)]²⁺ (M = Ir^{III} (3), Rh^{III} (4)), two octahedral *fac(S)*-[M(aet)₃] units are linked by a coordinated disulfide bond. Although the bonds of disulfide sulfur atoms and metals are generally weak, the disulfide sulfur atoms are bound to the iridium or rhodium atoms more strongly than thiolato sulfur atoms in 3 and 4. The S-bridged pentanuclear complex, [Mo^V₂O₃{Rh(aet)₃}₃]⁴⁺ (7) consists of Mo₂O₂(μ-O)⁴⁺ unit and three *fac(S)*-[Rh(aet)₃] units. Two *fac(S)*-[Rh(aet)₃] units bound to one molybdenum atom, while another unit bridges between two molybdenum atoms, remaining one non-bridging thiolato sulfur atom. This bridging *fac(S)*-[Rh(aet)₃] unit is significantly distorted from regular octahedral. Although a single crystal suitable for X-ray analysis could not be obtained unfortunately, 8 was assigned by the ¹³C NMR, infrared, and Raman spectroscopy, the plasma emission spectral analysis, and molar conductivity. Namely, 8 would involve Mo₂O₂(μ-O)₂²⁺ unit and two *fac(S)*-[Co(aet)₃] units.

From the spectroscopic investigation, the structures of the obtained complexes except 7 in solid state retain in aqueous solution. The electronic absorption and CD spectral pattern of the trinuclear MCr^{III}M complexes 1 and 2 were similar to those of the corresponding MCo^{III}M complexes, indicating the similarity of a Cr^{III}S₆ and a Co^{III}S₆ chromophore. The other isomers (1b and 2b) for the MCr^{III}M complexes were characterized by comparing their absorption and CD spectra, the molar conductivity, and the magnetic susceptibility to 1a, 2a, and the corresponding MCo^{III}M complexes. The electronic absorption, ¹³C NMR, infrared, and Raman spectra of the dinuclear disulfide complexes 3 and 4 exhibit characteristic behavior in relation to the coordinated disulfide bond. Especially, the electronic absorption bands of 3 are much intensified because of the short Ir-S bonds. The electronic absorption spectra of the trinuclear Ir^{III}Mo^{IV}Ir^{III} complex 5 and Rh^{III}Mo^{III}Rh^{III} complex 6 show a characteristic unique intense band at visible region, implying the metal-metal interaction in the complexes. These electronic absorption spectral patterns of 5 and 6 were not similar to those of 1 and 2.

The vibrational spectra of the pentanuclear $\text{Rh}^{\text{III}}_3\text{Mo}^{\text{V}}_2$ complex 7 and the tetranuclear $\text{Co}^{\text{III}}_2\text{Mo}^{\text{V}}_2$ complex 8 exhibit a characteristic strong band attributed to Mo-O double bonds. These complex 7 and 8 indicate diamagnetism because of the exist of the superexchange coupling or the metal - metal interaction.

In this work, the chromium(III) ion, whose incorporation into the S-bridged polynuclear structures have been believed difficult, gave the appearance of various interesting properties in relation to the weak chromium-sulfur bonds. For the mononuclear thiolato complexes, *fac(S)*-[M(aet)₃] (M = Co^{III}, Rh^{III}, and Ir^{III}), the differences of some property depending upon M were clearly observed. Namely, the redox property of the thiolato sulfur atoms and the stability of M-S bonds could be elucidated. Moreover, novel dinuclear iridium complex 3 with a coordinated disulfide bond could be obtained. It has been recognized that the oxidation reaction of *fac(S)*-[M(aet)₃] (M = Co^{III} and Rh^{III}) give the sulfenato or sulfinato complexes, *fac(S)*-[M(aese)_n(aesi)_{3-n}] (n = 0 - 3). Formation of 4 as well as 3 was achieved by using equivalent strong oxidizing agents. Considering the redox reaction of the obtained dinuclear disulfide complexes, it was elucidated that the coordinated disulfide bond is cleaved by both of reduction and oxidation reaction, which do not involve the M-S bond cleavage. Moreover, the conversion of the coordinated thiolato to the coordinated bridging disulfide is reversible, and [M₂(aet)₄(cysta)]²⁺ can act as not only oxidation agents but also building blocks. The reactions of the molybdenum(III) ion with *fac(S)*-[M(aet)₃] gave the trinuclear Ir^{III}Mo^{IV}Ir^{III} and Rh^{III}Mo^{III}Rh^{III} complexes containing different valence of central molybdenum ion depending upon the terminal building blocks. Moreover, the trinuclear Rh^{III}Mo^{III}Rh^{III} complex was converted into the pentanuclear Rh^{III}₃Mo^V₂ complex involving Mo₂O₂(μ-O)⁺ unit by spontaneous oxidation. This structural change was monitored by absorption spectra. The formation of Mo₂O₂(μ-O)₂²⁺ and Mo₂O₂(μ-O)⁴⁺ units are generally depending upon concentration of acid. Considering the reaction of the molybdenum(V) ion with *fac(S)*-[M(aet)₃], it is suggested that the present molybdenum-containing S-bridged polynuclear structures are controlled by the building blocks, *fac(S)*-[M(aet)₃] units.

In the cyclic voltammetry experiments, a reversible redox couple (M(IV)/M(III)) and an irreversible reduction wave (Cr(III)/Cr(II)) were shown in the trinuclear $M\text{Cr}^{\text{III}}M$ complexes **1** and **2**. Although the present $M\text{Cr}^{\text{III}}M$ complexes indicated similar stereochemical and spectrochemical property to the corresponding $M\text{Co}^{\text{III}}M$ complexes, the electrochemical property of the chromium complexes is highly different from that of the cobalt complexes. In the dinuclear disulfide complexes **3** and **4**, an irreversible oxidation wave (M(IV)/M(III)) and an irreversible reduction wave of sulfur-sulfur bond cleavage were observed. Since only irreversible waves are observed, the dinuclear structures decompose in both of reduction and oxidation process. In both trinuclear $\text{Ir}^{\text{III}}\text{Mo}^{\text{IV}}\text{Ir}^{\text{III}}$ complex **5** and $\text{Rh}^{\text{III}}\text{Mo}^{\text{III}}\text{Rh}^{\text{III}}$ complex **6**, a quasi-reversible redox couple (Mo(III)/Mo(II)) was measured. Interestingly, a quasi-reversible redox couple (Mo(IV)/Mo(III)) for **5**, while an irreversible oxidation wave (Mo(V)/Mo(III)) for **6**, was also shown. This result indicates that a trinuclear $\text{Ir}^{\text{III}}\text{Mo}^{\text{III}}\text{Ir}^{\text{III}}$ complex incorporate trivalent molybdenum ion would be electrochemically unstable in iridium system, while the corresponding $\text{Rh}^{\text{III}}\text{Mo}^{\text{III}}\text{Rh}^{\text{III}}$ complex was obtained in rhodium system. Moreover, a trinuclear $\text{Rh}^{\text{III}}\text{Mo}^{\text{IV}}\text{Rh}^{\text{III}}$ structure could not formed and structural conversion to the pentanuclear $\text{Rh}^{\text{III}}_3\text{Mo}^{\text{V}}_2$ complex was taken place by the oxidation reaction.

During the course of this research,¹⁻⁶⁾ many interesting and important information for the obtained complexes were obtained. Especially, I could elucidate not only the stereochemical, spectrochemical, and electrochemical properties of the S-bridged polynuclear complexes containing the group 6 metal ions¹⁻³⁾ but also apparent difference of the reactivity of the mononuclear and polynuclear complexes depending upon the group 9 metal ions in the building blocks.²⁻⁴⁾ To control such properties of the S-bridged polynuclear structures by the building blocks is interesting, which will be valuable as basis for the construction of suitable polynuclear complexes.

References and Notes

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