

「論文内容の要約」

Bottom-up Syntheses and Properties of Trinuclear Sulfido Complexes with
N-Heterocyclic Carbene Metal Units as Tunable Components

(N-ヘテロ環カルベン金属部位を持つ三核スルフィド錯体の
ボトムアップ合成と電子的・立体的性質制御)

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Chapter 1 *Syntheses and Reactions of Bis-hydrosulfido Platinum and Palladium Complexes With Chelated Bis-N-heterocyclic Ligands*

A hydrosulfido platinum complex with a chelate NHC ligand was prepared and structurally characterized. The complex reacted with molecular oxygen in the presence of excess hydrogen sulfide affording a tetrasulfide complex via oxidation of sulfide. On the other hand the complex was oxidized by molecular oxygen in the absence of hydrogen sulfide, a dinuclear complex with thiosulfato bridging ligands was generated via oxidation and oxygenation of sulfides besides the formation of the tetrasulfido complex. X-ray structure analysis of the thiosulfato dinuclear complex showed the butterfly shape of the Pt_2S_2 core, which would generate more than four possible isomers with the arrangements of the thiosulfato and chelate ligands. However, the steric repulsion of the thiosulfato ligands and the methyl groups in the chelate ligand allowed only one of the isomers to exist.

Although the generation of hydrosulfide palladium complexes in the reaction of the corresponding chloro complexes with NaSH was confirmed by using ^1H NMR spectroscopic measurements, isolation of the complexes has not been succeeded probably due to the higher reactivity of the palladium complexes attributed to more labile nature of palladium(II) ions. In the case of the reaction of the palladium chloro complex with H_2S gas, the formation of the hydrosulfide complex was not confirmed by ^1H NMR spectra and elemental sulfur formed in air oxidation, implying the catalytic oxidation of sulfides by the palladium bisNHC units.

The hydrosulfido complex was used to synthesize homometallic trinuclear platinum complex, which was obtained by the reaction of the hydrosulfide complex with 2 equiv. of the acetato complex. Only the C_{3h} -isomer between the two possible C_{3h} - and C_s -isomers was crystallized and structurally characterized by X-ray crystallography revealing the Pt_3S_2 core with the pseudo- D_{3h} . These two isomers are in equilibrium, which depends on temperatures and

solvents, in solution. This equilibrium attributed to the flip around motion of the chelate ligands in the trinuclear complex.

Chapter 2 *Rational Syntheses and Properties of Heterometallic Trinuclear Complexes With a Chelated Bis-N-heterocyclic Carbene Platinum or Palladium Unit*

A bottom up method to construct sulfido-bridged trinuclear complexes with N-heterocyclic carbene ligands using the hydrosulfido platinum or palladium complexes, $[M'(\text{bisNHC-C}_n\text{-R})(\text{SH})_2]$ ($n = 1-3$; $M' = \text{Pt}$, $\text{R} = \text{Me}$, $i\text{-Pr}$, Bn ; $M' = \text{Pd}$, $\text{R} = \text{Me}$), was performed. From X-ray structural analyses of the trinuclear complexes, the metal–metal bond lengths were flexible and then affected by environment around the complexes such as crystal packing interaction.

The formation of trinuclear complexes in relation to the structures of the hydroxo-bridged dinuclear complexes in solution was also investigated. Thus, M_2M' -type heterometallic trinuclear complexes, $[(\text{MCp}^*)_2\{M'(\text{bisNHC-C}_n\text{-R})\}(\mu_3\text{-S})_2](\text{BPh}_4)_2$ ($M = \text{Rh}$, Ir ; $M' = \text{Pt}$, Pd), were synthesized by treating the hydrosulfido complexes with hydroxo-bridged dinuclear Rh and Ir complexes, whose dimeric structures remain intact in methanol during the formation of the trinuclear complexes. Reactions of the hydroxo dinuclear complexes with the hydrosulfido complex in acetonitrile gave different products from those obtained in methanol, due to the monomer-dimer equilibrium of the Rh and Ir hydroxo complexes in acetonitrile. The monomeric complexes in acetonitrile reacted with the hydrosulfido platinum complex to afford MPt_2 -type trinuclear and pseudo-cubane-type $M_2\text{Pt}_2$ tetranuclear complexes, whose formation was confirmed by using ESI mass spectrometry.

The complexes exhibited the absorptions around 620–680 and 560–600 nm for the Rh_2M'

and Ir₂M' complexes, respectively. No significant differences were observed for the absorption maxima with the variation of N-substituents but small differences were found with the different chain lengths of the bridging parts of the bisNHC ligands, which were reproduced via TD-DFT calculations.

The heterometallic complexes, except for those containing the platinum unit with the ethylene-bridged bisNHC ligands, showed dynamic behavior in solution attributed to the flapping-wing motion of the NHC ligand moieties. Activation parameters obtained from line shape analyses of variable temperature ¹H NMR spectra of the complexes suggested the flapping-wing motion occurred without bond-cleavages, except for the complexes having the palladium unit with the ethylene-bridged ligand that exhibited the large negative ΔS^\ddagger values suggesting the Pd–C_{carbene} bond cleavages accompanied by coordination of solvent molecules. Additionally, these results about the dynamic motion of chelated bisNHC ligands could provide useful information about the environments around active sites on metal ions, which are affected by the orientation of surrounded N-substituents on NHC ligands, for the development of catalysts using metal complexes having chelated bisNHC ligands.

Chapter 3 *Electrochemical Properties of Heterometallic Trinuclear Complexes With a Chelated Bis-N-heterocyclic Carbene Platinum or Palladium Unit*

The electrochemical properties of the heterometallic M₂M' trinuclear complexes were examined. While the complexes showed two reversible 1e-reduction couples in CVs in an organic solvent, acetonitrile, complicate waves appeared in CV measurements in aqueous solutions.

Electrocatalytic proton reduction ability of the heterometallic trinuclear complexes in both organic and aqueous solutions were also investigated.