

氏名 都 日 沫

学位（専攻分野） 博士（理学）

学位記番号 総研大甲第122号

学位授与の日付 平成7年3月23日

学位授与の要件 数物科学研究科 構造分子科学専攻
学位規則第4条第1項該当

学位論文題目 Transformation of Framework of Triple Cubane-
Type Rh-Mo Oxide Cluster by Using Mercaptans:
Dynamic Behavior of Linear-Type Tetranuclear
Complexes in Solution

論文審査委員 主査教授 北川 禎 三

教授 田 中 晃 二

助教授 宮 島 清 一

助教授 高 橋 保

教授 磯 邊 清

（大阪市立大学）

助教授 中 島 清 彦

（愛知教育大学）

In recent years the research concerning with the reaction of structurally characterized discrete metal oxide clusters has been received considerable attention with the hope that this knowledge can be transferred to the actual catalyst system of solid oxides to understand the transformation of small organic molecules on the active sites of the catalysts. In addition, single or integrated cubane-type clusters have been successfully used as models of oxide solids in recent theoretical works. The triple cubane-type oxide cluster $[(\text{Cp}^*\text{Rh})_4\text{Mo}_4\text{O}_{16}]$ ($\text{Cp}^* = \eta^5\text{-C}_5(\text{CH}_3)_5$) (1) synthesized by our group recently shows interesting reactivities toward protic reagents such as CH_3OH . The reactions of this triple cubane-type oxide cluster with mercaptans such as methanethiol and 1,2-benzenedithiol provoke our interest since the mercaptans with proton and soft sulfur may lead to different reactions and supply valuable information to deepen our understanding about the chemistry occurred on the surface of oxides.

A reaction of 1 with methanethiol was carried out in methanol. It was found that the triple cubane framework was collapsed and a series of complexes of $[(\text{Cp}^*\text{Rh}(\mu\text{-SCH}_3)_3\text{MoO}_2)_2(\mu\text{-O})]$ (2), $[(\text{Cp}^*\text{Rh}(\mu\text{-SCH}_3)_3\text{MoO})_2(\mu\text{-O})_2]$ (3), $[(\text{Cp}^*\text{Rh}(\mu\text{-SCH}_3)_3\text{MoO})_2(\mu\text{-O})(\mu\text{-S})]$ (4), $[(\text{Cp}^*\text{Rh})_2(\mu\text{-SCH}_3)_3]_4[\text{Mo}_8\text{O}_{26}]$ (5), and $[(\text{Cp}^*\text{Rh})_2(\mu\text{-SCH}_3)_3]_2\text{Mo}_6\text{O}_{19}]$ (6), were isolated under different conditions. The structures of these complexes were determined by X-ray analyses and their properties were characterized by NMR and IR spectroscopies as well as FAB mass spectrometry.

Complexes 2, 3, and 4 are linear-type tetranuclear complexes formed through the rearrangement of the triple cubane framework by attacking of methanethiol. Among them 4 has a bridging sulfur atom which is from the methanethiol by cleaving of S-C bond. The cleavage process relating to industrially important desulfurization reaction provides a rare example for the polynuclear cluster formation with bridging sulfur atoms coming from a mercaptan. In the ^1H and ^{13}C NMR spectra 2 shows two series signals which are attributed to the existence of two isomers, asymmetric isomer and symmetric isomer, in the solution. The two isomers were considered to arise from different relative orientations of methyl groups on bridging sulfurs. Through dissolving the crystals of 2 in CDCl_3 at low temperature and then measuring ^1H and ^{13}C NMR spectra the assignments were made successfully for asymmetric and symmetric isomers. The forward and reverse rate constants of the interconversion process of the two isomers were obtained by studying ^1H NMR spectra at different temperatures. And then the activation free energies of inversion reaction of the sulfur were calculated by Eyring plots as 66.4kJmol^{-1} for forward reaction and 67.7kJmol^{-1} for reverse reaction.

Complexes 2, 3 and 4 show very interesting fluxional behavior in solu-

tion. ^{17}O NMR spectral data of 2, 3, and 4 are well consistent with corresponding solid structures and indicate that the structural units of $\text{O}_2\text{Mo}(\mu\text{-O})\text{MoO}_2$ for 1, $\text{OMo}(\mu\text{-O})_2\text{MoO}$ for 2, and $\text{OMo}(\mu\text{-O})(\mu\text{-S})\text{MoO}$ for 3, are retained in the solution. The variable-temperature ^1H NMR measurements of 2, 3, and 4 show that the complete averaging of methyl groups are achieved at higher temperatures. The averaging processes are fully reversible upon cooling for all the three complexes. The computer-generated spectra were iteratively fitted to the observed spectra to evaluate the rate constants for the exchange processes at different temperatures. The activation parameters were calculated by using Eyring plots. The small entropic contributions obtained are consistent with intramolecular mechanisms. The variable-temperature ^{17}O NMR studies show that the resonances of all the three complexes become sharpen with increasing temperature. This indicates that the averaging processes are not realized by the exchange between terminal and bridging oxygen atoms. Accordingly a mechanism was put forward with the first breaking of a $\text{Mo-S}(\text{CH}_3)$ bond trans to the terminal oxygen atom, followed by an intramolecular scrambling to achieve the average of environments through five coordinate intermediate and then recombine to restore to the original configuration. Since 2 has two weak $\text{Mo-S}(\text{CH}_3)$ bonds resulted from two trans terminal oxygen atoms, we have suggested a second mechanism for 2 in which the breaking of two weak $\text{Mo-S}(\text{CH}_3)$ bonds takes place as the first step followed by the rotation of resulted species along the remaining $\text{Mo-S}(\text{CH}_3)$ bond. Finally, the recombination occurs to recover the original framework to achieve averaging of SCH_3 groups.

Complexes 5 and 6 are formed through the rearrangements of the triple cubane framework of 1 by separating organometallic group Cp^*Rh and oxometalate part completely. Complex 5 has a characteristic structure which is different from those of α , β , and γ -octamolybdates and therefore is a new isomer of octamolybdate. This complex is structurally similar to an intermediate suggested previously in the interconversion process of α , β , and γ -octamolybdates. The IR spectrum of 5 was measured in CH_3NO_2 and the evidence was provided for the intermediate nature of 5.

Furthermore through the reaction of 1 with 1,2-benzenedithiol, a rhodium dimer $[(\text{Cp}^*\text{Rh})(\mu\text{-S}_2\text{C}_6\text{H}_4)]_2$ (7) and a corresponding sulfinato complex $[(\text{Cp}^*\text{Rh})(\mu\text{-S}_2(\text{O})\text{C}_6\text{H}_4)]_2$ (8) were obtained. In addition, an iridium monomer $[(\text{Cp}^*\text{Ir})(\mu\text{-S}_2\text{C}_6\text{H}_4)]$ (9) were isolated from a reaction of $[(\text{Cp}^*\text{IrCl}_2)]_2$ with 1,2-benzenedithiol. Complexes 7, 8, and 9 were characterized by X-ray structural analyses and NMR, IR and FAB-MS. The complex 7 was found to show the interesting monomer and dimer interconversion in solution. The complex 8 can be also obtained through the oxidation of 7 by molecular oxygen in the air at room temperature which has an important meaning in understanding the deactivated

processes of some enzymes.

審査結果の要旨

邨 日沫君の博士論文は、三重立方体型酸化物クラスター $[(\text{Cp}^*\text{Rh})_4\text{Mo}_4\text{O}_{16}]$ ($\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) (1) と含硫黄有機小分子との反応、そしてその反応に伴うクラスター骨格のユニークな構造変換を明らかにしたものである。更に、その反応で得られた生成物の固体分子構造ならびに溶液内動的挙動もあわせて明らかにしている。

本研究の要点は次の (i) ~ (vi) にまとめられる。(i) 含硫黄有機物として CH_3SH を用いた場合には、1 の三重立方体骨格の切断・再編が起こり、新型の四核クラスター $[(\text{Cp}^*\text{Rh}(\mu\text{-SCH}_3)_3\text{MoO}_2)_2(\mu\text{-O})]$ (2), $[(\text{Cp}^*\text{Rh}(\mu\text{-SCH}_3)_3\text{MoO})_2(\mu\text{-O})_2]$ (3), $[(\text{Cp}^*\text{Rh}(\mu\text{-SCH}_3)_3\text{MoO})_2(\mu\text{-O})(\mu\text{-S})]$ (4) 及び新奇なオクタモリブデート $[(\text{Cp}^*\text{Rh})_2(\mu\text{-SCH}_3)_3]_4[\text{Mo}_8\text{O}_{26}]$ (5), そしてヘキサモリブデート $[(\text{Cp}^*\text{Rh})_2(\mu\text{-SCH}_3)_3]_2[\text{Mo}_6\text{O}_{19}]$ (6) が生成することを見いだした。X-線結晶解析により、それらの化合物の固体構造を明らかにした。(ii) クラスター 2 では溶液中、symmetric structure asymmetric structure の異性化反応が起こっていることを見つけ、その反応を速度論的に解析した。このような反応が実際に解析されたのは、今回が初めてである。(iii) 四核クラスターである 2, 3, 4 のいずれも、溶液中で SCH_3 基の磁氣的平均化を起こすことを見いだした。 ^1H , ^{13}C , ^{17}O , NMR スペクトル及び ^1H シグナルの line-shape analysis をもとに、その平均化が Mo-S 結合の切断によって誘発されることを提案した。(iv) Mo-Mo 間に架橋 S 原子を持つクラスター 4 を見出した事により、三重立方体型酸化物クラスター 1 が、比較的穏やかな条件下で C-S 結合活性化を行うことを示した。(v) クラスター 5 が、新型のオクタモリブデート構造を持つこと、及び α 型 β 型のオクタモリブデート異性化反応における重要な中間体であることを、X 線結晶解析ならびに IR スペクトルより明らかにした。(vi) 含硫黄有機化合物として 1, 2- $\text{C}_6\text{H}_4(\text{SH})_2$ を用いた場合には、三重立方体型酸化物クラスター 1 中の Rh 原子と Mo 原子とが完全に分離し、二核構造を持つ錯体 $[(\text{Cp}^*\text{Rh})(\mu\text{-S}_2\text{C}_6\text{H}_4)]_2$ (7) と $\{[(\text{Cp}^*\text{Rh})_2(\mu\text{-S}_2\text{C}_6\text{H}_4)[\mu\text{-S}(\text{SO}_2)(\text{C}_6\text{H}_4)]\}$ (8) が、生成することを見いだした。そして X 線結晶解析によりそれらの化合物の構造を確立した。また 7 が、溶液中で単量体 二量体の平衡混合物として存在していることを明らかにした。

以上、本研究は、三重立方体型酸化物クラスター 1 とメルカプタン類との反応の特異性を明らかにすると共に、その反応系より新型の化合物を単離し、X 線結晶解析によりそれらの固体構造を確立する一方で、line-shape analysis 等を用いて複雑な溶液内動的挙動を解明したものであり、理学博士の学位論文に値すると認められた。また、申請者は学位論文の内容を 1 時間余りかけて英語で説明した。試験官はその発表に関し約 2 時間質問した。トリプルキューバン Mo 錯体の研究バックグラウンド、錯体の合成と精製、 ^1H 及び ^{17}O -NMR や X-線結晶解析による物質の同定など、この分野の専門知識を十分に備えていることが質疑応答より明らかになった。申請者は日本語も十分に話せるが、質疑応答は全部英語で行い、また論文も英語で書かれていたので語学力に関しては問題ないと判断された。公開發表での発表もよく準備されたわかりやすいものであり、一般の質疑応答も問題なかった。従って学位論文の試験には合格と判断した。