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Fragmentation of Triple Cubane-Framework in $[(Cp^*Rh)_4Mo_4O_{16}]$ ($Cp^*=\eta^5$-C_5Me_5) by MeSH into Tetranuclear Parts in $[\{Cp^*Rh(\mu\text{-}SMe)_3MoO\}_2(\mu\text{-}O)_2]$ and $[\{Cp^*Rh(\mu\text{-}SMe)_3MoO\}_2(\mu\text{-}O)(\mu\text{-}S)]$ Providing a Novel System for Studying Stereodynamics of Thiolate Complexes

Rimo XI, Bateer WANG,† Masaaki ABE, Yoshiki OZAWA,†† and Kiyoshi ISOBE*
Institute for Molecular Science, Department of Structural Molecular Science,
The Graduate University for Advanced Studies, Myodaiji, Okazaki 444
†Institute of Coordination Chemistry, Inner Mongolia Normal University,
Huhhot, Inner Mongolia 010022, China
††Department of Material Science, Himeji Institute of Technology, Harima Science Park City, Hyogo 678-12

Reaction of the triple cubane-type cluster $[(Cp^*Rh)_4Mo_4O_{16}]$ with MeSH gave two tetranuclear complexes of $[\{Cp^*Rh(\mu\text{-}SMe)_3MoO\}_2(\mu\text{-}O)_2]$ and $[\{Cp^*Rh(\mu\text{-}SMe)_3MoO\}_2(\mu\text{-}O)(\mu\text{-}S)]$ which were characterized by X-ray structural analysis. The stereodynamics of the two complexes was studied by variable-temperature ^1H and ^{17}O NMR as well as ^{13}C NMR spectroscopy.

Recently we found that triple cubane-framework in $[(Cp^*Rh)_4Mo_4O_{16}]$ is broken partly by methanol to give an incomplete double cubane-type cluster $[(RhCp^*)_2Mo_3O_9(OMe)_4]$.1) The triple cubane-framework, however, is reconstructed by methanethiol with formation of $[\{Cp^*Rh(\mu\text{-}SMe)_3MoO_2\}_2(\mu\text{-}O)]$ 2) and $[(Cp^*Rh)_2(\mu\text{-}SMe)_3]_4[Mo_8O_{26}]$.3) In the same system under different reaction conditions, we have found formation of other two new tetranuclear complexes $[\{Cp^*Rh(\mu\text{-}SMe)_3MoO\}_2(\mu\text{-}O)_2]$ (**1**) and $[\{Cp^*Rh(\mu\text{-}SMe)_3MoO\}_2(\mu\text{-}O)(\mu\text{-}S)]$ (**2**), both of which have two $Rh(\mu\text{-}SMe)_3Mo$ groups in the molecules. These tetranuclear complexes provide a novel system to investigate the stereodynamics of thiolate complexes.4)

A solution of $[(Cp^*Rh)_4Mo_4O_{16}]\cdot 2H_2O$ (0.600 g, 0.368 mmol) in MeOH (60 cm^3) was exposed to a vapor of MeSH (30 cm^3, 150 mmol, 30% in MeOH). Red crystals of complex **1**5) were collected in a 19% (0.140 g) yield6) after one week. Complex **2**5) was synthesized by adding a solution of $[(Cp^*Rh)_4Mo_4O_{16}]\cdot 2H_2O$ (0.200 g, 0.123 mmol) in MeOH (20 cm^3) to a refluxing solution of MeSH (5 cm^3, 25 mmol, 30% in MeOH) in MeOH (20 cm^3). After stirring for an hour the solvent was removed and the resulting orange powder was dissolved in a minimum of CH_2Cl_2 and chromatographed on a column of silica gel 60 with CH_2Cl_2-Me_2CO (15:1 by volume) as an eluent. The first fraction was evaporated to give an orange solid of **2** in a 17% (0.044 g) yield.6) The stoichiometries of reactions were based on the following equations (eq. 1 for **1** and eq. 2 for **2**).

$$[(Cp^*Rh)_4Mo_4O_{16}]\cdot 2H_2O + 16MeSH \rightarrow 2[\{Cp^*Rh(\mu\text{-}SMe)_3MoO\}_2(\mu\text{-}O)_2] + 2MeSSMe + 10H_2O \qquad \text{(eq. 1)}$$

$$[(Cp^*Rh)_4Mo_4O_{16}]\cdot 2H_2O + 20MeSH \rightarrow 2[\{Cp^*Rh(\mu\text{-}SMe)_3MoO\}_2(\mu\text{-}O)(\mu\text{-}S)] + 3MeSSMe + 2Me\bullet + 12H_2O \qquad \text{(eq. 2)}$$

In **2** the μ-S ligand may arise from the cleavage of the C–S bond of MeSH, but organic species from the resulting alkyl moieties is not detected yet. The dimethyl disulfide in eq. 1 and eq. 2 was confirmed by ^1H NMR in CD_3OD (δ 2.40). Complexes **1** and **2** were recrystallized from CH_2Cl_2 at room temperature and characterized by single crystal X-ray analysis.7) The molecular structures are shown in Fig. 1. The OMo(μ-O)(μ-X)MoO (X=O or S) framework was found to have a syn arrangement similar to those in all known cases.8) The three SMe ligands in both **1** and **2** link two different metal atoms, Rh(III) and Mo(V), to make $Cp^*Rh(\mu\text{-}SMe)_3Mo$ moieties which are bridged by O(1) and O(4) atoms for **1** or O(1) and S(7) atoms for **2** in a syn arrangement. In each complex, all six sulfur atoms of the SMe ligands prefer the Rh atoms in unequal bridging of the Rh····Mo spacing. The complexes have metal-metal bonds (2.564(1) Å for **1** and 2.666(1) Å for **2**) between the molybdenum atoms with a d^1-d^1 configuration, and hence are diamagnetic. Two sets of the three bridging SMe groups are disposed as in anticlockwise symmetric arrangements9) for **1** and **2**, viewed along the Rh(1)····Mo(1) and Rh(2)····Mo(2) axes. Although the enantiomers, the molecules with the clockwise symmetric arrangement, exist equally in the crystals, no molecule with an asymmetric arrangement9) was observed. This is probably due to one small terminal oxygen ligand in each Mo atom in **1** or **2**, which does not induce the serious terminal-bridge (μ-SR) interligand interaction described for $[\{Cp^*Rh(\mu\text{-}SMe)_3MoO_2\}_2(\mu\text{-}O)]$2) and $[Mo_2(CO)_2(L)(\mu\text{-}SR)_3(\eta^7\text{-}C_7H_7)]$ (L=CO, $P(OMe)_3$, R=Me, Et, Pr^i, Bu^t). The latter prefers for the asymmetric arrangement over the symmetric one when R is a large substituent.9b)

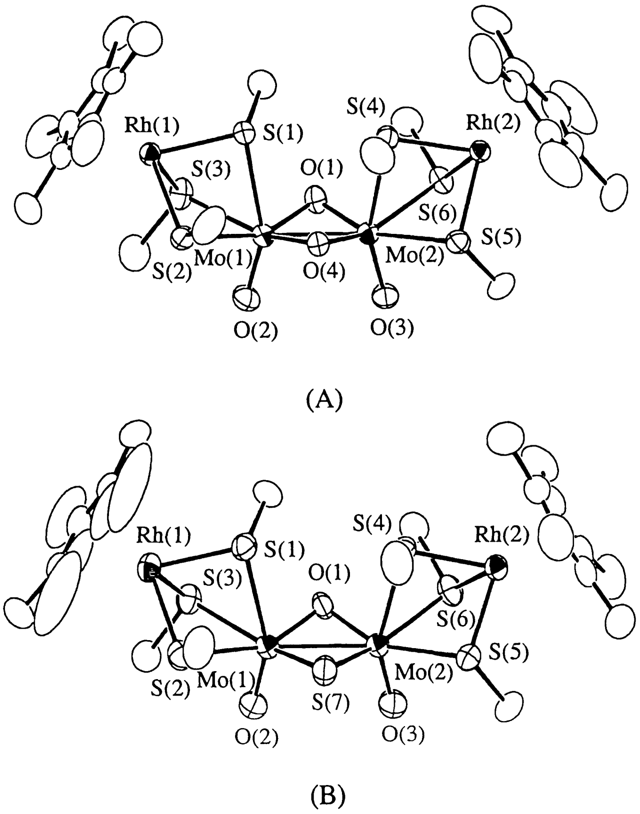
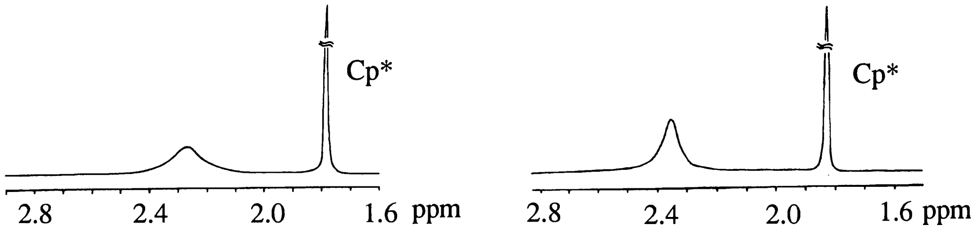


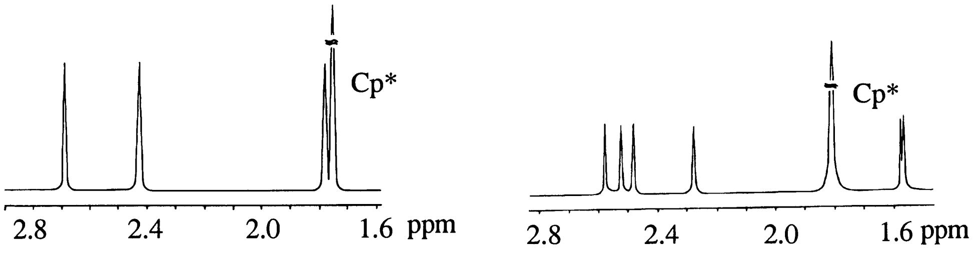
Fig. 1. ORTEP drawings of complex **1** (A) and **2** (B).

Complexes **1** and **2** show temperature-dependent ^1H NMR spectra in $CDCl_3$ and $C_6D_5NO_2$. On warming in $C_6D_5NO_2$, broadening then coalescence of the μ-SMe signals occurs at respective temperatures of 100 °C and 80 °C, then the signals become sharper with increases in temperature (Fig. 2A for **1** and Fig. 2B for **2**). These changes, which are reversed on cooling, may not simply be interpreted as the onset of rapid pyramidal inversion of the bridging sulfur atoms effecting a symmetry asymmetry arrangement interconversion such as that found in $L_nMo(\mu\text{-}SR)_3MoL_n$9) and $[\{Cp^*Rh(\mu\text{-}SMe)_3MoO_2\}_2(\mu\text{-}O)]$2) systems. The asymmetric isomers of **1** or **2**, even if produced at higher temperature, may also give three or six signals for the μ-SMe ligands, but such an interconversion would not attain the observed averaging of the μ-SMe ligands. A rapid isomerization between the syn and the anti configuration of the OMo(μ-O)(μ-X)MoO (X=O or S) framework in **1** and **2** is also not consistent with the results of the NMR measurements. The ^{17}O NMR spectra of **1** and **2** show no temperature-dependence for the oxygen signals of the Mo–O(terminal) and Mo–O (bridging) bonds. This indicates that the framework of OMo(μ-O)(μ-X)MoO (X=O or S) is strong enough so as not to undergo any dynamic behavior even at high temperature. An explanation of the complete averaging of the protons of μ-SMe ligands is the cleavage of the Mo–S(μ-SMe) bond. The μ-SMe ligands in **1** and **2** form weak bonds with Mo atoms: molybdenum-sulfur distances generally fall within the range 2.411-2.549 Å,[9b)] but the corresponding distances in both **1** and **2** are much longer (2.556(2)-2.736(3) Å) except for Mo(2)–S(6) (2.548(2) Å) in **1**. This is particularly true for the Mo–S bond which is trans to the Mo–O (terminal) bond. This bond is very long (2.736(3) and 2.704(3) Å for **1**; 2.734(2) and 2.717(2) Å for **2**) and is likely to be broken at high temperature. It is also worthwhile to note that in many known cases the Mo atoms of the OMo(μ-O)(μ-X)MoO (X=O or S) framework can achieve either 5 or 6 coordination, and that the terminal oxo group has the ability to weaken the bond trans to it, and in the extreme this trans ligand is absent.[8a)] We believe that this bond cleavage induces the complete averaging of all protons of the μ-SMe ligands. M–μ-SR bond cleavage has also been proposed for the cis $\rightleftharpoons$ trans isomerization in the double bridged μ-SR system of $[\{M(CO)(\mu\text{-}SR)(\eta^5\text{-}C_5H_5)\}_2]$ (M=Fe and Ru; R=Me, CH_2Ph, Ph).[10)] The details of this averaging process are currently under investigation.



1 in $C_6D_5NO_2$ (at 120 °C)

2 in $C_6D_5NO_2$ (at 120 °C)



1 in $C_6D_5NO_2$ (at 23 °C)

2 in $CDCl_3$ (at -20 °C)

(A)

(B)

Fig. 2. ^1H NMR spectra of complex **1** (A) in $C_6D_5NO_2$ and complex **2** (B) in $C_6D_5NO_2$ and $CDCl_3$.

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5) Complex **1**: Anal. Found: C, 30.96; H, 4.76%. Calcd for $C_{26}H_{48}Mo_2O_4Rh_2S_6$ (M.W.=1014.72): C, 30.77; H, 4.77%. IR (KBr, cm^{-1}) 940 (s, ν(Mo–O)), 723(m, ν(Mo–O)); (in $CHCl_3$, cm^{-1}) 940 (s, ν(Mo–O)), the 723 cm^{-1} band overlapping with those of chloroform. ^1H NMR ($CDCl_3$, 23 °C, δ): 2.54 (6H, s, SMe), 2.20 (6H, s, SMe) 1.81(30H, s, C_5Me_5), 1.60 (6H, s, SMe). ^{13}C NMR ($CDCl_3$, 23 °C, δ): 96.9 (d, $J_{Rh\text{-}C}$=6.1 Hz, C_5Me$_5$), 17.3 (s, SMe), 13.0 (s, SMe), 12.5 (s, SMe), 9.4 (s, C_5*Me*$_5$). ^{17}O NMR ($CDCl_3$, 23 °C, δ relative to H_2O): 938 (s, Mo–O_T), 595 (s, Mo–O_B) (O_T=terminal oxygen; O_B=bridging oxygen). Complex **2**: Anal. Found: C, 30.04; H, 4.56%. Calcd for $C_{26}H_{48}Mo_2O_3Rh_2S_7$ (M.W.=1030.78): C, 30.06; H, 4.66%. IR (KBr, cm^{-1}) 948 (sh, ν(Mo–O)), 927 (s, ν(Mo–O)), 708 (m, ν(Mo–O)); (in $CHCl_3$, cm^{-1}) 948 (sh, ν(Mo–O)), 927 (s, ν(Mo–O)), the 708 cm^{-1} band overlapping with those of chroform. ^1H NMR ($CDCl_3$, 23 °C, δ): 2.60 (3H, s, SMe), 2.51 (3H, s, SMe), 2.47 (3H, s, SMe), 2.27 (3H, s, SMe), 1.80 (30H, s, C_5Me_5), 1.57 (6H, s, SMe). ^{13}C NMR ($CDCl_3$, 23 °C, δ): 96.8 (d, $J_{Rh\text{-}C}$=6.1 Hz, C_5Me$_5$), 18.7 (s, SMe), 17.5 (s, SMe), 16.4 (s, SMe), 15.0 (s, SMe), 13.6 (s, SMe), 12.8 (s, SMe), 9.4 (s, C_5*Me*$_5$). ^{17}O NMR ($CDCl_3$, 23 °C, δ relative to H_2O): 954 (s, Mo–O_T), 944 (s, Mo–O_T), 578 (s, Mo–O_B).

6) Along with the formation of complex **1**, a prolonged reaction also gives a hexamolybdate $[(Cp^*Rh)_2(\mu\text{-}SMe)_3]_2[Mo_6O_{19}]$. The relatively low yield of complex **2** is due to the formation of the hexamolybdate (in a 16% yield, 0.041 g), **1** (in a 22% yield, 0.054 g), and some other unidentified decomposition products.

7) Crystal data **1**: monoclinic, space group *C*2/*c* (No. 15), *a*=25.334(4), *b*=21.271(2), *c*=17.831(3) Å, β=129.70(5)°, *V*=7393(2) Å^3, *Z*=8, D_c=1.823 g·cm^{-3}. **2**: orthorhombic, space group *Pcab* (No. 61), *a*=16.902(3), *b*=26.631(3), *c*=16.855(2) Å, *V*=7587(3) Å^3, *Z*=8, D_c=1.805 g·cm^{-3}. A total of 11088 (**1**) (the range $2° < 2\theta < 60°$) and 10249 (**2**) (the range $2° < 2\theta < 55°$) reflections were collected on a Rigaku AFC-5 diffractometer using graphite-monochromated Mo Kα (λ=0.71073 Å) radiation at 296 K. The structures were solved by usual heavy-atom methods. Crystallographic calculations of **1** and **2** were carried out using SHELXS-86 and UNICS III program packages on a HITAC M680 computer at the IMS Computer Centre. The final *R* values are 0.045 (**1**, 8807 independent reflections) and 0.044 (**2**, 5051).

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