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New Linear-Type Tetranuclear Complex, [{Cp*Rh(μ-SMe)$_3$Mo(O)$_2$}$_2$(μ-O)] (Cp* = η^5-C$_5$Me$_5$)

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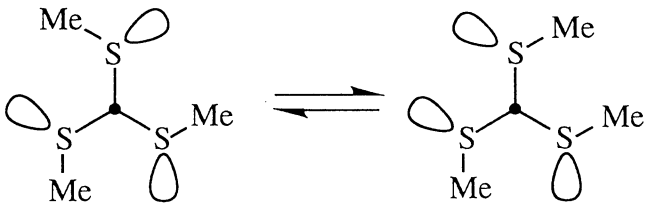
A mixed metal tetranuclear complex with two Mo^{VI}(μ-SMe)$_3$Rh^{III} groups, [{Cp* Rh(μ- SMe)$_3$Mo(O)$_2$}$_2$(μ-O)] has been obtained from the reaction of the triple-cubane type oxide cluster [(Cp*Rh)$_4$Mo$_4$O$_{16}$] with MeSH. The complex has been characterized by X-ray analysis and variable-temperature ^{1}H NMR spectroscopy. The latter has revealed that the complex exists as a mixture of isomers which show interconversion due to the inversion at the pyramidal sulfur center.

Several low valent molybdenum binuclear complexes with three bridging μ-SR groups, such as [(η^7-C$_7$H$_7$) Mo(μ-SR)$_3$Mo(η7-C$_7$H$_7$)]$^+$ (R = Et, Pr, Bu, Ph, CH$_2$Ph),[1] and [(CO)$_2$(L)Mo(μ-SR)$_3$Mo(η7-C$_7$H$_7$)] (L= CO, P(OMe)$_3$, R = Me, Et, Pr^i, Bu^t),[2] have been synthesized. These complexes exist as two isomers in solution and the isomerism arises from different relative orientations of the R groups of μ-SR. These isomers interconvert rapidly, via inversion at the pyramidal sulfur atom (Scheme 1). In the course of studying the reactivity of the triple-cubane type oxide cluster, [(Cp*Rh)$_4$Mo$_4$O$_{16}$],[3] toward MeSH, we have found formation of a new Rh$_2$Mo$_2$ tetranuclear complex, [{Cp*Rh(μ-SMe)$_3$ Mo(O)$_2$}$_2$(μ-O)] (**1**). This compound



symmetric asymmetric

Scheme 1.

contains two [Rh(μ-SMe)$_3$Mo] groups in which the μ-SMe ligands link different metal atoms, Rh^{III} and Mo^{VI} (the highest oxidation state for molybdenum). In this paper we report the synthesis and the molecular structure of the tetranuclear complex as well as its fluxionality in solution.

A solution of $[(Cp^*Rh)_4Mo_4O_{16}]\cdot 2H_2O$ (0.35 g, 0.21 mmol) in CH_2Cl_2 (15 cm^3) was added dropwise to a solution of MeSH (0.720 g, 15 mmol) in CH_2Cl_2 (10 cm^3). After stirring for 30 min, the solvent was removed in vacuo to leave an orange residue. It was dissolved in a minimum of CH_2Cl_2 and chromatographed on a silica gel column. Elution with CH_2Cl_2: Me_2CO (15:1 by volume) gave two orange fractions. From the first fraction an orange solid of **1** was obtained in a 23.3% yield (90 mg) based on eq. 1.[4] The second fraction gave an orange red solid of $[\{Cp^*Rh(\mu\text{-}SMe)_3MoO\}_2(\mu\text{-}O)_2]$[5] in a 9.2% yield (40 mg).

$$[Cp^*RhMoO_4]_4\cdot 2H_2O + 12MeSH \rightarrow 2[\{Cp^*Rh(\mu\text{-}SMe)_3Mo(O)_2\}_2(\mu\text{-}O)] + 8H_2O \qquad \text{(eq. 1)}$$

Complex **1** was recrystallized from MeCN at room temperature. The molecular structure is shown in Fig. 1.[6] An oxygen atom (O1) connects two moieties of $Cp^*Rh(\mu\text{-}SMe)_3Mo(O)_2$ where three SMe ligands bridge Rh^{III} and Mo^{VI} atoms, metals whose formal oxidation states are notably different from each other. The two molybdenum atoms are also incorporated into the $(O)_2Mo\text{-}O\text{-}Mo(O)_2$ framework. Each molybdenum and rhodium atom is six co-ordinate with a distorted octahedral geometry. The Mo1-O1-Mo2 bond angle is slightly bent (175(1)°). The two terminal oxygens bound to each Mo are situated in cis positions similar to those in other known dioxo Mo^{VI} compounds.[7] The overall geometry of **1**, however, is transoid around the Mo1····Mo2 axis. The bulkiness of the $Cp^*Rh(\mu\text{-}SMe)_3Mo(O)_2$ groups does not allow **1**

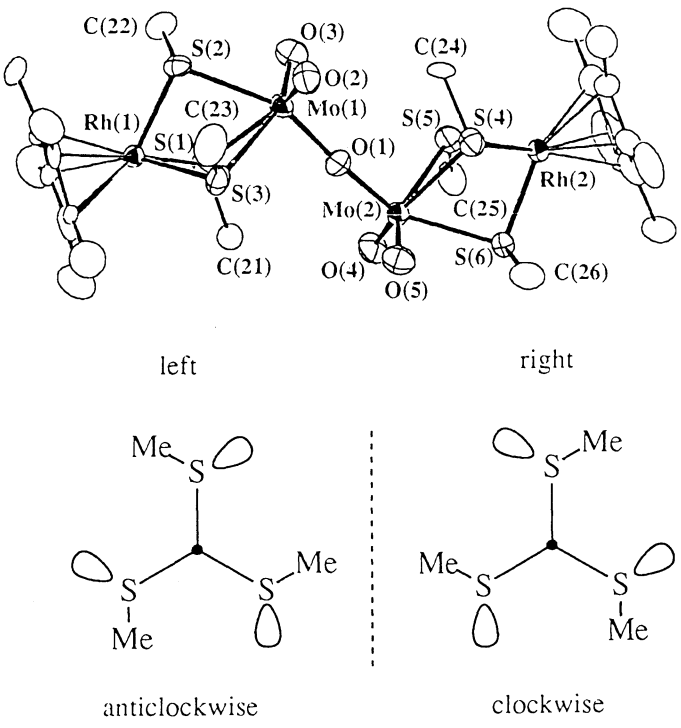


Fig. 1. ORTEP drawing of complex **1** and view of the geometry of three SMe ligands down the Rh····Mo axis.

to take a cisoid geometry. All of the six sulfur atoms prefer the Rh atoms in unequal bridging of the Rh····Mo spacing. In particular, the Mo-S bonds trans to the Mo-O(terminal) bonds are substantially longer (mean distance 2.696 Å) than the others (mean distance 2.554 Å). Two sets of the three bridging SMe groups are disposed in anticlockwise and clockwise symmetric arrangement, as viewed along the axes of Rh1····Mo1 and Rh2····Mo2, respectively (Fig. 1).

Although hydrogen atoms of the μ-SMe ligands were not located in the structural determination, we have found close interligand (terminal-bridge) contacts between O2····C23 (3.12(3) Å), O3····C22 (3.02(3) Å), O4····C25 (3.08(3) Å), and O5····C26 (2.96(3) Å). Their distances are below the O····Me van der Walls sum (3.4 Å[2]). The minimization of interligand contacts is attained by adoption of asymmetric arrangement in the M(μ-SR)$_3$M group. The complex of [(CO)$_2$(L)Mo(μ-SR)$_3$Mo(η^7-C$_7$H$_7$)] (L = CO, PR'$_3$) with interligand contacts between L and SR exists as two isomers with symmetric and asymmetric arrangement (an increased proportion of the asymmetric isomer with increasing size of the R group in μ-SR), and interconvert rapidly at ambient temperature and above.[2)]

It therefore seems possible that complex **1** may also exist as a mixture of isomers with different μ-SMe arrangements in two [Rh(μ-SMe)$_3$Mo] groups. The IR spectrum of **1** was measured in CHCl$_3$ in the Mo-O(terminal) vibrational region at room temperature. It is nearly the same as that in solid except for the intensity ratio of 918 and 891 cm^{-1} bands (the band of 891 cm^{-1} is weaker than the 918 cm^{-1} band in solution, but this trend is opposite in the solid state). ^{1}H and ^{13}C NMR spectra in CDCl$_3$ solutions at -40 °C, however, clearly show the existence of the isomers which exhibit two series of three μ-SMe signals, ^{1}H NMR: δ 2.03, 2.19, and 2.22;[8)] δ 1.96, 2.22,[8)] and 2.26 (intensity ratio *ca.* 1:3), ^{13}C NMR: δ 12.72, 13.65, and 15.45; δ 13.18, 14.07, and 15.33.[8)] On warming, broadening and then coalescence of the μ-SMe signals occurs. Upon reaching the coalescence temperatures three proton signal pairs (δ 2.03 + δ 1.96, δ 2.19 + δ 2.22, and δ 2.22 + δ 2.26) for the μ-SMe groups of both symmetric and asymmetric arrangements have coalesced separately. However, since the chemical shifts of the last two signal pairs are close, they appeared as a broad single peak at δ 2.19 at 50 °C (Fig. 2), therefore their exact coalescence temperatures were not observed clearly.

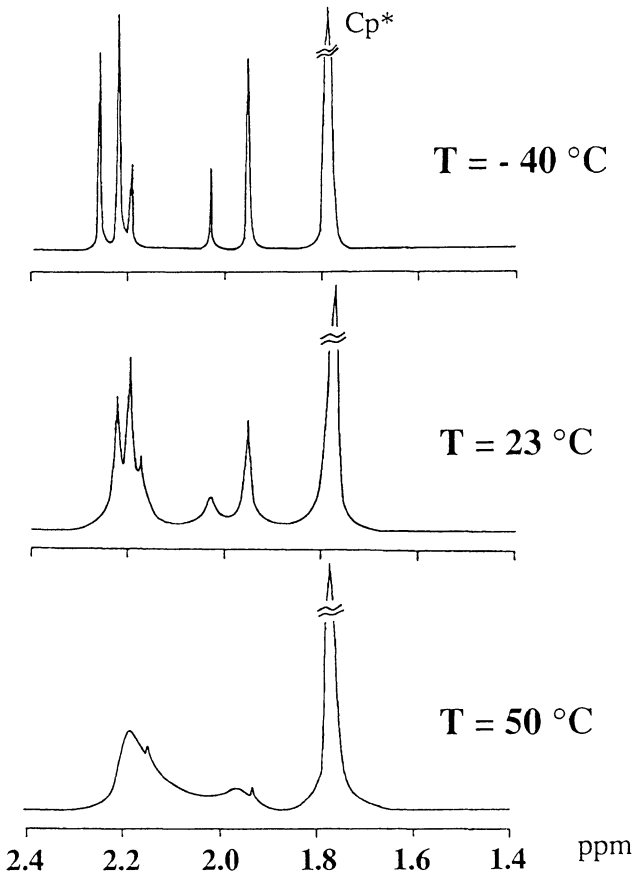


Fig. 2. Variable temperature ^{1}H NMR spectra of complex **1** in CDCl$_3$.

This dynamic behavior is due to interconversion of arrangements through

inversion at the sulfur atom (Scheme 1). For the signal pair at δ 2.03 and δ 1.96 (the coalescence temperature is 45 °C) the activation parameters of the dynamic process are estimated by the coalescence temperature method.[9] The estimated $\Delta G^{\neq}$ value (66.4 ± 1.0 kJ / mol) is slightly larger by *ca.* 10 kJ / mol than those of the $Mo(\mu\text{-}SR)_3Mo$ systems in $[(\eta^5\text{-}C_7H_7)Mo(\mu\text{-}SR)_3Mo(\eta^7\text{-}C_7H_7)][BF_4]$ and $[(CO)_2(L)Mo(\mu\text{-}SR)_3Mo(\eta^7\text{-}C_7H_7)]$.[1,2] The details of the fluxinality of related tetranuclear complexes are currently under investigation.

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References

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3) Y. Hayashi, K. Toriumi, and K. Isobe, *J. Am. Chem. Soc.*, **110**, 3666 (1988).

4) **1**: Anal. Found: C, 30.56; H, 4.68%. Calcd for $C_{26}H_{48}Mo_2O_5Rh_2S_6$ (M.W. = 1030.72): C, 30.30; H, 4.69%. IR (KBr, cm^{-1}) Mo-O stretching region: 951(m), 919(s), 891(s), 750(s). ^1H NMR ($CDCl_3$, 23 °C): C_5Me_5 δ 1.78 (s), SCH_3 δ 1.95 (s), δ 2.03(s), δ 2.17(s), δ 2.19(s), δ 2.22(s). ^{13}C NMR ($CDCl_3$, 23 °C): $C_5\mathit{Me}_5$ δ 9.41(s), SCH_3 δ 12.89(s), δ 13.56(s), δ 13.83(s), δ 15.29(s), C_5Me_5 δ 97.25 (d, $J_{Rh\text{-}C}$ = 6.1 Hz).

5) This compound will be reported elsewhere.

6) Crystal data are as follows: monoclinic, space group $P2_1/n$, a = 15.348(3) Å, b = 14.059(3) Å, c = 17.879(3) Å, β = 107.11(2)°, Z = 4, V = 3690(1) $Å^3$, Dx = 1.855 g cm^{-3}. Intensity data were collected on a Rigaku AFC-5 diffractometer with graphite-monochromated MoKα radiation in the $2\theta \leq 60°$ range. The structure was solved by Patterson methods (SHELXS-86) and refined by a block-diagonal least-squares technique using UNICS III program. The current R value of **1** is 0.064 for 2378 independent absorption-corrected reflections.

7) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," 5th ed, John Wiley & Sons, New York (1988), p. 828.

8) In ^1H NMR spectrum, the signals of δ 2.22 are accidentially overlapped in the two series. The isomers may involve three possible conformers with respect to the arrangements of the SMe groups in two $[Rh(\mu\text{-}SMe)_3Mo]$ units in **1**: two symmetric arrangements, two asymmetric arrangements, and one symmetric and the other asymmetric arrangement, in the two units. Within the same arrangement the corresponding S-methyl signals give almost the same chemical shifts both in ^1H and in ^{13}C NMR spectra. At the present stage of the study, we cannot determine which series of signals arises from which arrangement.

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