

Synthesis and Reactivity of a Bis(disulfide)-Bridged RuMo_3S_4 Double-Cubane Cluster: A New Family of Nona- or Decanuclear Mixed-Metal Sulfide Clusters with Two RuMo_3S_4 Units

Izuru Takei,[†] Koji Kobayashi, Keita Dohki, and Masanobu Hidai*

Department of Materials Science and Technology, Faculty of Industrial Science and Technology, Tokyo University of Science, Noda, Chiba 278-8510, Japan

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A bis(disulfide)-bridged RuMo_3S_4 double-cubane cluster $[\{(\text{Cp}^*\text{Mo})_3(\mu_3\text{-S})_4\text{Ru}\}(\mu_2\text{-}\eta^2\text{-}\eta^1\text{-S}_2)]_2[\text{PF}_6]_2$ (**2**, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) is readily available from cluster $[(\text{Cp}^*\text{Mo})_3(\mu_3\text{-S})_4\text{RuH}_2(\text{PPh}_3)][\text{PF}_6]$ (**1**) and S_8 . The reactions of cluster **2** with $[\text{M}(\text{PPh}_3)_4]$ ($\text{M} = \text{Pd}, \text{Pt}$) give rise to the formation of a new family of nona- or decanuclear mixed-metal sulfide clusters, $[\{(\text{Cp}^*\text{Mo})_3(\mu_3\text{-S})_4\text{Ru}\}_2(\mu_3\text{-S})_2\{\text{Pd}(\text{S})(\text{PPh}_3)\}]_2[\text{PF}_6]_2$ (**3**), $[\{(\text{Cp}^*\text{Mo})_3(\mu_3\text{-S})_4\text{Ru}\}_2(\mu_3\text{-S})_2\{\text{Pd}(\text{PPh}_3)_2(\mu_2\text{-S})\}]_2[\text{PF}_6]_2$ (**4**), and $[\{(\text{Cp}^*\text{Mo})_3(\mu_3\text{-S})_4\text{Ru}\}_2(\mu_3\text{-S})_2\{\text{Pt}(\text{PPh}_3)_2\}]_2[\text{PF}_6]_2$ (**5**), with two RuMo_3S_4 cubane units, the structures of which have been determined by X-ray diffraction studies.

Iron sulfide based clusters are observed in metalloproteins such as ferredoxin, nitrogenase, $[\text{Fe}]$ -hydrogenase, and carbon monoxide dehydrogenase (CODH). To date, a variety of metal sulfide clusters have been prepared as synthetic models and their reactivity has been extensively investigated in order to shed light on the functions of metalloproteins.¹ The M_4S_4 cubane structure is a fundamental unit found in those metalloproteins. In the early 1970s, Holm discovered the spontaneous formation of $[\text{Fe}_4\text{S}_4(\text{SR})_4]^{2-}$ clusters from reaction mixtures of FeCl_3 , NaSH , and NaSR .² Later, double-cubane clusters containing two MoFe_3S_4 units potentially related to FeMo-co were prepared by a similar self-assembly route using the reaction system of FeCl_3 , RS^- , and $[\text{MoS}_4]^{2-}$.³

Further, extensive investigations have been performed on the synthesis and reactivity of cubane-type metal sulfide clusters.⁴ We have long been interested in the rational synthesis and reactivity of metal sulfide clusters containing especially noble metals because we are aware that metalloproteins do not contain noble metals but the unique catalysis of noble metal sulfide clusters is expected.⁵ Actually, PdMo_3S_4 cubane clusters exhibit remarkable catalytic activity for some reactions of alkynes including intramolecular cyclization of alkyneic acids and aminoalkynes to form enol lactones and cyclic imines, respectively.⁶ It is to be noted that those reactions occurring at the unique Pd atom embedded in the Mo_3S_4 aggregate have some resemblance to catalysis of aconitase containing a Fe_4S_4 unit.⁷

We now report the synthesis and reactivity of a bis-(disulfide)-bridged RuMo_3S_4 double-cubane cluster, leading to the formation of a new family of palladium or platinum sulfide clusters with the two RuMo_3S_4 units. Noteworthy is the fact that the Pd or Pt atom in these clusters is connected to the two RuMo_3S_4 cubane units through bridging sulfide ligands, whereas an Fe atom is bound to a Fe_4S_4 cubane unit

* To whom correspondence should be addressed. E-mail: hidai@rs.noda.tus.ac.jp.

[†] Current address: Mitsubishi Kagaku Institute of Life Science (MITILS), Machida, Tokyo 194-8511, Japan.

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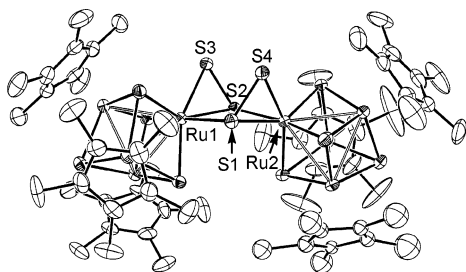
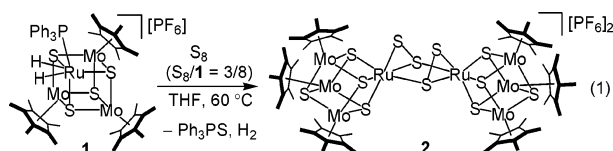


Figure 1. Structure of the cationic part of cluster **2** showing 30% thermal ellipsoids. H atoms and half of the disordered C atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Ru–Mo_{av}, 2.876(1); Mo–Mo_{av}, 2.863(1); Ru1–S1, 2.457(2); Ru1–S2, 2.412(3); Ru1–S3, 2.381(2); Ru2–S4, 2.372(2); Ru2–S1, 2.408(3); Ru2–S2, 2.445(2); S1–S4, 2.013(3); S2–S3, 2.016(3); S1–Ru1–S2, 78.14(9); S1–Ru2–S2, 78.43(9); S2–Ru1–S3, 49.74(8); S1–Ru2–S4, 49.82(9).

via the S atom of a cysteinyl ligand in [Fe]–hydrogenase,⁸ an Fe atom is coordinated to a NiFe₃S₃ unit via two sulfide ligands in the [NiFe]–CODH C cluster,^{9a} and a Ni atom is connected to a Fe₄S₄ unit via the S atom of a cysteinyl ligand in the [NiFe]–CODH A cluster.^{9b}

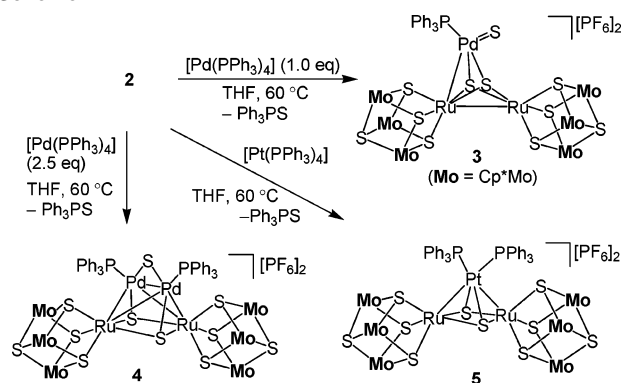
Recently, we reported that the RuMo₃S₄ cubane cluster, [(Cp*Mo)₃(μ₃-S)₄RuH₂(PPh₃)] [PF₆] (**1**, Cp* = η⁵-C₅Me₅), is readily available from the reaction of the trimolybdenum sulfide cluster [(Cp*Mo)₃(μ₂-S)₃(μ₃-S)] [PF₆] with [RuH₄(PPh₃)₃].¹⁰ When cluster **1** was allowed to react with S₈ (molar ratio: S₈/1 = 3/8) at 60 °C for 24 h in tetrahydrofuran (THF), the RuMo₃S₄ double-cubane cluster bridged by two disulfide (S₂²⁻) ligands, [(Cp*Mo)₃(μ₃-S)₄Ru}(μ₂-η²:η¹-S₂)₂] [PF₆]₂ (**2**), was obtained in 55% yield, concurrent with the formation of Ph₃PS and the evolution of H₂, as shown in eq 1.¹¹ The molecular structure of **2** has been determined



by an X-ray diffraction study.¹² Cluster **2** has two RuMo₃S₄ cores in which the two Ru atoms are separated at a Ru1···Ru2 distance of 3.7499(12) Å and bridged by two μ₂-η²:η¹-disulfide groups (Figure 1). Therefore, the three Cp* groups are nonequivalent in the solid state. In accordance with this structure, the ¹H NMR spectrum of **2** exhibits three broad singlets at δ 2.01, 2.11, and 2.14. The nonbridging S atoms in cluster **2** are in a syn arrangement, and the two planes containing a Ru and a bridging disulfide ligand are nearly parallel with the dihedral angle 174°. Previously,

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 (11) The formation of Ph₃PS was confirmed by ³¹P{¹H} NMR analysis.
 (12) Crystallographic data for **2**: monoclinic, P2₁/c (No. 14), *a* = 17.102(6) Å, *b* = 30.512(11) Å, *c* = 17.102(6) Å, β = 108.1390(16)°, *V* = 8890(6) Å³, *Z* = 4, *D*_{calcd} = 1.778 g cm⁻³, *R*₁ = 0.0568, *wR*₂ = 0.1956, GOF = 1.025.

Scheme 1



Holm and co-workers prepared [Et₄N]₄[[{Fe(S-*p*-C₆H₄X)}₃-(μ₃-S)₄Mo](μ₂-η²:η¹-S₂)₂] (X = Cl, Br), in which the two [MoFe₃S₄]³⁺ cores are bridged by the two S₂²⁻ ligands in the same bridging mode as that of cluster **2**.¹³

The results of the reactions of cluster **2** with group 10 noble metal complexes [M(PPh₃)₄] (M = Pd, Pt) are summarized in Scheme 1. When cluster **2** was allowed to react with an equimolar amount of [Pd(PPh₃)₄] at 60 °C for 18 h in THF, a heterotrimetallic PdRu₂Mo₆ cluster [(Cp*Mo)₃(μ₃-S)₄Ru₂}(μ₃-S)₂{Pd(S)(PPh₃)}] [PF₆]₂ (**3**)¹⁴ was obtained in 38% yield.¹¹ Cluster **3** consists of two RuMo₃S₄ cubane cores unsymmetrically connected by two μ₃-S ligands and a Pd(S)(PPh₃) fragment (Figure 2a). The Pd–Ru1 [2.932(1) Å] and Ru–Ru [3.105(2) Å] distances indicate the presence of a metal–metal bond (Table 1). The long Pd···Ru2 distance [3.368(2) Å] suggests the absence of a direct Pd–Ru interaction. On the other hand, treatment of cluster **2** with 2.5 equiv of [Pd(PPh₃)₄] under the same reaction conditions resulted in the formation of a novel Pd₂Ru₂Mo₆ cluster containing two Pd(PPh₃) fragments between two RuMo₃S₄ cubane cores, formulated as [(Cp*Mo)₃(μ₃-S)₄Ru₂}(μ₃-S)₂-(Pd(PPh₃))₂(μ₂-S)] [PF₆]₂ (**4**),¹⁵ as dark-brown crystals in 42% yield.¹¹ Interestingly, the reaction of cluster **3** with an excess amount of [Pd(PPh₃)₄] did not afford cluster **4** under the same or more forcing conditions. In contrast to cluster **3**, a sulfur ligand is bridging between the two Pd(PPh₃) fragments in a μ₂-S mode (Figure 2b). Cluster **4** has a tetrahedral Pd₂Ru₂ framework having two capping μ₃-S ligands on both PdRu₂ planes, in which the Ru–S and Pd–S bond lengths are in the range of 2.290–2.384 Å and are not exceptional (Table 1). Among the six edges of the Ru₂Pd₂ tetrahedron, only the Ru···Ru separation of 3.500(1) Å corresponds to a nonbonding interaction. In the ¹H and ³¹P-

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 (14) Crystallographic data for **3**: triclinic, P1̄ (No. 2), *a* = 11.4628(7) Å, *b* = 18.1960(9) Å, *c* = 26.855(2) Å, α = 95.954(2)°, β = 100.126(3)°, γ = 97.109(2)°, *V* = 5426.3(5) Å³, *Z* = 2, *D*_{calcd} = 1.801 g cm⁻³, *R*₁ = 0.0680, *wR*₂ = 0.0840, GOF = 1.047.
 (15) Crystallographic data for **4**: triclinic, P1̄ (No. 2), *a* = 18.241(3) Å, *b* = 18.610(3) Å, *c* = 22.053(4) Å, α = 72.338(7)°, β = 87.748(8)°, γ = 69.835(6)°, *V* = 6678.5(20) Å³, *Z* = 2, *D*_{calcd} = 1.738 g cm⁻³, *R*₁ = 0.0670, *wR*₂ = 0.2020, GOF = 1.027. The structure refinement has essentially converged except for some coordinates corresponding to the solvent molecules (largest shift/error ~ 0.5). For further information, please see the Supporting Information.

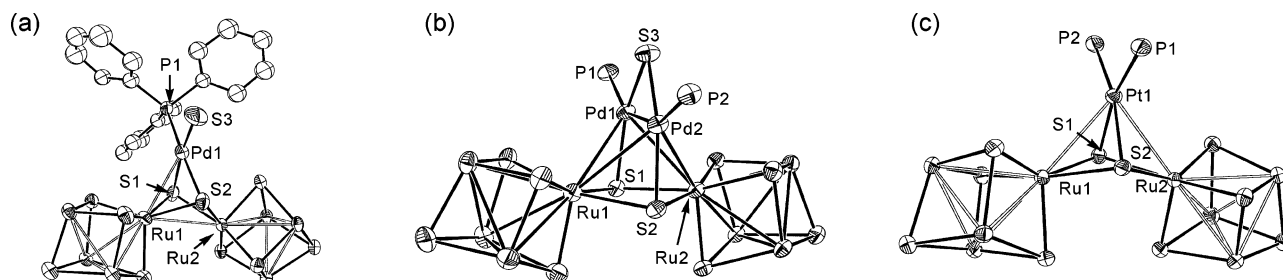


Figure 2. Structures of the cationic parts of clusters **3** (a), **4** (b), and **5** (c). Thermal ellipsoids are shown at the 30% probability level. Cp* groups and half of the disordered C and P atoms in **3** as well as phenyl groups and Cp* groups in **4** and **5** are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) for **3–5**

	3 (M = Pd)	4 (M = Pd)	5 (M = Pt)
Ru1–M1	2.932(1)	2.9659(9)	3.0155(7)
Ru2–M1		3.057(1)	3.0155(7)
Ru1–Pd2		3.0436(9)	
Ru2–Pd2		3.057(1)	
Pd1–Pd2		2.655(1)	
Ru1–Ru2	3.105(2)		
Ru1–S1	2.376(4)	2.361(3)	2.388(2)
Ru1–S2	2.341(4)	2.384(2)	2.368(2)
Ru2–S1	2.350(4)	2.360(2)	2.371(2)
Ru2–S2	2.342(4)	2.377(3)	2.378(2)
M1–S1	2.314(4)	2.310(2)	2.344(2)
M1–S2	2.356(4)		2.347(2)
M1–S3	2.373(7)	2.245(3)	
Pd2–S2		2.290(2)	
Pd2–S3		2.232(2)	
Ru–Mo _{av}	2.901(3)	2.895(3)	2.913(1)
Mo–Mo _{av}	2.863(3)	2.855(3)	2.861(1)
Ru1–M1–Ru2		71.03(3)	75.80(2)
Ru1–Pd2–Ru2		70.01(3)	
M1–Ru1–Ru2	67.76(2)		
S1–M1–S2	78.7(2)		73.44(6)
S1–Ru1–S2	77.7(2)	83.97(9)	72.27(6)
S1–Ru1–S2	78.2(2)	84.14(9)	72.39(6)

{¹H} NMR spectra (CD₂Cl₂), the protons of the six Cp* groups and the two P atoms are observed as singlets, indicating a symmetrical structure with two mirror planes for cluster **4** in solution. Previously, Rauchfuss et al. showed versatility of the bis(disulfide)-bridged diruthenium complex [(Cp**Ru*)₂(μ₂-η²:η²-S₂)(μ₂-η¹:η¹-S₂)] as a precursor for the synthesis of polynuclear transition-metal sulfur clusters containing homonuclear Ru₃ or Ru₄ and heteronuclear Ru₂-Rh cores.¹⁶ Ogino et al. succeeded in the preparation of early late heterobimetallic Ru₂W₂ or Ru₂W clusters by reacting [(Cp**Ru*)₂(μ₂-η²:η²-S₂)(μ₂-η¹:η¹-S₂)] with [W(CO)₃(MeCN)₃].¹⁷ We also demonstrated the synthesis of heterobimetallic Pd₂-Ru₂ and PtRu₂ clusters from the reaction of [(Cp**Ru*)₂(μ₂-

η¹:η¹-S₂)(μ₂-SP^r)₂] with [Pd(PPh₃)₄] and [Pt(PPh₃)₄], respectively.¹⁸ We thus treated cluster **2** with [Pt(PPh₃)₄] (1.0–2.5 equiv) in a manner similar to the reaction with [Pd(PPh₃)₄], which resulted in the formation of the heterotrimetallic PtRu₂-Mo₆ cluster [(Cp**Mo*)₃(μ₃-S)₄Ru]₂(μ₃-S)₂{Pt(PPh₃)₂}[PF₆]₂ (**5**)¹⁹ in moderate yield.¹¹ It is to be noted that no cluster similar to cluster **4** was obtained by treatment of cluster **2** with an excess of [Pt(PPh₃)₄]. Figure 2c depicts the X-ray structure of **5**, which has an almost isosceles PtRu₂ triangle capped by two μ₃-sulfide ligands from both sides. The Pt–Ru distances [3.0155(7) Å] are relatively long, which suggests weak Pt–Ru bonding interactions (Table 1). Regardless of these Pd–Ru interactions, the coordination geometry around the Pt atom is square-planar. Finally, it is to be emphasized that these new clusters reported here can be described in terms of the 18e[−] rule.

In summary, a bis(disulfide)-bridged RuMo₃S₄ double-cubane cluster **2** is readily available from cluster **1** and S₈. The reactions of cluster **2** with [M(PPh₃)₄] (M = Pd, Pt) give rise to the formation of a new family of nona- or decanuclear mixed-metal sulfide clusters, **3–5**, with two RuMo₃S₄ cubane units. Investigations on the reactivity of these clusters as well as the reaction of cluster **2** with other transition-metal complexes are now in progress.

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Supporting Information Available: Experimental details for the preparation of **2–5** (PDF) and detailed crystallographic data for **2–5** in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (19) Crystallographic data for **5**: monoclinic, *P*2₁/*n* (No. 14), *a* = 17.4712(9) Å, *b* = 30.631(2) Å, *c* = 23.555(2) Å, β = 100.6230(8)°, *V* = 12390.0(12) Å³, *Z* = 4, *D*_{calcd} = 1.793 g cm^{−3}, *R*₁ = 0.0640, *wR*₂ = 0.1880, GOF = 1.050.