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Article

Synthesis and Characterization of a Twin Cubane-Type Molybdenum−Rhodium−Sulfur Cluster, [{Mo₃RhCp*S₄(H₂O)₇(O)}₂]⁸⁺. X-ray Structure of [{Mo₃RhCp*S₄(H₂O)₇(O)}₂](CH₃C₆H₄SO₃)₈·14H₂O

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The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ (**1**) with $[(Cp*RhCl_2)_2]$ afforded a novel rhodium–molybdenum cluster, $[\{Mo_3RhCp*S_4(H_2O)_7(O)\}_2]^{8+}$ (**2**). X-ray structure analysis of [**2**](pts)₈·14H₂O (pts⁻ = $CH_3C_6H_4SO_3^-$) has revealed the existence of a new oxo-bridged twin cubane-type core, $(Mo_3RhCp*S_4)_2(O)_2$. The high affinity of the Cp*Rh group for sulfur atoms in **1** seems to be the main driving force for this reaction. The strong Lewis acidity of the Cp*Rh group in intermediate **A**, $[Mo_3RhCp*S_4(H_2O)_9]^{6+}$, caused a release of proton from one of the water molecules attached to the molybdenum atoms to give intermediate **B**, $[Mo_3RhCp*S_4(H_2O)_8(OH)]^{5+}$. The elimination of two water molecules from two intermediate **B** molecules, followed by the deprotonation reaction of hydroxo bridges, generated the twin cubane-type cluster **2**. The formal oxidation states of rhodium and molybdenum atoms are the same before and after the reaction (i.e., Mo(IV)₃, Rh(III)). The Mo–O–Mo moieties in [**2**](pts)₈·14H₂O are nearly linear with a bond angle of 164.3(3)°, and the basicity of the bridging oxygen atoms seems to be weak. For this reason, protonation at the bridging oxygen atoms does not occur even in a strongly acidic aqueous solution. The binding energy values of Mo $3d_{5/2}$, Rh $3d_{5/2}$, and C 1s obtained from X-ray photoelectron spectroscopy measurements for [**2**](pts)₈·14H₂O are 229.8, 309.3, and 285 eV, respectively. The XPS measurements on the Rh $3d_{5/2}$ binding energy indicate that the oxidation state of Rh is 3+. The binding energy of Mo $3d_{5/2}$ (229.8 eV) compares with that observed for [**1**](pts)₄·7H₂O (230.7 eV, Mo $3d_{5/2}$). A lower energy shift (0.9 eV) is observed in the binding energy of Mo $3d_{5/2}$ for [**2**](pts)₈·14H₂O. This energy shift may correspond to the coordination of an oxygen atom having a negative charge to the molybdenum atom.

Introduction

Mixed-metal cubane-type sulfide clusters have drawn much attention, primarily owing to their relevance to metalloenzymes,[1] vital functions in vivo,[2] and industrial heterogeneous metal sulfide catalysts.[3] Studies of these clusters are usually carried out with clusters containing the metals in the first-row transition series.[4] Moreover, clusters containing molybdenum (in the second row) and tungsten (in the third row) have been investigated.[5] It is very difficult to synthesize the desired sulfide clusters containing noble metals using self-assembly approaches because noble metals are highly reactive with sulfur and have intricate side reactions. Only a few attempts have been made to study clusters containing noble metals.[6]

We have focused on the reactivity of lone pair electrons of μ-S atoms in $[Mo_3S_4(H_2O)_9]^{4+}$ (**1**) and its ability to incorporate heterometals to afford a series of mixed-metal

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(1) For example, see: Beinert, H.; Holm, R. H.; Munck, E. *Science* **1997**, *277*, 653.
(2) For example, see: Aikoh, H.; Tagawa, T.; Shibahara, T. *Physiol. Chem. Phys. Med. NMR* **2002**, *34*, 83.
(3) For example, see: (a) Tatsumi, T.; Taniguchi, M.; Ishige, H.; Ishii, Y.; Murata, T.; Hidai, M. *Appl. Surf. Sci.* **1997**, *121/122*, 500. (b) Riaz, U.; Curnow, O. J.; Curtis, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 4357. (c) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1.
(4) For example, see: Holm, R. H. *Adv. Inorg. Chem.* **1992**, *38*, 1.
(5) (a) Shibahara, T. *Coord. Chem. Rev.* **1993**, *123*, 73. (b) Llusar, R.; Uriel, S. *Eur. J. Inorg. Chem.* **2003**, 1271.
(6) Hidai, M.; Mizobe, Y. *Acc. Chem. Res.* **2000**, *33*, 46.

cubane-type sulfide clusters containing Mo_3MS_4 cores (M = Fe,[7] Co,[8] Ni,[7b] Cu,[9] Zn,[10] Ga,[11] Cd,[12] In,[13] Sn,[14] Sb,[15] Hg,[8] Sn^{2+},[14] and Cu^+ [9]). Some papers related to the metal incorporation reaction of **1** or its derivatives have been published by other researchers.[16] While developing a new method to prepare cubane-type sulfide clusters containing noble metals, we successfully isolated clusters, $[\{Mo_3\text{-}RhCp*S_4(H_2O)_7(O)\}_2]^{8+}$ (**2**), containing the Mo_3RhS_4 core from the reactions of **1** with the Cp*Rh group.[17] Some molybdenum−rhodium complexes containing a Mo_3RhS_4 core are known: the preparation and X-ray structure of $[(\eta^5\text{-}Cp')_3Mo_3S_4RhCl(PPh_3)](CH_3C_6H_4SO_3)\cdot1/2THF$ (**3**)[18] and the formation of $[Mo_3RhCl_3S_4(H_2O)_9]^{4+}$ (**4**)[19] have been reported so far. The molecular formula of **4** was given by the results of elemental analyses and the separation of **1** as the thermal decomposition product of **4**. A detailed comparison of the characteristics of **2** with those of **4** is presented in this paper.

In addition, a different methodology for preparing cubane-type sulfido clusters containing noble metals has been presented. Preassembled dinuclear sulfido complexes are used as building blocks to achieve cubane-type sulfido clusters with target metal compositions. The sulfur-bridged cubane-type noble metal molybdenum clusters prepared by this method have been reported.[20−23] Other sulfur-bridged noncubane-type noble metal molybdenum clusters have also

been reported.[22−25] Since knowledge of the preparation and reactivity of cubane-type noble metal clusters is still limited, it is necessary to develop new preparation methods. This study focuses on the preparation and characterization of **2** and the X-ray structure of $[2](pts)_8\cdot14H_2O$.

Experimental Section

Preparation of $[\{Mo_3RhCp*S_4(H_2O)_7(O)\}_2](CH_3C_6H_4SO_3)_8\cdot14H_2O$ ($[2](pts)_8\cdot14H_2O$). $[(Cp*RhCl_2)_2]$ (340 mg, 1.1 mmol) was introduced into a conical flask containing the aqua ion **1** (200 mL, 5×10^{-3} M per Mo_3) in 0.1 M HCl with stirring. The color of the solution turned from green to red-purple in ca. 6 h. After 2 days of stirring, the solution was filtered and absorbed on a Dowex 50W-X2 cation exchanger (length 4 cm, diameter 2 cm). The resin was washed with 0.1 M Hpts to remove the chloride ion, and slow elution with 4 M Hpts ($pts^- = CH_3C_6H_4SO_3^-$) gave only a red-purple solution of $[\{Mo_3RhCp*S_4(H_2O)_7(O)\}_2]^{8+}$ (**2**, yield 93%, determined by ICP). The resultant solution was kept in a refrigerator, and red-purple crystals of $[2](pts)_8\cdot14H_2O$ were obtained in a few days (yield 30%). Anal. Found (Calcd for $C_{76}H_{142}Mo_6O_{54}Rh_2S_{16}$, fw = 3214.42): C, 28.43 (28.40); H, 4.46 (4.45).

X-ray Structure Analysis for $[2](pts)_8\cdot14H_2O$. A crystal of $[2](pts)_8\cdot14H_2O$ was mounted in a cryoloop (Hampton Research Corp.) with liquid paraffin and frozen in liquid nitrogen. Data collection was performed (at 93 K) on a Rigaku/MSC Mercury CCD two-dimensional detector equipped with a low-temperature apparatus by use of Mo Kα radiation ($\lambda = 0.71073$ Å). Empirical absorption correction using the program REQABA was applied.[26] The structure of $[2](pts)_8\cdot14H_2O$ was solved by the direct method (Sir 97[27]) with the aid of successive difference Fourier maps and refined by the full-matrix least-squares method on F^2. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were at the calculated positions and fixed at the initial positions. Isotropic thermal parameters of hydrogen atoms were constrained to $1.2U_{eq}$, to which they were attached. All calculations were performed with the Crystal Structure crystallographic software package.[28] In the last cycles of the refinement, all parameters shifted by less than 1% of their esd's, and the final difference Fourier maps showed no significant electron density. Crystallographic and refinement data are summarized in Table 1.

Electronic and Reflectance Spectroscopy. Electronic spectra of $[2](pts)_8\cdot14H_2O$ were measured on a Hitachi U-2000 spectrophotometer. The reflection spectrum of $[2](pts)_8\cdot14H_2O$ was measured on a Hitachi U-3310 spectrophotometer equipped with an integrating sphere attachment. Crystals of $[2](pts)_8\cdot14H_2O$ were ground in an agate mortar, and the powder of the sample was diluted 150 times by weight with powder K_2SO_4. A plate of Al_2O_3 was used for reference.

X-ray Photoelectron Spectroscopy. X-ray photoelectron spectra of $[2](pts)_8\cdot14H_2O$ were measured on a Shimazu/Kratos AXIS-HS using Mg Kα and Kβ radiations (15 kV, 10 mA) for wide-range

(7) (a) Shibahara, T., Akashi, H., Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 1342. (b) Shibahara, T., Sakane, G.; Naruse, Y.; Taya, K.; Akashi, H.; Ichimura A.; Adachi, H. *Bull. Chem. Soc. Jpn.* **1995**, *68*, 2769.
(8) Shibahara; T.; Akashi, H.; Yamasaki, M.; Hashimoto, K. *Chem. Lett.* **1991**, 689.
(9) Akashi H.; Shibahara, T. *Inorg. Chim. Acta* **2000**, *300/302*, 572.
(10) Sakane, G.; Kawasaki, H.; Oomori, T.; Yamasaki, M.; Adachi, H.; Shibahara, T. *J. Cluster Sci.* **2002**, *13*, 75.
(11) Shibahara, T.; Kobayashi, S.; Tuji, N.; Sakane G.; Fukuhara, M. *Inorg. Chem.* **1997**, *36*, 1702.
(12) Sakane, G.; Kawasaki, H.; Yamasaki, M.;. Adachi, H.; Shibahara, T. *Chem. Lett.* **1999**, 631.
(13) (a) Sakane, G.; Shibahara, T. *Inorg. Chem.* **1993**, *32*, 777. (b) Sakane, G.; Yao Y.; Shibahara, T. *Inorg. Chim. Acta* **1994**, *216*, 13.
(14) Akashi H.; Shibahara, T. *Inorg. Chem.* **1989**, *28*, 2906.
(15) (a) Sakane, G.; Hashimoto, K.; Takahashi, M.; Takeda M.; Shibahara, T. *Inorg. Chem.* **1998**, *37*, 4231. (b) Shibhara, T.; Hashimoto K.; Sakane, G. *J. Inorg. Biochem.* **1991**, 43.
(16) For example, see: (a) Sokolov, M. N.; Hernandez-Molina, R.; Dybtsev, D. N.; Chubarova, E. V.; Solodovniko, S. F. *Z. Anorg. Allg. Chem.* **2002**, *628*, 2335. (b) Herbst, K.; Rink, B.; Dahlenburg, L.; Brorson M. *Organometallics* **2001**, *20*, 3655. (c) Masui, D.; Ishii, Y.; Hidai M. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 931. (d) Varey, J. E.; Lamprecht, G. J.; Fedin, V. P.; Holder, A.; Clegg, W.; Elsegood M. R. J.; Sykes, A. G. *Inorg. Chem.* **1996**, *35*, 5525. (e) Murata, T.; Mizobe, Y.; Gao, H.; Ishii, Y.; Wakabayashi, T.; Nakano, F.; Tanase, T.; Yano, S.; Hidai, M.; Echizen, I.; Nanikawa H.; Motomura, S. *J. Am. Chem. Soc.* **1994**, *116*, 3389.
(17) Preliminary results of the reactions were reported: Akashi, H.; Nakao, A. Shibahara, T. XVIIIth IUCr Congress, Glasgow, Scotland, August 1999; P07.07.041.
(18) Brorson and co-workers reported on a reaction of $[(\eta^5\text{-}Cp')_3Mo_3S_4]$-$(CH_3C_6H_4SO_3)$ with $[RhCl(cyclooctene)_2]_2$ and triphenylphosphane in methanol to give the molybdenum−rhodium single cubane-type cluster $[(\eta^5\text{-}Cp')_3Mo_3S_4RhCl(PPh_3)](CH_3C_6H_4SO_3)\cdot^1/_2THF$: Herbst, K.; Monari, M.; Brorson, M. *Inorg. Chem.* **2001**, *40*, 2979.
(19) Sokolov, M. N.; Villagra, D.; El-Hendawy, A. M.; Kwak, C.-H.; Elsegood, M. R. J.; Clegg, W.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **2001**, 2611.
(20) Masumori, T.; Seino, H.; Mizobe, Y.; Hidai M. *Inorg. Chem.* **2000**, *39*, 5002.
(21) Ikeda, T.; Kuwata, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1998**, *37*, 5793.
(22) Ikeda, T.; Kuwata, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1999**, *38*, 64.
(23) Ikeda, T.; Kuwata, S.; Mizobe, Y.; Hidai, M. *Inorg. Chem.* **1998**, *37*, 5793.
(24) Xi, R.; Wang, B.; Ozawa, Y.; Abe, M.; Isobe, K. *Chem. Lett.* **1994**, 323.
(25) Xi, R.; Wang, B.; Ozawa, Y.; Abe, M.; Isobe, K. *Chem. Lett.* **1994**, 1178.
(26) Jacobson, R. Private communication, 1995−1998.
(27) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, *27*, 435.
(28) Molecular Structure Corp.; Rigaku Corp. Single Crystal Structure Analysis Software. Version 1.11. MSC, 9009 New Trails Dr., The Woodlands, TX 77381-5209; Rigaku, 3-9-12 Matsubara, Akishima, Tokyo, 196-8666, Japan, 2000.

**Table 1.** Crystal and Structure Refinement Data for [**2**](pts)$_8$·14H$_2$O

empirical formula	C$_{38}$H$_{71}$O$_{27}$Mo$_3$S$_8$Rh	μ(Mo Kα)	12.28 cm^{-1}
fw	1607.17	temp	$-$180.0 °C
cryst syst	triclinic	no. of reflns measured	total: 33644
space group	P$\bar{1}$ (No. 2)		unique: 21219 (R_{int} = 0.073)
lattice params	a = 12.2631(8) Å	corrections	Lorentz polarization
	b = 15.911(1) Å		absorption (trans factors: 0.6959−0.9405)
	c = 17.389(3) Å	no. of variables	694
	α = 63.704(3)°	residuals: R1^a ($I > 2.0\sigma(I)$)	0.060
	β = 78.688(2)°	residuals: $R_w{}^a$	0.169
	γ = 81.038(2)°	no. of reflns to calc R1	7804
	V = 2973.5(5) Å^3	GOF indicator	1.006
Z value	2	max shift/error in final cycle	0.001
D_{calcd}	1.764 g/cm^3	max peak in final diff map	2.17 e$^-$/Å^3
F_{000}	1628.00	min peak in final diff map	$-$1.25 e$^-$/Å^3

^{a} R1 = $\Sigma||F_o| - |F_c||/\Sigma|F_o|$, R_w = $[(\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2)]^{1/2}$.

measurement and monochromated Al Kα radiation (15 kV, 5 mA) for narrow-range measurement (C 1s, Mo 3d, Rh 3d, S 2p). Crystals of [**2**](pts)$_8$·14H$_2$O were ground in an agate mortar, and the powder of the sample was mounted on the sample table using a copper-plated cloth tape X7001 (Sumitomo 3M Ltd.). The binding energy of Rh 3d$_{5/2}$ for [(Cp*RhCl$_2$)$_2$] was also measured. A small quantity of crystals of Hpts was added to the crystals of [(Cp*RhCl$_2$)$_2$] as the standard. A charge neutralizer was applied to prevent charging of the sample. A binding energy value of C 1s (=285.0 eV) for the pts$^-$ anion was employed as a standard.

Results and Discussion

Preparation and Spectroscopic Characterization. The reaction of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ (**1**) with [(Cp*RhCl$_2$)$_2$] in 0.1 M HCl afforded [{Mo$_3$RhCp*S$_4$(H$_2$O)$_7$(O)}$_2$]$^{8+}$ (**2**; 93% based on **1**) in excellent yields. Red-purple crystals of [**2**](pts)$_8$·14H$_2$O were obtained from the solution of **2** in 4 M Hpts (yield 30%). The high yield shows that the reaction proceeds in 0.1 M HCl stoichiometrically, as shown in eq 1.

(1a^{29})

[{Mo$_3$RhCp*S$_4$(H$_2$O)$_7$(O)}$_2$]$^{8+}$ (**2**) + 4H$^+$ + 8H$_2$O   (1b)
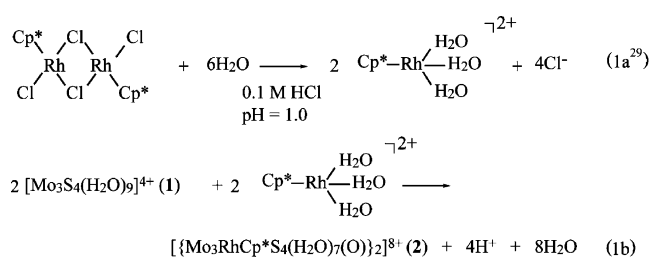
As the reaction proceeds the hydrogen ion concentration of the reaction mixture increases: the pH of the solution changed from 1.0 to 0.7. Since the reaction yields hydrochloric acid, the high acidity of the solvent hinders the reaction of **1** with [(Cp*RhCl$_2$)$_2$].

The concentration of chloride ions is another important factor for the reaction. When the concentration of chloride ions becomes 0.5 M or above in the reaction system, the incorporation reaction of the Cp*Rh group into **1** does not take place. This is because a high concentration of chloride ions inhibits the dissociation from [(Cp*RhCl$_2$)$_2$] to give [Cp*Rh(H$_2$O)$_3$]$^{2+}$.

The reducing power of the metal is an important factor whether the reaction proceeds: in many cases, the molybdenum atoms in the Mo$_3$S$_4$ core are reduced on the metal incorporation reaction of **1**.[7−16] In addition to this factor, the

Scheme 1. Mechanism of Formation of Oxo Bridges in [**2**](pts)$_8$·14H$_2$O
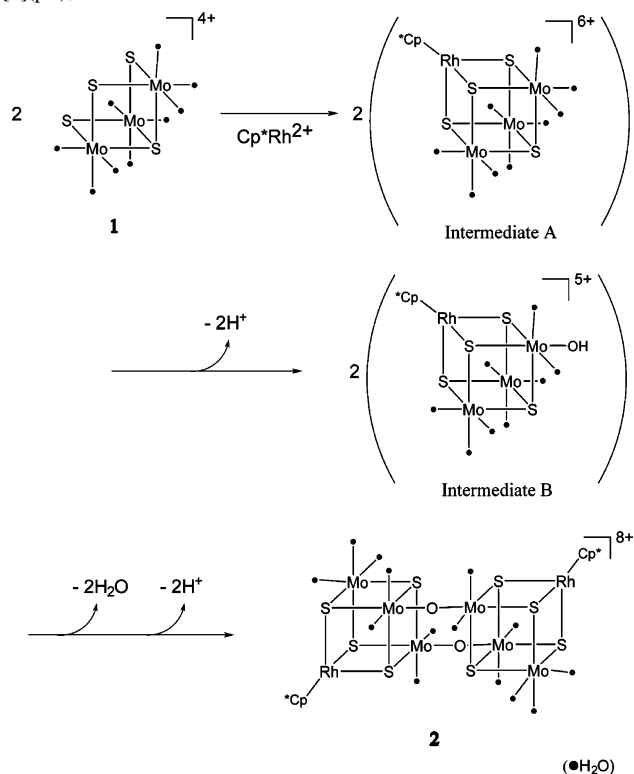
affinity of metal for sulfur atoms in **1** becomes an important driving force for the reactions.[8] Since the formal oxidation states of the molybdenum and rhodium atoms in **2** do not change before or after the reaction of **1** with [(Cp*RhCl$_2$)$_2$], the affinity of the Cp*Rh group for sulfur atoms appeared to be the driving force for this reaction (see the XPS section below).

An oxo bridge formation mechanism is shown in Scheme 1. The high affinity of Cp*Rh^{2+} for the sulfur atoms in **1** gives intermediate **A**. The deprotonation reaction of the water molecules attached to the molybdenum atoms is induced by the high acidity of the Cp*Rh moiety and the high oxidation state of molybdenum atoms in intermediate **A**. Intermediate **B**, [Mo$_3$RhCp*S$_4$(H$_2$O)$_8$(OH)]$^{5+}$, would be formed at this stage. The elimination of two water molecules from two intermediate **B** molecules, followed by the deprotonation reaction of hydroxo bridges, generates the twin cubane-type cluster **2**. The structures of Cp*Rh aqua complexes, as a
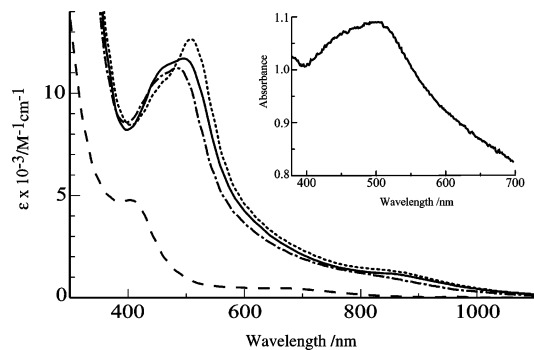
Figure 1. Electronic spectra of [**2**](pts)$_8$·14H$_2$O in an aqueous solution of 0.1 M HCl (solid line), in 2 M HCl (dashed line), in 0.1 M Hpts (dashed−dotted line), and in CH$_2$Cl$_2$ (dotted line). The inset shows the reflection spectrum of [**2**](pts)$_8$·14H$_2$O.

Figure 2. ORTEP diagram of [**2**](pts)$_8$·14H$_2$O. Counteranions and water of crystallization are removed for clarity.

function of pH, are reported in detail by Fish and Ogo.[29] As the pH of the solution with [Cp*M(H$_2$O)$_3$]$^{2+}$ (M = Rh, Ir) complexes increases, the complexes dimerize into [Cp*M-(μ-OH)$_3$MCp*]$^+$ (eq 2).

$$2[Cp*M(H_2O)_3]^{2+} \rightleftarrows [Cp*M(\mu\text{-}OH)_3MCp*]^+ + 3H^+ + \\ 3H_2O \ (M = Rh, Ir) \ (2)$$
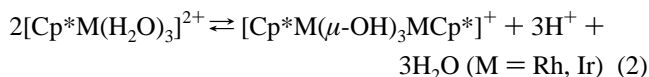
We have previously reported the synthesis and properties of the oxo-bridged twin cubane-type molybdenum−cupper cluster [{(NH$_3$)$_6$(H$_2$O)(OH)Mo$_3$CuS$_4$(O)}$_2$]Cl$_4$·8H$_2$O.[30] This synthesis was carried out in a concentrated ammonia solution, and the formation of oxo bridges occurred by the dehydration condensation of water molecules between two intermediates, [Mo$_3$CuS$_4$(NH$_3$)$_6$(H$_2$O)$_2$(OH)$_2$]$^{2+}$, followed by the oxidative elimination of dihydrogen from the hydroxo bridges. This is in contrast to the formation of oxo bridges in **2**, which takes place in a strong acid solution.

The electronic spectra of [**2**](pts)$_8$·14H$_2$O are shown in Figure 1. The peak positions and ϵ values are largely dependent on the solvents: λ_{max}, nm (ϵ, M^{-1} cm^{-1}), in 0.1 M Hpts, 484 (11220); in 0.1 M HCl, 496 (11700); in 2 M HCl, 402 (4770); in CH$_2$Cl$_2$, 508 (12600). A reflection spectrum of [**2**](pts)$_8$·14H$_2$O is shown in the inset of Figure 1. The reflection spectrum is similar to the spectrum of **2** in 0.1 M Hpts and in 0.1 M HCl, which indicated that **2** exists as a twin cubane-type cluster in these solutions.

The absorbance of **2** in 0.1 M HCl in the visible region decreases in a few seconds by the addition of concentrated HCl to make 2 M HCl. When **2** was dissolved in 0.5 M HCl, the same spectrum as that of **2** in 0.1 M HCl was obtained; however, the initial red-purple color of the solution of **2** in 0.5 M HCl gradually changed to yellow (after 3.5 h) and finally became identical with that of **2** in 2 M HCl. The addition of sodium chloride to a 0.1 M HCl solution of **2** to make the concentration of the chloride ion 2 M caused an immediate spectral change. This spectral change is revers-
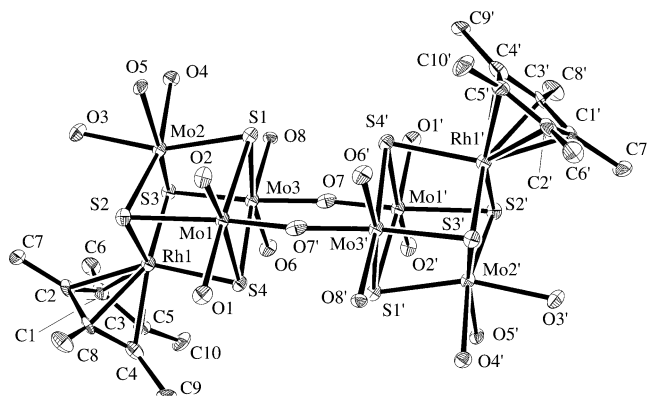
ible: as the chloride ion concentration was decreased to 0.1 M by dilution with water, the spectrum showed the peak at 496 nm again after 4 h. This indicates that the oxo bridges in **2** are cleaved by the coordination of chloride ions to the molybdenum atoms under a high concentration of chloride ions (>0.5 M Cl$^-$) to afford a single cubane-type cluster, [Mo$_3$RhCp*S$_4$(H$_2$O)$_7$Cl$_2$]$^{4+}$ (**5**) (see eq 3).

$$[\{Mo_3RhCp*S_4(H_2O)_7(O)\}_2]^{8+} \ (\mathbf{2}) + 4HCl \rightleftarrows \\ 2[Mo_3RhCp*S_4(H_2O)_7Cl_2]^{4+} \ (\mathbf{5}) + 2H_2O \ (3)$$
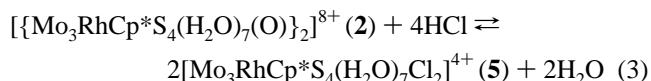
The addition of 2, 4-dinitrophenol as a proton source to the dichloromethane solution of **2** caused no spectral change ([**2**](pts)$_8$·14H$_2$O:2,4-dinitrophenol = 1:20). It is clear that no protonation of the oxygen atoms in the oxo bridges in **2** occurred in the dichloromethane solution.

The addition of tetrabutylammonium chloride as a chloride ion source to the dichloromethane solution of **2** caused no spectral change ([**2**](pts)$_8$·14H$_2$O:tetrabutylammonium chloride = 1:20). In contrast to the case of the aqueous solution of **2**, it is clear that the attack of the chloride ions on the molybdenum atoms does not cleave the oxo bridge in dichloromethane.

X-ray Structure of [2](pts)$_8$·14H$_2$O. X-ray structure analysis of [**2**](pts)$_8$·14H$_2$O revealed that a new twin cubane-type core, (Mo$_3$RhCp*S$_4$)$_2$(O)$_2$, exists. An ORTEP drawing of the cluster cation is shown in Figure 2. The center of symmetry resides on the midpoint of two oxo bridges in the (Mo$_3$RhCp*S$_4$)$_2$(O)$_2$ core. Selected bond distances and angles are listed in Table 2. The O7 and O7′ atoms in **2** are assigned to oxo bridges rather than hydroxo bridges: the distances of Mo1−O7′ (1.900(6) Å) and Mo3−O7 (1.891(6) Å) are closer to the Mo−O$_{bridge}$ distance in Ba[Mo$_2$O$_4$(C$_2$O$_4$)$_2$]·5H$_2$O[31] (1.93(3) Å) than to the Mo−OH$_{bridge}$ distance in K$_2$[Mo$_2$(OH)$_2$(CH$_3$CO$_2$)(edta)][32] (2.08 Å). The Mo−O−Mo angle (164.3(3)°) in **2** is close to 180°, and the basicity of the bridging oxygen atoms seems to be weak. For this reason, protonation at the bridging oxygen atoms does not occur even in a strongly acidic aqueous solution. The Mo1−S2 (2.394(2)

(29) Rh: (a) Eisen, M. S.; Haskel, A.; Chen, H.; Olmstead, M. M.; Smith, D. P.; Maester, M. F.; Fish, R. H. *Organometallics* **1995**, *14*, 2806. (b) Ogo, S.; Chen, H.; Olmstead, M. M.; Fish, R. H. *Organometallics* **1996**, *15*, 2009. Ir: (c) Ogo, S.; Makihara, N.; Watanabe, Y. *Organometallics* **1999**, *18*, 5470.
(30) Akashi H.; Shibahara, T. *Inorg. Chim. Acta* **1998**, *282*, 50.

(31) Cotton, F. A.; Morehouse, S. M. *Inorg. Chem.* **1965**, *10*, 1377.
(32) Shibahara, T.; Sheldrick, B.; Sykes, A. G. *J. Chem. Soc., Chem. Commun.* **1976**, 523.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [**2**](pts)8·14H₂O

Rh(1)	Mo(1)	3.1123(7)	Mo(1)	Rh(1)	Mo(2)	55.47(2)
Rh(1)	Mo(2)	2.9379(8)	Mo(1)	Rh(1)	Mo(3)	53.04(2)
Rh(1)	Mo(3)	3.080(1)	Mo(2)	Rh(1)	Mo(3)	55.88(2)
Mo(1)	Mo(2)	2.8201(8)	S(2)	Rh(1)	S(3)	100.06(7)
Mo(1)	Mo(3)	2.765(1)	S(2)	Rh(1)	S(4)	95.62(7)
Mo(2)	Mo(3)	2.823(1)	S(3)	Rh(1)	S(4)	96.57(8)
Rh(1)	S(2)	2.390(2)	Mo(2)	Mo(1)	Mo(3)	60.70(3)
Rh(1)	S(3)	2.361(2)	Mo(1)	Mo(2)	Mo(3)	58.69(3)
Rh(1)	S(4)	2.410(2)	Mo(1)	Mo(3)	Mo(2)	60.61(3)
Mo(1)	S(1)	2.352(2)	Rh(1)	S(2)	Mo(1)	81.16(8)
Mo(2)	S(1)	2.359(2)	Rh(1)	S(2)	Mo(2)	77.38(8)
Mo(3)	S(1)	2.335(2)	Rh(1)	S(3)	Mo(2)	77.55(7)
Mo(1)	S(2)	2.394(2)	Rh(1)	S(3)	Mo(3)	80.83(6)
Mo(1)	S(4)	2.325(2)	Rh(1)	S(4)	Mo(1)	82.18(7)
Mo(2)	S(2)	2.308(2)	Rh(1)	S(4)	Mo(3)	81.30(6)
Mo(2)	S(3)	2.329(2)	Mo(1)	S(1)	Mo(2)	73.53(7)
Mo(3)	S(3)	2.390(2)	Mo(1)	S(1)	Mo(3)	72.30(5)
Mo(3)	S(4)	2.318(2)	Mo(2)	S(1)	Mo(3)	73.92(5)
Mo(1)	O(7)ᵃ	1.900(6)	Mo(1)	S(2)	Mo(2)	73.68(7)
Mo(3)	O(7)	1.891(6)	Mo(2)	S(3)	Mo(3)	73.45(5)
S(2)	S(3)	3.643(3)	Mo(1)	S(4)	Mo(3)	73.12(5)
S(2)	S(4)	3.556(3)	S(1)	Mo(3)	O(7)	86.6(2)
S(3)	S(4)	3.561(2)	S(3)	Mo(3)	O(7)	160.7(2)
Mo	O(aqua)(av)	2.184[27]	S(4)	Mo(3)	O(7)	94.4(2)
Rh	C(av)	2.188[11]	Mo(1)ᵃ	O(7)	Mo(3)	164.3(4)

ᵃ Symmetry operation: $-x, -y + 1, -z + 1$.

Å) and Mo3−S3 (2.390(2) Å) distances are longer compared with other Mo−S distances; the elongation seems to be due to the *trans* influence of the oxo bridges. The Rh1−Mo2 (2.9379(8) Å) distance is shorter than the Rh1−Mo1 (3.1123(7) Å) and Rh1−Mo3 (3.080(1) Å) distances. In addition, the Mo1−Mo3 (2.765(1) Å) distance is shorter than those of Mo1−Mo2 (2.8201(8) Å) and Mo3−Mo2 (2.823(1) Å). These differences reflect the distortion of the core caused by the existence of the *trans* influence of the oxo bridges. The metal−metal interactions between the rhodium atom and molybdenum atoms seem very weak, since the Rh−Mo distances (3.1123(7)−2.9379(8) Å) are longer than the sum (2.71 Å) of the metallic radius of each atom.

A comparison of the Mo₃RhS₄ core structures of **3** and [**2**](pts)₈·14H₂O shows that the distortion of the core in **3** is smaller than that of the core in [**2**](pts)₈·14H₂O. For example, the Mo−Rh distances in [**2**](pts)₈·14H₂O show a larger scatter than those of the cubane-type core in **3** (2.883(1)−2.954(1) Å). No significant difference in other bond distances can be seen between the Mo₃S₄ moieties in [**2**](pts)₈·14H₂O and **3**.

X-ray Photoelectron Spectra of [2](pts)₈·14H₂O. The binding energy values of Mo 3d₅/₂ and Rh 3d₅/₂ obtained from the X-ray photoelectron spectroscopy measurement for [**2**](pts)₈·14H₂O are 229.8 and 309.3 eV, respectively. The binding energy of Rh 3d₅/₂ for [(Cp*RhCl₂)₂] is 309.5 eV. The XPS measurements on the Rh 3d₅/₂ binding energy indicate that the oxidation state of Rh is 3+. The lower energy shift of Mo 3d₅/₂ (230.3 eV) upon Ni incorporation into **1** was associated with a reductive addition of the metal.[7b] The binding energy of Mo 3d₅/₂ (229.8 eV) for [**2**](pts)₈· 14H₂O shows a lower energy shift compared with that observed for [**1**](pts)₄·7H₂O (Mo 3d₅/₂ = 230.7 eV), though no formal reduction of the molybdenum atoms occurred. This lower energy shift may be due to the coordination of the bridging oxygen atoms having a negative charge to the molybdenum atom.

Comparison between 2 and 4. Sykes and co-workers have reported the preparation of a single cubane-type cluster, **4**, which has not been characterized crystallographically;[19] they suggested the formation of [Mo₃RhS₄(H₂O)₁₂]⁷⁺ (**4′**) on a cation-exchange resin (Dowex 50W−X2), since once **4** was absorbed on the cation-exchange resin, **4** was not eluted with 4 M Hpts solution. On the other hand, the behavior of **2** having a +8 charge on the cation-exchange resin is significantly different from that reported for **4**; that is, a red-purple solution of **2** was eluted with the 4 M Hpts. The crystals of [**2**](pts)₈·14H₂O were deposited from the solution. Although cluster **4** is stable in 2 M HCl, cluster **2** changes to cluster **5** immediately in 2 M HCl. The spectrum of **5** in 2 M HCl is significantly different from that of **4** (λ_{max} = 370 nm in 2 M HCl). These differences in the characters and the core structures (twin in **2** vs single in **4**) of **2** and **4** are most likely due to the coordination of the Cp* group to the Rh site in **2** instead of the coordination of three chloride anions to the Rh site in **4**.

Supporting Information Available: X-ray crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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