Inorg. Chem. **2001,** *40,* 2111−2119

Adduct of Acetylene at Sulfur in an Oxygen- and Sulfur-Bridged Open Cubane Cluster Complex of Tungsten

Masataka Maeyama,[†] Genta Sakane,[†] Roberta Pierattelli,[‡] Ivano Bertini,[‡] and Takashi Shibahara*[,†]

Department of Chemistry, Okayama University of Science, Ridai-cho, Okayama 700-0005, Japan, and Department of Chemistry, University of Florence, Via Gino Capponi, 9-50121 Florence, Italy

Received October 24, 2000

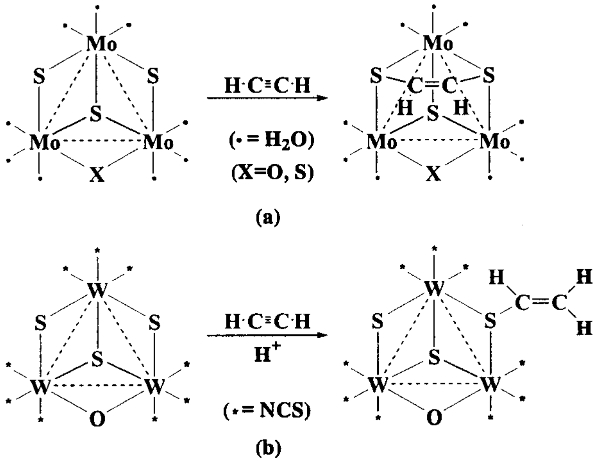
Formation of a single carbon−sulfur bond is described. The reaction of incomplete cubane-type sulfur and oxygen-bridged isothiocyanato tungsten cluster $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(NCS)_9]^{5-}$ (**7**) with acetylene affords $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})(\mu\text{-SCH{=}CH_2})(NCS)_9]^{4-}$ (**8**). The cluster **8** has been isolated as $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})(\mu\text{-SCH{=}CH_2})(NCS)_9]$ (**8′**), whose structure has been characterized by X-ray crystallography, electronic spectra, and ^{1}H and ^{13}C NMR spectroscopy. Crystal data of **8′**: triclinic system, space group $P\bar{1}$, $a = 14.465(5)$ Å, $b = 17.353(3)$ Å, $c = 10.202(2)$ Å, $\alpha = 90.98(1)°$, $\beta = 108.59(2)°$, $\gamma = 98.13(2)°$, $V = 2397.6(10)$ Å^3, $Z = 2$, $D_c = 2.096$ g cm^{-3}, $D_m = 2.08$ g cm^{-3}, R (R_w) = 3.6 (5.5)% for 8786 reflections ($I > 1.50\,\sigma(I)$). The carbon−carbon distance is 1.27(1) Å and is almost equidistant between ethylene (1.339 Å) and acetylene (1.203 Å). The electronic spectrum of **8′** in 1.0 M HCl containing 1.5 M KSCN has a characteristic broad peak in the near-infrared region [λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 840 (650), 575 (1450)]. ^{1}H NMR and HH correlation spectroscopy (COSY) of **8′** in CD_3CN support the results of the X-ray structural analysis. The ^{1}H NMR spectrum shows three signals at 2.42 (1H, dd), 4.84 (1H, d, $J = 8.8$ Hz), and 4.89 (1H, d, $J = 16.2$ Hz) ppm due to the μ-SCH=CH$_2$ moiety of **8′**. The correlation spectrum shows spin couplings of the signal at 2.42 ppm with the signals at 4.84 and 4.89 ppm. The mechanism of the formation of **8** is suggested to proceed through an intermediate with acetylene bridging two of the sulfur atoms.

Introduction

We have previously reported carbon−sulfur bond formation through the reaction of incomplete cubane-type oxygen- and sulfur-bridged molybdenum aqua clusters $[Mo_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(H_2O)_9]^{4+}$ (**1**) and $[Mo_3(\mu_3\text{-S})(\mu\text{-S})_3(H_2O)_9]^{4+}$ (**2**) with acetylene to afford clusters with alkenedithiolate ligands $[Mo_3(\mu_3\text{-S})(\mu\text{-O})(\mu_3\text{-SCH{=}CHS})(H_2O)_9]^{4+}$ (**3**) and $[Mo_3(\mu_3\text{-S})(\mu\text{-S})(\mu_3\text{-SCH{=}CHS})(H_2O)_9]^{4+}$ (**4**), respectively (Scheme 1a).[1,2] We tried to extend the chemistry to the corresponding tungsten aqua clusters $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(H_2O)_9]^{4+}$ (**5**)[3] and $[W_3(\mu_3\text{-S})(\mu\text{-S})_3(H_2O)_9]^{4+}$ (**6**)[4] but found no reaction of the tungsten aqua clusters with acetylene. When we used the tungsten isothiocyanato cluster $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(NCS)_9]^{5-}$ (**7**) obtained from **5** and NCS$^-$ instead of using the tungsten aqua cluster **5**, we found a novel reaction, that is, a single carbon−sulfur bond formation through the reaction of **7** with acetylene to give $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})(\mu\text{-SCH{=}CH_2})(NCS)_9]^{4-}$ (**8**) (Scheme 1b).

Rakowski DuBois and her colleagues reported that the reaction of the dinuclear molybdenum complex $[(CpMo)_2(\mu\text{-S}_2CH_2)(\mu\text{-S})_2]$ with acetylene or phenylacetylene gave the complexes with $Mo_2(\mu\text{-SCH{=}CH_2})$[5] or $Mo_2(\mu\text{-SC(Ph){=}CH_2})$[6] moieties, respectively. Each of the complexes has a single carbon−sulfur bond. To our knowledge, the former complex is the only example with the moiety $Mo_2(\mu\text{-SCH{=}CH_2})$ so far reported that is obtained from the reaction of any complexes with acetylene. They reported that each single carbon−sulfur bond formation was obtained by H$^+$-severing of one of the two C−S bonds in the intermediate complex (Scheme 2). Examples

Scheme 1. Reaction of (a) $[Mo_3(\mu_3\text{-S})(\mu\text{-X})(\mu\text{-S})_2(H_2O)_9]^{4+}$ (X = O, **1**; X = S, **2**) and (b) $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(NCS)_9]^{5-}$ (**7**) with Acetylene, Respectively, in 1.0 M HCl



[†] Okayama University of Science.

[‡] University of Florence.

(1) Shibahara, T.; Akashi, H. *Inorg. Synth.* **1992**, *29*, 260−269.

(2) Shibahara, T.; Sakane, G.; Mochida, S. *J. Am. Chem. Soc.* **1993**, *115*, 10408−10409.

(3) Shibahara, T.; Takeuchi, A.; Kuroya, H. *Inorg. Chim. Acta* **1987**, *127*, L39−L40.

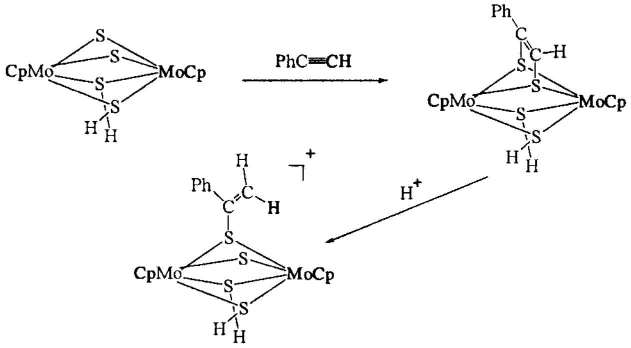
(4) Shibahara, T.; Yamasaki, M.; Sakane, G.; Minami, K.; Yabuki, T.; Ichimura, A. *Inorg. Chem.* **1992**, *31*, 640−647.

(5) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1−9.

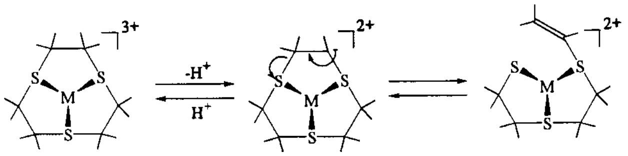
(6) Laurie, J. C. V.; Duncan, L.; Haltiwanger, R. C.; Weberg, R. T.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6234−6241.

10.1021/ic001174k CCC: $20.00

Scheme 2. Reaction of $[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-}S)_2]$ with Phenylacetylene



Scheme 3. Deprotonation of $[M([9]aneS_3)_2]^{3+}$ ($[9]aneS_3$ = 1,4,7-Trithiacyclononane; M = Co, Rh, Ir,)



of complexes having single carbon−sulfur bonds such as $M-SCH=CH_2$ (M = metals) are not so many, and only several complexes are known that were obtained by the ring-opening of 1,4,7-trithiacyclononane ($[9]aneS_3$) ligand in the complexes $[M([9]aneS_3)_2]^{3+}$ and related ones (M = Co, Ru, Rh, Ir)[7−10] through deprotonation (Scheme 3). There are a number of other metal complexes with vinyl thiolate ligands that have been reported.[11−15] These include derivatives prepared from vinyl halides and by S−H addition to acetylenes.[11,12,14] The chemistry of vinyl sulfide metallacycle complexes of molybdenum has also been reported.[16]

We have characterized the trinuclear complex **8** and discussed the formation mechanism mainly with X-ray crystallography and NMR spectroscopy, suggesting the presence of an intermediate having two carbon−sulfur bonds $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu_3\text{-}SCH=CHS)(NCS)_9]^{5-}$ (**A**). It is very interesting to know how ligand(s) and/or solvent change affects the reactivity of metals and other ligands.[17] A preliminary report of portions of this work has appeared.[18]

Experimental Section

Materials. The tungsten cluster $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (**5**) was obtained according to published procedures.[3] Other chemicals were used as purchased.

Measurements. ICP emission analysis was applied to the analyses of tungsten and potassium, a Shimadzu ICPS-500 analyzer being used. Electronic spectra were measured by use of a Hitachi U-2000 double-beam spectrophotometer. Spectra from ^1H NMR, ^{13}C NMR, and HH correlation spectroscopy (COSY) were obtained with Bruker DRX 500 and Bruker ARX-400R spectrometers.

Syntheses of Compounds. 1. $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(NCS)_9]^{5-}$ (7) and $(Hpy)_5[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(NCS)_9]\cdot 2H_2O$ (7′). To a conical flask containing a red-purple solution of **5** (3.32×10^{-3} M in 1.0 M HCl, 100 mL) was added KSCN (14.6 g) to make 1.5 M KSCN solution. The resultant blue-green solution was then heated in a water bath for 90 min at 50 °C. The color of the solution remained blue-green. The solution was kept in a refrigerator overnight and filtered to remove white precipitates. Addition of a small amount of pyridine (0.50 mL, 6.18×10^{-3} mol) and allowing the solution to stand at room temperature for a few days gave dark-green platelike crystals of **7′**; yield, 0.402 g (75%). Anal. of **7′** Found (Calcd for $W_3S_{12}O_3N_{14}C_{34}H_{34}$): N, 12.09 (12.08); C, 25.05 (25.16); H, 2.40 (2.11).

2. $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH=CH_2)(NCS)_9]^{4-}$ (8) and $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH=CH_2)(NCS)_9]$ (8′). To a conical flask containing **5** (2.92×10^{-3} M in 1.0 M HCl, 100 mL) was added KSCN (14.6 g) to make a 1.5 M KSCN solution through which a stream of acetylene gas was passed for 15 min, and then the flask was sealed at room temperature (1 atm). The resultant blue-green solution was then heated in a water bath for 3 days at 50 °C, and the color turned to brownish green. The solution was kept in a refrigerator overnight and filtered to remove white precipitates. Addition of a small amount of pyridine (0.10 mL, 1.24×10^{-3} mol) and allowing the solution to stand at room temperature for a few days gave brown platelike crystals of **8′**; yield, 0.259 g (59%). Anal. of **8′** Found (Calcd for $W_3K_{0.5}S_{12}ON_{12.5}C_{28.5}H_{24}$): W, 36.16 (36.44); K, 1.40 (1.29); N, 11.47 (11.57); C, 22.14 (22.62); H, 1.49 (1.60).

Reactivity of $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(NCS)_9]^{5-}$(7) with Acetylene Depending on the Concentration of HCl. 1. Experiement a. The aqua cluster **5** (3.48×10^{-3} M) in 1.0 M HCl containing 1.5 M KSCN was heated for 90 min at 50 °C to give **7** (the electronic spectrum was taken). After a stream of acetylene gas was passed through the resultant solution for 15 min, the vessel was sealed and kept at 50 °C. A small portion of the solution was diluted to 10 times its volume with 1.0 M HCl containing 1.5 M KSCN, and the electronic spectra were taken after 1, 2, and 3 days.

2. Experiment b1. The same procedures as those in experiment a were used except the use of 0.1 M HCl containing 1.5 M KSCN, concentration of **5** being 3.48×10^{-3} M. The solution was diluted, and the spectra were taken after 1, 2, 3, 5, and 7 days.

3. Experiment b2. The aqua cluster **5** (3.01×10^{-3} M) in 0.1 M HCl containing 1.5 M KSCN was heated for 90 min at 50 °C, followed by the addition of LiCl to the resultant solution to make a 0.9 M LiCl solution. After a stream of acetylene gas was passed through the solution for 15 min, the vessel was sealed and kept at 50 °C. A small portion of the solution was diluted to 10 times its volume with 0.1 M HCl containing 1.5 M KSCN, and the electronic spectra were taken after 1, 2, 3, 5, and 7 days.

4. Experiment c1. A solid sample of **7′** was dissolved (1.02×10^{-3} M) in pH 3 HCl containing 1.5 M KSCN and through which acetylene was passed for 10 min. The electronic spectra were taken after 12 h and 2, 5, and 7 days.

5. Experiment c2. The same procedures as those in experiment c1 were used except that a of higher concentration of **7′** was used here (3.56×10^{-3} M). The electronic spectra were taken after 12 h and 2, 5, and 7 days.

6. Experiment c3. The same procedures as those in experiment c2 were used but with the concentration of **7′** being 3.02×10^{-3} M, through which acetylene was passed for 15 min. The vessel was sealed and was kept heated at 50 °C. The electronic spectra were taken after 1, 2, and 5 days.

---

(7) Blake, A. J.; Holder, A. J.; Hyde, T. I.; Küppers, H.-J.; Schröder, M.; Stötzel, S.; Wieghardt, K. *J. Chem. Soc., Chem. Commun.* **1989**, 1600−1602.

(8) Sellmann, D.; Barth, I.; Knoch, F.; Moll, M. *Inorg. Chem.* **1990**, *29*, 1822−1826.

(9) Bennett, M. A.; Goh, L. Y.: Willis, A. C. *J. Am. Chem. Soc.* **1996**, *118*, 4984−4992.

(10) Chakraborty, P.; Karmakar, S.; Chandra, S. K.; Chakravorty, A. *Inorg. Chem.* **1994**, *33*, 816−822.

(11) Casewit, C. J.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 5482−5489.

(12) Kaneko, Y.; Suzuki, N.; Nishiyama, A.; Suzuki, T.; Isobe, K. *Organometallics* **1998**, *17*, 4875−4883.

(13) Bae, J.-Y.; Lee, Y.-J.; Kim, S.-J.; Ko, J.; Cho, S.; Kang, S.-O. *Organometallics* **2000**, *19*, 1514−1521.

(14) Weberg, R. T.; Haltiwanger, R. C.; Laurie, J. C. V.; Rakowski DuBois, M. *J. Am. Chem. Soc.* **1986**, *108*, 6242−6250.

(15) Casewit, C. J.; Haltiwanger, R. C.; Noordik, J.; Rakowski DuBois, M. *Organometallics* **1985**, *4*, 119−129.

(16) Coucouvanis, D. *Adv. Inorg. Chem.* **1998**, *45*, 1−73.

(17) Constable, E. C. *Metals and Ligands Reactivity*; VCH: Weinheim, 1996.

(18) Maeyama, M.; Sakane, G.; Pierattelli, R.; Bertini, I.; Shibahara, T. Recent Development and Future Prospects on Metal-Assembled and Metal-Cluster Compounds. Presented at Okazaki, Japan, October 1998; Abstr. P15.

Table 1. Crystallographic Data for $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (**8′**)

empirical formula	$W_3K_{0.5}S_{12}ON_{12.5}C_{28.5}H_{24}$
fw	1513.44
space group	$P\bar{1}$ (No. 2)
a, Å	14.465(5)
b, Å	17.353(3)
c, Å	10.202(2)
α, deg	90.98(1)
β, deg	108.59(2)
γ, deg	98.13(2)
V, Å^3	2397.6(10)
Z	2
R (R_w)^a	0.036(0.055)
ρ_{obsd}, g cm^{-3}	2.08
ρ_{calcd}, g cm^{-3}	2.096
radiation^b	Mo Kα
λ,^{b} Å	0.710 69
μ, cm^{-1}	78.9
T, °	9

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$; $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|]^{1/2}$; $w = 1/[\sigma^2(|F_o|) + g|F_o|^2]$; $g = 0.001$. ^{b} Graphite monochromated.

7. Experiment c4. The same procedures as those in experiment c3, up to the sealing of the vessel, were used, but the concentration of **7′** was 2.99×10^{-3} M. The resultant solution was kept at room temperature (ca. 20 °C) with stirring, and the electronic spectra were taken after 1 and 3 days. Then the solution was cooled in an ice bath, acetylene gas was passed for 15 min, and the solution was sealed and kept in a refrigerator with stirring (2 °C). Electronic spectra of the solutions were taken after 1, 2, and 9 days, respectively.

8. Experiment c5. The same procedures as those in experiment c4 were used, up to the solution being kept at room temperature (ca. 20 °C) with stirring, the concentration of **7′** being (2.84×10^{-3} M). After 1 day electronic spectra were taken to ensure the completion of the reaction, and then dinitrogen gas was passed for 5 min. The spectra collection and dinitrogen gas procedure was repeated two more times. Then, after introduction of acetylene followed by sealing, electronic spectra were taken after 1 and 3 days.

Measurements of NMR Spectra of $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (8′). 1. Experiment d. The cluster **8′** (20.0 mg, 1.23×10^{-5}mol) was dissolved in CD_3CN (1 mL) for the measurement of ^1H and ^{13}C NMR and for HH COSY at 20 °C, 400 MHz.

2. Experiment e. The cluster **8′** (20.0 mg, 1.23×10^{-5}mol) was dissolved in CD_3CN (1 mL) for the measurement of ^1H NMR at 0, 10, and 20 °C, 400 MHz.

3. Experiment f. The cluster **7′** (20.4 mg, 1.26×10^{-5}mol) was dissolved in a mixture (1 mL) of 1.0 M DCl containing 1.5 M KSCN and CD_3CN (1:1), through which a stream of acetylene gas was passed for 5 min. The flask was then sealed and kept at room temperature. NMR spectra were taken after 1 h and 1, 2, 4, and 7 days at 20 °C, 400 MHz. The HH correlation spectrum was also measured after 7 days.

Structural Determination of $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (8′). The diffraction data were collected on RIGAKU AFS-6S diffractometer and analyzed, the teXsan system being used.[19] A brown platelike crystal of **8′** (approximate dimensions of 0.34 mm × 0.27 mm × 0.18 mm) was mounted in a glass capillary. Crystal data and collection and refinement parameters for **8′** are summarized in Table 1 (and also in Table S1 of Supporting Information). The atomic coordinates (Table S2), thermal parameters (Table S3), and $F_o - F_c$ Tables (Table S6) for **8′** are listed in the Supporting Information. A decay (8.9%) was observed, and a correction was applied.

Chart 1. Abbreviations and Formula Numbers

$[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (**1**), $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9](pts)_4\cdot 7H_2O$ (**1′**)

pts *p*-toluenesulfonate, $CH_3C_6H_4SO_3^-$

$[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (**2**), $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9](pts)_4\cdot 9H_2O$ (**2′**)

$[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu_3\text{-}SCH{=}CHS)(H_2O)_9]^{4+}$ (**3**)

$[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)(\mu_3\text{-}SCH{=}CHS)(H_2O)_9]^{4+}$ (**4**)

$[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (**5**)

$[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (**6**), $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9](pts)_4\cdot 9H_2O$ (**6′**)

$[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(NCS)_9]^{5-}$ (**7**), $(Hpy)_5[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(NCS)_9]\cdot 2H_2O$ (**7′**)

Hpy pyridinium ion, $C_5H_6N^+$

$[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]^{4-}$ (**8**),

$K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (**8′**)

$Ba[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(ida)_3]\cdot 7H_2O$ (**9′**) (ida = $NH(CH_2CO_2)_2$)

$K_2[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(Hnta)_3]\cdot KCl\cdot 7H_2O$ (**10′**) (Hnta = $N(CH_2CO_2)_2(CH_2CO_2H)$)

$Na_2[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(Hnta)_3]\cdot 5H_2O$ (**11′**)

$(Hbpy)_5[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(NCS)_9]\cdot 3H_2O$ (**12′**)

Hbpy 2,2′-bipyridinium ion, $C_{10}H_9N_2^+$

The structure of **8′** was solved by SHELXS-86, and all the remaining non-hydrogen atoms were located from difference maps except for some of the disordered pyridinium ions. Of the three-and-a-half pyridinium ions, two (N81, C811−C815; N82, C821−C825) are refined normally, and a rigid model is applied to the remaining one-and-a-half pyridinium ions: two groups, (N83, C831−C835) and (N84, C841−C845), are in general positions close to each other; therefore, the occupancy factor 0.5 was assigned to each of the groups. The last group, (N85, C851−C855), lies around a center of symmetry and is inevitably disordered.

The positions of three hydrogen atoms attached to C1 and C2 originating from acetylenic carbon atoms were found by difference Fourier maps, and those of hydrogen atoms attached to pyridinium groups were obtained by calculation. The rigid model of Hpy was obtained by the use of the dimensions of $C_5H_5N\cdot 2HF$.[20] The temperature factors for hydrogen atoms were assigned values 1.2 times greater than the isotropic temperature factor of the C to which it is bonded. An empirical absorption correction based on azimuthal scans of several reflections was applied. All calculations for the refinement were performed using the teXsan crystallographic software package.[19] Although the residual electron densities are rather large, they are within 1.00 Å from tungsten atoms.

Results and Discussion

The abbreviations and formula numbers are summarized in Chart 1.

Synthesis of $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (8′) and Reactivity of Incomplete Cubane-Type Sulfur- and Oxygen-Bridged Tungsten Clusters with Acetylene. The incomplete cubane-type oxygen- and sulfur-bridged molybdenum aqua clusters **1** and **2** in 1.0 M HCl react with acetylene to produce clusters with alkenedithiolate ligands, **3** and **4**, respectively (Scheme 1a),[2] while the corresponding tungsten aqua clusters **5**[3] and **6**[4] in 1.0 M HCl do not react with acetylene. There are no significant dimensional differences between **2′** and **6′** and between **9′**[21] and **10′**[22] (see Table 2). Although the X-ray structure of **1** (determined as **1′**) has been determined, that of **5** is unknown. We thought that a change of the aqua ligand to other ligands might change the bridging sulfur from nonreactive to reactive, and we tried to find reactive

---

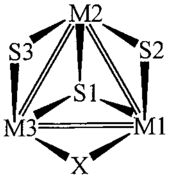
(19) *Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.

(20) Boenigk, D.; Mootz, D. *J. Am. Chem. Soc.* **1988**, *110*, 2135−2139.

(21) Shibahara, T.; Miyake, H.; Kobayashi, K.; Kuroya, H. *Chem. Lett.* **1986**, 139−142.

(22) Shibahara, T.; Takeuchi, A.; Kuroya, H. *Inorg. Chim. Acta* **1987**, *127*, L39−L40.

Table 2. Bond Distances (Å) in $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9](pts)_4\cdot 9H_2O$ (**2′**), $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9](pts)_4\cdot 9H_2O$ (**6′**) $Ba[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(ida)_3]\cdot 7H_2O$ (**9′**), $K_2[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(Hnta)_3]\cdot KCl\cdot 7H_2O$ (**10′**), $Na_2[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(Hnta)_3]\cdot 5H_2O$ (**11′**), $(Hbpy)_5[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(NCS)_9]\cdot 3H_2O$(12′), and $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$(**8′**)[a]



(M=Mo, W; X=O1, S1)

	(**2′**)	(**6′**)	(**9′**)	(**10′**)	(**11′**)	(**12′**)	(**8′**)
M1−M2	2.742(2)	2.713(1)	2.716(2)	2.728(1)	2.728(1)	2.760(1)	2.8363(5)
M1−M3	2.727(2)	2.704(1)	2.612(2)	2.620(1)	2.728(1)	2.767(1)	2.6611(7)
M2−M3	2.737(2)	2.707(1)	2.733(2)	2.719(1)	2.759(1)	2.764(1)	2.7151(3)
M1−S1	2.343(4)	2.347(4)	2.361(4)	2.353(6)	2.347(4)	2.343(4)	2.361(2)
M2−S1	2.333(5)	2.331(4)	2.336(4)	2.343(6)	2.348(3)	2.344(4)	2.351(2)
M3−S1	2.336(3)	2.336(3)	2.358(4)	2.336(6)	2.351(4)	2.362(5)	2.386(2)
M1−S2	2.277(5)	2.287(4)	2.298(5)	2.308(6)	2.308(4)	2.295(5)	2.418(2)
M2−S2	2.282(5)	2.286(4)	2.317(5)	2.318(6)	2.316(4)	2.322(6)	2.421(2)
M2−S3	2.285(3)	2.288(3)	2.325(5)	2.319(6)	2.296(4)	2.291(5)	2.265(2)
M3−S3	2.289(4)	2.287(4)	2.294(5)	2.313(6)	2.306(4)	2.309(6)	2.274(2)
M1−X	2.285(3)	2.278(3)	1.938(11)	1.956(14)	2.291(4)	2.312(5)	2.045(5)
M3−X	2.279(4)	2.280(4)	1.949(11)	1.947(14)	2.310(4)	2.309(5)	2.059(6)

[a] The numbering of atoms in the clusters is different from those in the original papers.

derivatives of **5**. In the initial stage we found that the tungsten cluster **10** did not react with acetylene in water, but at high hydrochloric acid concentrations **5** reacted with acetylene. Since it was difficult to isolate or treat tungsten chloro clusters $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2Cl_{9-x}(H_2O)_x]^{(5-x)-}$, we used tungsten thiocyanato cluster **7** obtained from **5** and NCS^-, and we did find the reaction to give **8**. It is interesting that the reactivity of the bridging sulfur atom μ-S toward acetylene is controlled by the change to other ligands.

For the synthesis of **7′** and **8′**, KSCN (1.5 M) was added to **5** in 1.0 M HCl solution to keep the full coordination of nine NCS^- to W_3OS_3 cores. The peak positions of the spectra of **7′** and **8′** in water with no addition of KSCN shifted to shorter wavelengths. To accelerate the reaction of **5** with NCS^-, the temperature was maintained at 50 °C. At higher temperatures a side reaction of NCS^- with H^+ occurred and white precipitates were deposited. The acidity of HCl was kept at 1.0 M; lower acidity slowed the reaction of **7** with acetylene to give **8**, and higher acidity caused the formation of white precipitates (see the section on the reaction of **7** with acetylene).

The reaction of **7** with acetylene to give **8** took 3 days at 50 °C, while the reaction of **1** and **2** to give **3** and **4**, respectively, was completed within 2 h at room temperature. As for stability, the electronic spectrum of the sample either in 1.5 M KSCN solution or in acetonitrile did not change for 1 month while **3** and **4** in 1.0 M HCl decomposed completely in a few days to give precipitates, the supernatant solution being colorless.

The electronic spectra of **8′**, **7′**, and **5** (in 1.0 M HCl) are shown in Figure 1′, and their absorption maxima and ϵ values are listed in Table 3. The reaction of **7** with acetylene to give **8** causes large spectral changes in the visible and near-infrared regions when no isosbestic points are maintained, while isosbestic points were maintained in the reaction of either **1** or **2** with acetylene.

Presence of an Intermediate $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu_3\text{-}SCH{=}CH\text{-}S)(NCS)_9]^{5-}$ (A). Acidity has a large influence on the formation rate of **8**. Three different kinds of media were used in the reaction of **7** with acetylene to give **8** at 50 °C (experiements a−c), and the results are shown in Figure 2. The reaction in 1.0 M HCl proceeds at least 3 times faster than those of the reactions either in 0.1 M HCl or in 0.1 M HCl + 0.9 M LiCl. These results suggest participation of the hydrogen ion in the reaction.

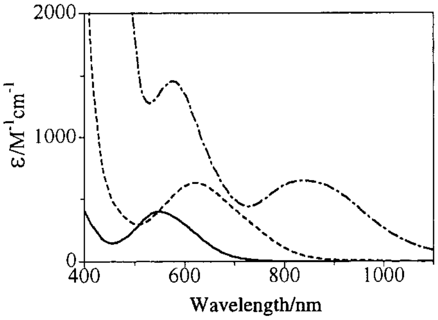


Figure 1. Electronic spectra of (—·—) $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (**8′**) in 1.0 M HCl containing 1.5 M KSCN, (- - -) $(Hpy)_5[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(NCS)_9]\cdot 2H_2O$ (**7′**) in 1.0 M HCl containing 1.5 M KSCN, and (−) $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (**5**) in 1.0 M HCl.

Table 3. Electronic Spectra of $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (**8′**), $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(H_2O)_9]^{4+}$ (**5**), and $(Hpy)_5[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(NCS)_9]\cdot 2H_2O$ (**7′**)

compound	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	solvent
5	547 (400)	1.0 M HCl
7′	620 (630)	1.0 M HCl containing 1.5 M KSCN
8′	844 (620), 574 (1390)	1.0 M HCl containing 1.5 M KSCN

Electronic spectral changes obtained in experiments c1−c5 are shown in parts a (experiment c1), b (experiment c2), c (experiment c3), andd (experiment c4) of Figure 3. The reaction of **7** with acetylene gives a new peak at ca. 900 nm at pH 3 and at a higher complex concentration (parts a and b of Figure 3). As is shown in Scheme 4, we propose the presence of an intermediate **A** and an equilibrium reaction between **7** and **A**. The reaction rate of **A** with H^+ should be very low at such a low acid concentration as pH 3, and we attribute the peak at 900 nm to **A**. Higher complex concentration and lower tem-

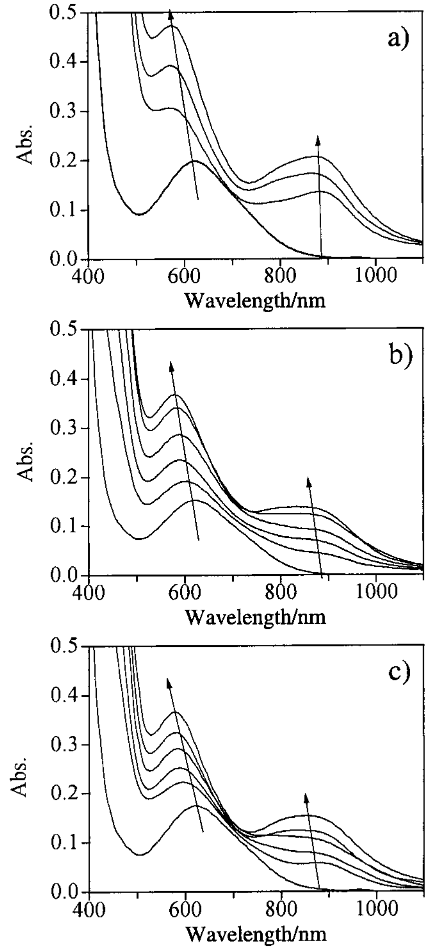
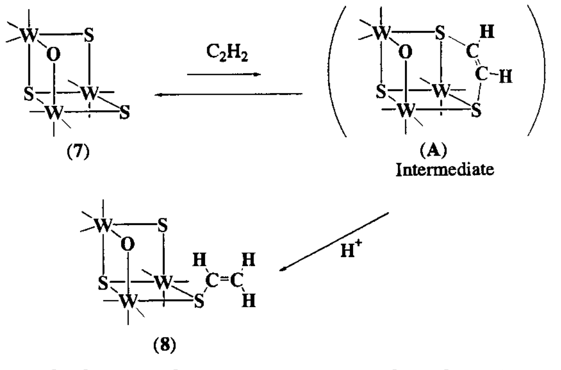


Figure 2. Electronic spectral change from the reaction of $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(NCS)_9]^{5-}$ (**7**) with acetylene to give the final product $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})(\mu\text{-SCH=CH}_2)(NCS)_9]^{4-}$ (**8**): (a) in 1.0 M HCl containing 1.5 KSCN; (b) in 0.1 M HCl containing 1.5 KSCN; (c) in 0.1 M HCl containing 1.5 KSCN and 0.9 M LiCl.

Scheme 4. Reaction of $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(NCS)_9]^{5-}$ (**7**) with Acetylene To Give $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})(\mu\text{-SCH=CH}_2)(NCS)_9]^{4-}$ (**8**) via an Intermediate $[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu_3\text{-SCH=CHS})(NCS)_9]^{5-}$ (**A**)



perature (higher acetylene concentration in the solution) increase the concentration of **A** (see parts b and c of Figure 3). The mechanism is supported by the reaction conducted in a refrigerator (Figure 3d), which gives a more distinct peak at 900 nm. Passing dinitrogen to the reaction mixture of **7** and acetylene suppressed the appearance of the peak at 900 nm and passing acetylene to the solution produced the peak. This also supports the mechanism. The reaction of **7** with acetylene to give **A** proceeds more quickly at lower temperature because of the better solubility of acetylene, but the reaction of **A** with proton is enhanced at higher temperature, which is a normal reaction.

Table 4. Bond Distances (Å) and Angles (deg) in $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})(\mu\text{-SCH=CH}_2)(NCS)_9]$ (**8′**)

W1−W2	2.8363(5)	W3−S3	2.274(2)
W1−W3	2.6611(7)	W1−O1	2.045(5)
W2−W3	2.7151(3)	W3−O1	2.059(6)
W1−S1	2.361(2)	S2−C1	1.769(9)
W2−S1	2.351(2)	C1−C2	1.27(1)
W3−S1	2.386(2)	C1−H1	1.06
W1−S2	2.418(2)	C2−H2	1.14
W2−S2	2.421(2)	C2−H3	0.83
W2−S3	2.265(2)		

W2−W1−W3	59.09(1)	W3−W1−O1	49.8(1)
W1−W2−W3	57.24(1)	W1−W3−O1	49.4(1)
W2−W3−W1	63.672(9)	W2−W3−O1	97.8(1)
W2−W1−S1	52.83(4)	W1−S1−W2	74.01(5)
W3−W1−S1	56.35(4)	W1−S1−W3	68.18(5)
W1−W2−S1	53.16(5)	W2−S1−W3	69.93(5)
W3−W2−S1	55.64(4)	W1−S2−W2	71.76(4)
W1−W3−S1	55.46(4)	W2−S3−W3	73.49(7)
W2−W3−S1	54.43(4)	W1−O1−W3	80.8(2)
W2−W1−S2	54.17(5)	W1−S2−C1	110.8(3)
W3−W1−S2	97.68(4)	W2−S2−C1	111.3(2)
W1−W2−S2	54.08(4)	S2−C1−C2	121.8(7)
W1−W2−S3	95.58(6)	S2−C1−H1	120.95
W3−W2−S2	96.19(4)	C2−C1−H1	115.36
W3−W2−S3	53.41(5)	C1−C2−H2	110.19
W1−W3−S3	100.34(5)	C1−C2−H3	134.41
W2−W3−S3	53.10(5)	H2−C2−H3	113.2
W2−W1−O1	94.5(1)		

X-ray Structures of $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})(\mu\text{-SCH=CH}_2)(NCS)_9]$ (8′). X-ray structural analysis of **8′** revealed the formation of a single carbon−sulfur bond as shown in Figure 4 (and Scheme 1b), where three ethylene hydrogen atoms were located by the Fourier difference maps. Interatomic distances and angles are collected in Table 4 (and in Tables S4 and S5 of Supporting Information). Table 5 indicates that the C1−C2 distance is 1.27(1) Å, which is almost equidistant between ethylene (1.339 Å) and acetylene (1.203 Å). The distances C1−C2 and C1−S2 in **8′** are close to the corresponding ones reported for the M−SCH=CH$_2$ moieties in the dinuclear complexes. The angles S2−C1−C2 (121.8(7)°), S2−C1−H1 (120.9°), C2−C1−H1(115.4°), C1−C2−H2 (110.2°), C1−C2−H3 (134.4°), and H2−C2−S3 (113.2°) are close to 120°, which also indicates the double bond character of C1−C2 bond.

Before discussing the geometrical change of the W_3OS_3 core before and after the reaction of **7** with acetylene, let us see how the change of ligands affects metal−metal and metal-bridging oxygen−sulfur distances. Bond distances of **8′** and related clusters are listed in Table 2. As for the two clusters $Na_2[W_3(\mu_3\text{-S})(\mu\text{-S})_3(Hnta)_3]\cdot 5H_2O$ (**11′**) and $(Hbpy)_5[W_3(\mu_3\text{-S})(\mu\text{-S})_3(NCS)_9]\cdot 3H_2O$ (**12′**) with W_3S_4 cores, the change of the ligand from $Hnta^{2-}$ to NCS^- caused elongation of W−W distances by only ca. 0.03 Å and no substantial change of W−S distances.

Now we can discuss the geometrical effect of the introduction of acetylene. The core geometries of the complexes **8′** and **10′** are compared, since the X-ray structure of the thiocyanato complex **7** has not yet been determined. The W1−S2 and W2−S2 distances in **8′**, where S2 is a component of μ-SCH=CH$_2$, are clearly elongated compared with those in **10′**. The W2−S3 and W3−S3 distances in **8′** became slightly shorter, and W1−O and W3−O distances in **8′** became longer compared with those of **10′**. In contrast, the Mo−(μ-O) distances (1.932(4), 1.907(4) Å) in $[Mo_3(\mu_3\text{-S})(\mu\text{-O})(\mu_3\text{-SCH=CHS})(H_2O)_9]^{4+}$ became shorter compared with the corresponding distances in $[Mo_3(\mu_3\text{-S})(\mu\text{-O})(\mu\text{-S})_2(H_2O)_9]^{4+}$ (2.150(3), 2.129(4) Å). The

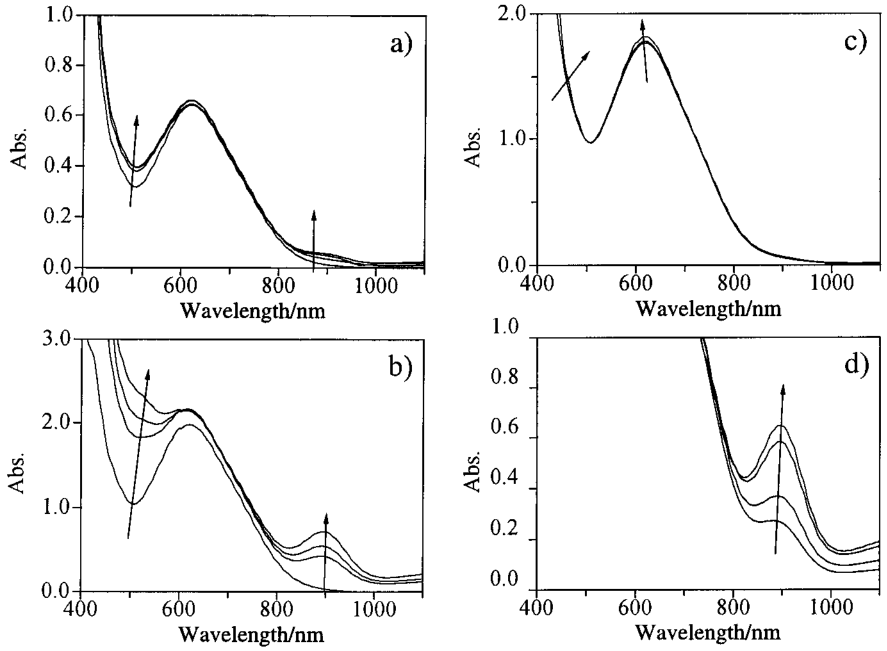


Figure 3. Electronic spectral change from reaction of $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(NCS)_9]^{5-}$ (**7**) with acetylene in pH 3 HCl containing 1.5 M KSCN to give the intermediate $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}SCH{=}CHS)(NCS)_9]^{5-}$ (**A**) (see Experimental Section): (a) experiment c1, lower complex concentration (**7′**, 1.02×10^{-3} M) at room temperature, where the electronic spectra were taken after 12 h and 2, 5, and 7 days; (b) experiment c2, higher complex concentration (**7′**, 3.56×10^{-3} M) at room temperature, where the electronic spectra were taken after 12 h and 2, 5, and 7 days; (c) experiment c3, higher complex concentration (**7′**, 3.56×10^{-3} M) at 50 °C, where the electronic spectra were taken after 1, 2, and 5 days; (d) experiment c4, higher complex concentration (**7′**, 2.99×10^{-3} M) at room temperature and then in a refrigerator, where the electronic spectra were taken after 1, 2, and 9 days.

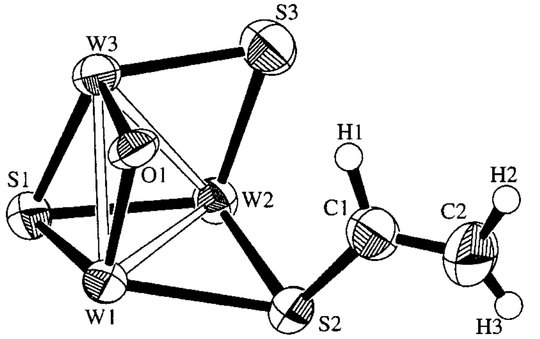


Figure 4. ORTEP drawing of the anion of $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (**8′**). The NCS^- ligands are omitted for clarity.

metal−metal bond distances also changed. The W1−W2 distance in **8′** became longer by more than 0.1 Å, W1 and W2 being bridged by μ-SCH=CH$_2$, while W2−W3 and W1−W3 distances remained almost unchanged.

The complex anions **8** are linked to each other by the cation K^+, creating a three-dimensional network (Figure 5).

NMR of $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (8′). ^{1}H NMR and HH correlation spectra of **8′** (experiment d) are shown in Figure 6, which support the results of the X-ray structural analysis. The ^{1}H NMR spectrum shows three signals at 2.42 (1H, dd), 4.84 (1H, d, $J = 8.8$ Hz), and 4.89 (1H, d, $J = 16.2$ Hz) ppm due to the μ-SCH=CH$_2$ moiety of **8′**. The first signal (2.42 ppm) is broad, but separation into a quartet can be seen. The HH COSY spectrum shows spin couplings of the signal at 2.42 ppm with the signals at 4.84 and 4.89 ppm. If the relationship $J_{\text{trans}} > J_{\text{cis}}$ holds in this species,[23] the three protons H1, H2, and H3 are assigned as shown in the figure. No geminal coupling between H2 and H3 was observed. The ^{13}C NMR signals assignable to the μ-SCH=CH$_2$ moiety of **8′** in acetonitrile appear at 149.9 (without decoupling, doublet) and 127.9 (without decoupling, triplet) ppm. The former signal is assigned to C1, and the latter is assigned to C2 (see Figure 4). The data from ^{1}H NMR spectra are consistent with the ^{13}C data. Other ^{1}H NMR signals at 2 ppm and 8−9 ppm are due to acetonitrile and pyridinium ions, respectively. The ratio of hydrogen combined with the carbon

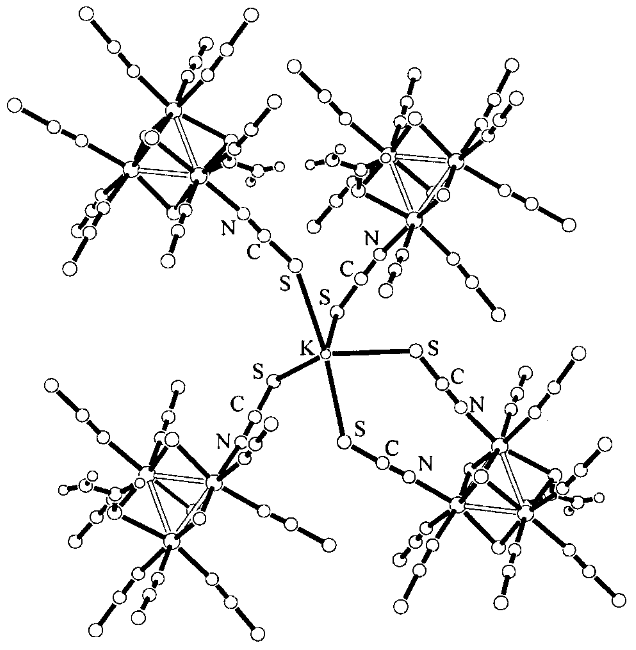
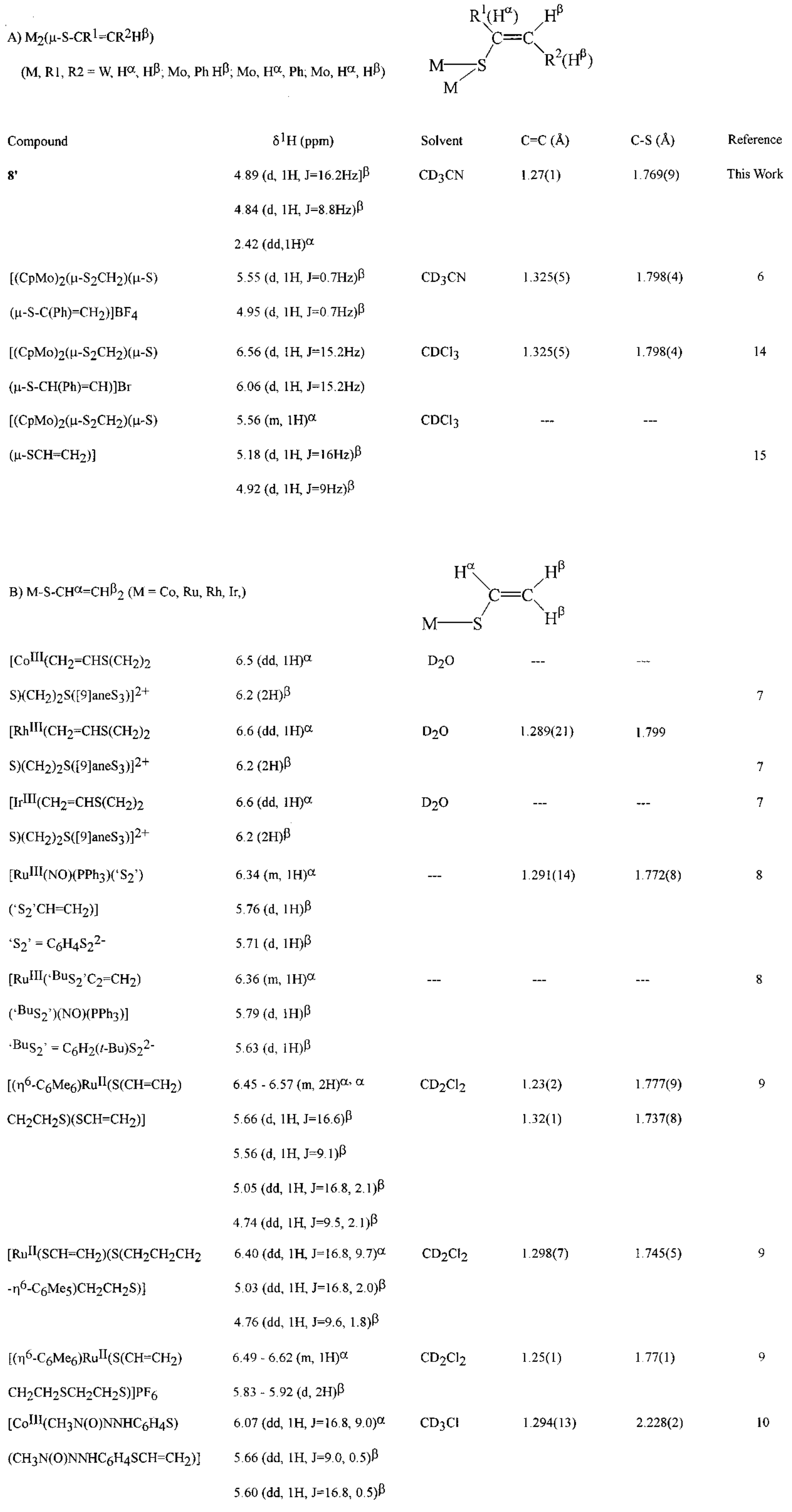


Figure 5. Crystal structure of $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (**8′**) showing the three-dimensional network, K^+ being involved.

---

[23] Pretsch, E.; Clerc, T.; Soible, J.; Simon, W. *Table of Spectral Data for Structure Determination of Organic Compounds*, 2nd ed.; Springer: New York, 1985.

Table 5. ^{1}H NMR and Atomic Distances in Complexes Having $M_2(\mu\text{-S-CR}^1{=}\text{CR}^2\text{H}^\beta)$ (M, R^1, R^2 = W, H$^\alpha$, H$^\beta$; Mo, Ph H$^\beta$; Mo, H$^\alpha$, Ph; Mo, H$^\alpha$, H$^\beta$) and $M{-}S{-}CH^\alpha{=}CH^\beta{}_2$ (M = Co, Ru, Rh, Ir) Moieties



A) $M_2(\mu\text{-S-CR}^1{=}\text{CR}^2\text{H}^\beta)$

(M, R1, R2 = W, H$^\alpha$, H$^\beta$; Mo, Ph H$^\beta$; Mo, H$^\alpha$, Ph; Mo, H$^\alpha$, H$^\beta$)

Compound	δ^1H (ppm)	Solvent	C=C (Å)	C-S (Å)	Reference
8'	4.89 (d, 1H, J=16.2Hz]$^\beta$ 4.84 (d, 1H, J=8.8Hz)$^\beta$ 2.42 (dd,1H)$^\alpha$	CD_3CN	1.27(1)	1.769(9)	This Work
$[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-S})$ $(\mu\text{-S-C(Ph)=CH}_2)]BF_4$	5.55 (d, 1H, J=0.7Hz)$^\beta$ 4.95 (d, 1H, J=0.7Hz)$^\beta$	CD_3CN	1.325(5)	1.798(4)	6
$[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-S})$ $(\mu\text{-S-CH(Ph)=CH})]Br$	6.56 (d, 1H, J=15.2Hz) 6.06 (d, 1H, J=15.2Hz)	$CDCl_3$	1.325(5)	1.798(4)	14
$[(CpMo)_2(\mu\text{-}S_2CH_2)(\mu\text{-S})$ $(\mu\text{-SCH=CH}_2)]$	5.56 (m, 1H)$^\alpha$ 5.18 (d, 1H, J=16Hz)$^\beta$ 4.92 (d, 1H, J=9Hz)$^\beta$	$CDCl_3$	---	---	15

B) $M\text{-S-CH}^\alpha{=}\text{CH}^\beta{}_2$ (M = Co, Ru, Rh, Ir,)

Compound	δ^1H (ppm)	Solvent	C=C (Å)	C-S (Å)	Reference
$[Co^{III}(CH_2{=}CHS(CH_2)_2$ $S)(CH_2)_2S([9]aneS_3)]^{2+}$	6.5 (dd, 1H)$^\alpha$ 6.2 (2H)$^\beta$	D_2O	---	---	7
$[Rh^{III}(CH_2{=}CHS(CH_2)_2$ $S)(CH_2)_2S([9]aneS_3)]^{2+}$	6.6 (dd, 1H)$^\alpha$ 6.2 (2H)$^\beta$	D_2O	1.289(21)	1.799	7
$[Ir^{III}(CH_2{=}CHS(CH_2)_2$ $S)(CH_2)_2S([9]aneS_3)]^{2+}$	6.6 (dd, 1H)$^\alpha$ 6.2 (2H)$^\beta$	D_2O	---	---	7
$[Ru^{III}(NO)(PPh_3)(\text{'}S_2\text{'})$ $(\text{'}S_2\text{'}CH{=}CH_2)]$ $\text{'}S_2\text{'} = C_6H_4S_2{}^{2-}$	6.34 (m, 1H)$^\alpha$ 5.76 (d, 1H)$^\beta$ 5.71 (d, 1H)$^\beta$	---	1.291(14)	1.772(8)	8
$[Ru^{III}(\text{'}^{Bu}S_2\text{'}C_2{=}CH_2)$ $(\text{'}^{Bu}S_2\text{'})(NO)(PPh_3)]$ $\text{'}^{Bu}S_2\text{'} = C_6H_2(t\text{-Bu})S_2{}^{2-}$	6.36 (m, 1H)$^\alpha$ 5.79 (d, 1H)$^\beta$ 5.63 (d, 1H)$^\beta$	---	---	---	8
$[(\eta^6\text{-}C_6Me_6)Ru^{II}(S(CH{=}CH_2)$ $CH_2CH_2S)(SCH{=}CH_2)]$	6.45 - 6.57 (m, 2H)$^{\alpha,\ \alpha}$ 5.66 (d, 1H, J=16.6)$^\beta$ 5.56 (d, 1H, J=9.1)$^\beta$ 5.05 (dd, 1H, J=16.8, 2.1)$^\beta$ 4.74 (dd, 1H, J=9.5, 2.1)$^\beta$	CD_2Cl_2	1.23(2) 1.32(1)	1.777(9) 1.737(8)	9
$[Ru^{II}(SCH{=}CH_2)(S(CH_2CH_2CH_2$ $\text{-}\eta^6\text{-}C_6Me_5)CH_2CH_2S)]$	6.40 (dd, 1H, J=16.8, 9.7)$^\alpha$ 5.03 (dd, 1H, J=16.8, 2.0)$^\beta$ 4.76 (dd, 1H, J=9.6, 1.8)$^\beta$	CD_2Cl_2	1.298(7)	1.745(5)	9
$[(\eta^6\text{-}C_6Me_6)Ru^{II}(S(CH{=}CH_2)$ $CH_2CH_2SCH_2CH_2S)]PF_6$	6.49 - 6.62 (m, 1H)$^\alpha$ 5.83 - 5.92 (d, 2H)$^\beta$	CD_2Cl_2	1.25(1)	1.77(1)	9
$[Co^{III}(CH_3N(O)NNHC_6H_4S)$ $(CH_3N(O)NNHC_6H_4SCH{=}CH_2)]$	6.07 (dd, 1H, J=16.8, 9.0)$^\alpha$ 5.66 (dd, 1H, J=9.0, 0.5)$^\beta$ 5.60 (dd, 1H, J=16.8, 0.5)$^\beta$	CD_3Cl	1.294(13)	2.228(2)	10

of Hpy$^+$ to that in μ-SCH=CH$_2$ is 6.00, which is in agreement with the results of elemental analyses.

An interesting feature of the spectra is the peculiar chemical shift of the H1 proton and the temperature dependence of both the line widths and the chemical shift of the μ-SCH=CH$_2$ protons resonances. The chemical shift of H1 (2.42 ppm) is close to that of acetylene protons, and the signal appears at much higher magnetic field compared with that of ethylene (5.28 ppm) and those of other complexes with $Mo_2(\mu\text{-SCH=CH}_2)$[5,15] or M-SCH=CH$_2$ moieties (M = metals) (see Table 5).[7-10] The carbon-carbon distances in complexes having $M{-}S{-}CH^\alpha{=}CH^\beta{}_2$[9] or $M{-}S(R){-}CH^\alpha{=}CH^\beta{}_2$ moieties[7,8,10] so far reported are slightly shorter than that of ethylene, while ^{1}H NMR signals of H$^\alpha$ and H$^\beta$ in these complexes appear in the region from 4.7 to 6.7 ppm, which is not so different from that of ethylene (5.28 ppm). The signals of H$^\alpha$ always appear at a lower field than

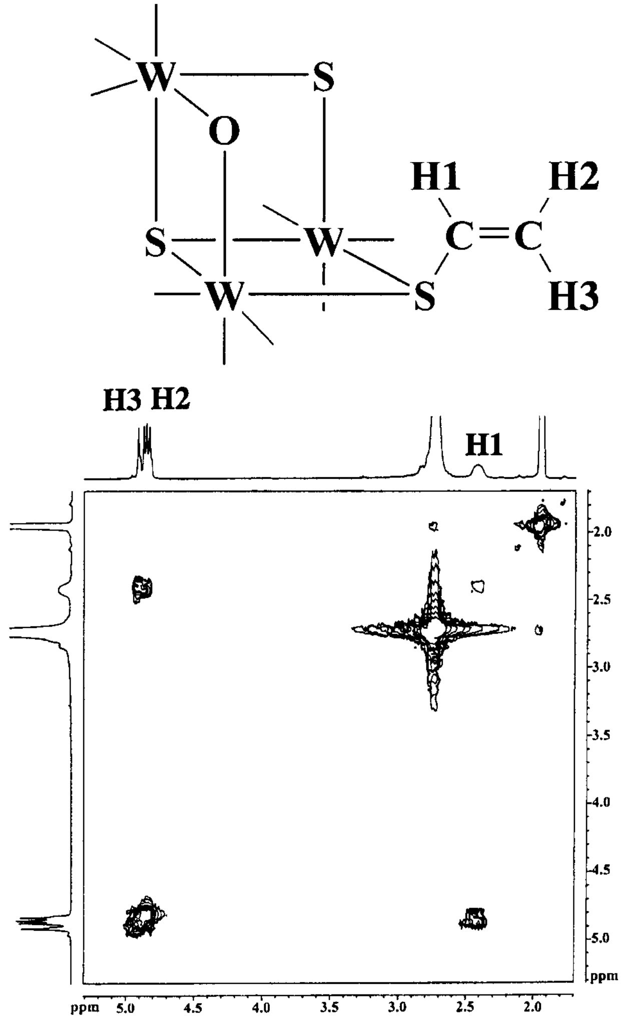


Figure 6. ^{1}H NMR and HH correlation spectra of $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (**8′**).

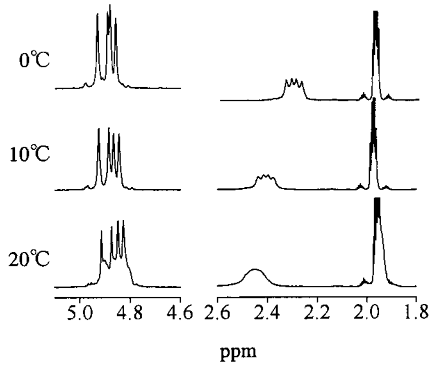


Figure 7. ^{1}H NMR spectra of $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (**8′**) at 0, 10, and 20 °C.

those of H^β.[7−10] As for the cluster **8′**, the C−C distance 1.27(1) Å follows the general tendency stated above; however, the signal of H1(H^α) appears at higher field than those of H2(H^β) and H3(H^β) as stated above.

The ^{1}H NMR spectra of **8′** obtained at lower temperatures (experiment e) are shown in Figure 7. The following values were obtained: at 20 °C, H1, δ 2.45 (1H, broad−m), H2, δ 4.84 (1H, d, J = 8.7 Hz), H3, δ 4.89 ppm (1H, d, J = 16.1 Hz); at 10 °C, H1, δ 2.41 (1H, q, J = 8.5, 15.6 Hz), H2, δ 4.86(1H, d, J = 8.7 Hz), H3, δ 4.91 (1H, d, J = 16.2 Hz); at 0 °C, H1, δ 2.30 (1H, q, J = 8.7, 15.9 Hz), H2, δ 4.87 (1H, d, J = 8.8 Hz), H3, δ 4.91 (1H, d, J = 16.3 Hz). Lowering the measurement temperature from 20 °C to 10 or 0 °C made the broad signal of H1 to a quartet, and the presence was made clear of couplings between H1 and H2 and between H1 and H3. The H1 signal is shifted considerably to the high magnetic field side, while those of H2 and H3 are shifted to the low ones, respectively.

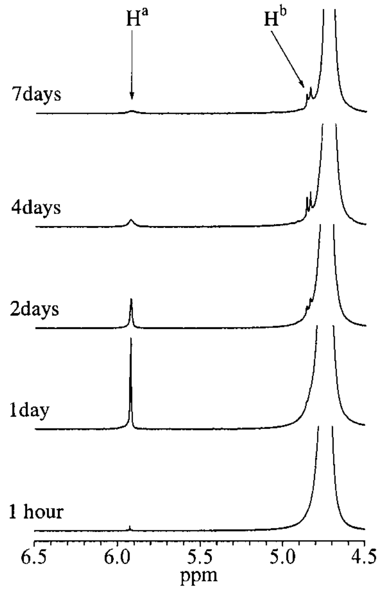


Figure 8. ^{1}H NMR spectral changes during the reaction of $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2(NCS)_9]^{5-}$(**7**) with acetylene in a mixture of 1.0 M DCl containing 1.5 M KSCN and CD_3CN (1:1): 1 h, 1, 2, 4, and 7 days.

The H1 proton is the closest to the cluster, and it is possible that it senses a shielding effect due to the W and the NCS moiety closest to it. This could give rise to the upfield shift. In addition, there is the possibility that the $CH{=}CH_2$ moiety is somehow distorted because of the steric effect; this could give rise to some conformational equilibria that have unpredictable effects in terms of chemical shift. This could be the origin also of the broadening of the resonances with increasing temperature. The ring current of the W_3OS_3 group, if any, might also be responsible.[24,25]

To clarify the reaction path from **7** to **8**, that is, to see the presence of any intermediates, a ^{1}H NMR experiment was done (see experiment f) where a mixed solvent of 1.0 M DCl (containing 1.5 M KSCN) and CH_3CN (1:1) was used because **8′** is hardly soluble in 1.0 M DCl containing 1.5 M KSCN. In experiment f, new signals other than signals due to **8** were observed (Figure 8); a signal, H^a (5.93(s) ppm), appears after 1 h and grows, but it decreases after 2 days with the appearance of another signal H^b (4.85(d, J = 8.8 Hz) ppm) due to **8**. After 4 days the signal H^a becomes weaker than that of H^b. Since the signal H^a is a singlet, the formation is confirmed of $[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu_3\text{-}SCH{=}CHS)(NCS)_9]^{5-}$(**A**) having two C−S bonds.[26] The signal H^b is due to **8** having one C−S bond, which was substantiated by results from experiment d. The signal H^b of **8** at ca. 2.4 ppm is obscured by the signal of free acetylene at 2.32 ppm, but the presence of H^b is verified by HH COSY. These results give the following reaction scheme from **7** to **8**.

---

(24) Kobayashi, H.; Shibahara, T.; Uryu, N. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 799−803.

(25) Chen, Z.; Lu, J.-X.; Liu, C.-W.; Zhang, Q.-N. *Polyhedron* **1991**, *10*, 2799−2807.

(26) The ^{1}H NMR spectrum of **3** (in 1.0 M CH_3SO_3H, 20 °C, 400 MHz) also shows a singlet signal at δ 6.73 due to the $-SCH{=}CHS-$ moiety of the cluster. The electronic spectrum of **3** in 1.0 M HCl shows a peak at. 810 nm (see ref 2).

The first stage is the reaction of **7** with acetylene to give **A**. Then the addition of a proton to **A** causes cleavage of one of the C−S bonds to give **8** as shown in Scheme 4. This mechanism is similar to that reported by Rakowski Dubois et al.[5,6]

Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (Grant No. 12023253, “Metal-Assembled Complexes”) from the Ministry of Education, Science, Sports and Culture, Japan, and by a Special Grant for Cooperative Research administered by Japan Private School Promotion Foundation.

Supporting Information Available: An X-ray crystallographic file in CIF format for compound $K_{0.5}(Hpy)_{3.5}[W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}SCH{=}CH_2)(NCS)_9]$ (**8′**). This material is available free of charge via the Internet at http://pubs.acs.org.

IC001174K