Syntheses and Electrochemistry of Incomplete Cubane-Type Clusters with M_3S_4 Cores (M = Mo, W). X-ray Structures of $[W_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4 \cdot 9H_2O$, $Na_2[W_3S_4(Hnta)_3] \cdot 5H_2O$, and $(bpyH)_5[W_3S_4(NCS)_9] \cdot 3H_2O$

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Facile synthetic methods for $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (**4′**) and $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ (**1′**) are described, $(NH_4)_2MoS_4$ (or $Na_2[Mo_2O_2S_2(cys)_2] \cdot 4H_2O$) and $(NH_4)_2WS_4$ being used for starting materials, respectively. Synthetic methods for derivative clusters with M_3S_4 cores (M = Mo, W), $[W_3S_4(Hnta)_3]^{2-}$, $[W_3S_4(NCS)_9]^{5-}$, and $[Mo_3S_4(Hnta)_3]^{2-}$, are also described. Crystal structures of $[W_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4 \cdot 9H_2O$ (**1**), $Na_2[W_3S_4(Hnta)_3] \cdot 5H_2O$ (**2a**), and $(bpyH)_5[W_3S_4(NCS)_9] \cdot 3H_2O$ (**3**) were determined. Compound **1** crystallized in the triclinic space group $P\bar{1}$ with $a = 15.353$ (7) Å, $b = 16.733$ (6) Å, $c = 12.003$ (5) Å, $\alpha = 95.49$ (3)°, $\beta = 108.42$ (3)°, $\gamma = 101.96$ (4)°, $V = 2818.7$ (22) Å^3, and $Z = 2$. Compound **2a** crystallized in the monoclinic space group $P2_1/a$ with $a = 21.712$ (6) Å, $b = 12.711$ (6) Å, $c = 13.378$ (4) Å, $\beta = 102.09$ (3)°, $V = 3610.1$ (23) Å^3, and $Z = 4$. Compound **3** crystallized in the triclinic space group $P\bar{1}$ with $a = 12.607$ (5) Å, $b = 24.893$ (9) Å, $c = 12.108$ (4) Å, $\alpha = 92.98$ (3)°, $\beta = 90.96$ (3)°, $\gamma = 77.34$ (3)°, $V = 3702.4$ (24) Å^3, and $Z = 2$. The cluster cation and anions have an approximate symmetry of C_{3v}. Current-sampled dc polarograms and cyclic voltammograms of $[M_3S_4(Hnta)_3]^{2-}$ (M = Mo (**5′**), W (**2′**)) show three consecutive one-electron reductive steps in alkaline solution (pH 11–12): $E_{1/2}$ (V vs Ag/AgCl) = −0.64, −1.08, −1.39; −1.12, −1.41, −1.88, respectively. These steps correspond to the change of oxidation states of the three metals in each cluster: (IV,IV,IV) → (IV,IV,III) → (IV,III,III) → (III,III,III). Electronic spectra of one-electron reduction products, the oxidation state being (IV,IV,III), obtained by bulk electrolyses of **5′** and **2′** have been reported for the first time, and the absorption maxima are 400, 620, and 720 sh nm for $[Mo_3S_4(Hnta)_3]^{3-}$ and 557, 597, and 708 nm for $[W_3S_4(Hnta)_3]^{3-}$.

Since the existence of incomplete cubane-type sulfur-bridged tungsten(IV) clusters with $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores was disclosed in 1986,[1] several reports have appeared on clusters with $W_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores.[2] Cotton et al. synthesized $[W_3S_4(\text{diphosphine})_3X_3]^+$ (diphosphine = dmpe, depe; X = Cl, H) by the reaction of WCl_4 with NaHS and diphosphine in THF, and determined those X-ray structures.[2b,c] They also synthesized $[W_3S_4Br_4(PEt_3)_3(OPEt_2H)(H_2O)]$ by the reaction of $W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_4$ with triethylphosphine in THF,[2d] where $W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_4$ was prepared from the elements, that is, tungsten metal, sulfur, and Br$_2$. Fedin et al. synthesized $[W_3S_4(H_2O)_9]^{4+}$ (**1′**) from $W_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3Br_4$, which was also utilized for the synthesis of $[W_3S_4(S_4)_3(NH_3)_3]^{2-}$.[2e,f] Zhan et al.[2h] and Zheng et al.[2g] reported the structures of $[W_3S_4(dtp)_3(\mu\text{-}O_2CCH_3)(py)] \cdot 0.5HCON(CH_3)_2$ and $[W_3S_4(dtp)_3(\mu\text{-}O_2CCH_3)(py)]$, respectively. Substitution reaction at W on **1′** was also investigated recently.[3] Many more reports on the molybdenum clusters with $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ cores[4] have appeared than those on the tungsten clusters with W_3S_4 cores. Some interesting reviews concerning clusters with Mo_3S_4 or W_3S_4 have been reported.[5]

We report here a facile synthetic method of **1′** obtained by the reduction of $(NH_4)_2WS_4$ with NaBH$_4$ in hydrochloric acid medium, from which the derivative clusters $[W_3S_4(Hnta)_3]^{2-}$ (**2′**) and $[W_3S_4(NCS)_9]^{5-}$ (**3′**) are easily prepared. By the reaction of $(NH_4)_2MoS_4$ with NaBH$_4$, the corresponding molybdenum(IV) aqua ion, $[Mo_3S_4(H_2O)_9]^{4+}$ (**4′**), has been synthesized in high yield and the method is also described here. A molybdenum(V) dimer, $Na_2[Mo_2O_2S_2(cys)_2] \cdot 4H_2O$ also is a useful source for the synthesis of **4′**. The redox chemistry is one of the most attractive parts of cluster chemistry, and we have investigated the redox properties of the clusters $[M_3S_4(Hnta)_3]^{2-}$ (M = Mo (**5′**), W (**2′**)). Three consecutive one-electron reductive steps are observed and, furthermore, the electronic spectra of the oxidation states of $M^{IV}_2M^{III}$ (M = Mo, W) have been obtained by bulk electrolyses of the corresponding clusters for the first time.

Experimental Section

Materials. *p*-Toluenesulfonic acid (HPTS) was used after recrystallization. Sodium borohydride, nitrilotriacetic acid, and tetraethylammonium chloride, as well as most other reagents, were commercial samples and were used as received. $(NH_4)_2WS_4$,[6] $(NH_4)_2MoS_4$,[6] and

$Na_2[Mo_2O_2S_2(cys)_2] \cdot 4H_2O$[7,8] were obtained by published procedures.

Syntheses of Compounds. All experiments were carried out in the air. $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3(H_2O)_9]^{4+}$ **Aqua Ion (1′) and $[W_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4 \cdot 9H_2O$ (1).** Sodium borohydride (9.0 g, 0.24 mol in 60 mL of H_2O) and 6 M HCl (60 mL) were pipetted alternately (ca. 4 mL each) into a yellow solution of $(NH_4)_2WS_4$ (9.0 g, 0.0258 mol in 150 mL of H_2O) with vigorous stirring at room temperature. Another quantity of HCl (6 M, 240 mL) was added to the resultant dark brown suspension, through which air was passed at a temperature above 90 °C for 5 h, which did not have to be continuous. During aeration the suspension turned to solution and the color of the solution became black. Also, 1 M HCl was added to the solution during air oxidation, if the volume of

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(4) For some papers giving earlier references, see: (a) Cotton, F. A.; Kibala, P. A.; Matusz, M.; McCaleb, C. S.; Sandor, R. B. W. *Inorg. Chem.* **1989,** *28,* 2623–2630. (b) Fedin, V. P.; Kolesov, B. A.; Mironov, Yu. V.; Fedorov, V. Ye. *Polyhedron* **1989,** *8,* 2419–2423. (c) Cheng, W.; Zhang, Q.; Huang, J.; Lu, J. *Polyhedron* **1989,** *8,* 2785–2789.

(5) Some recent reviews: (a) Lee, S. C.; Holm, R. H. *Angew. Chem., Int. Ed. Engl.* **1990,** *29,* 840–856. (b) Dance, I. G. *Polyhedron* **1986,** *5,* 1037–1104. (c) Zanello, P. *Coord. Chem. Rev.* **1988,** *83,* 199–275. (d) Cotton, F. A. *Polyhedron* **1986,** *5,* 3–14.

(6) McDonald, J. M.; Frisen, G. D.; Rosenheim, L. D.; Newton, W. E. *Inorg. Chim. Acta* **1983,** *72,* 205–210. Samples freshly prepared (or having been stored under dinitrogen atmosphere) should be used for the synthesis of **4′**: old samples will not dissolve in water and therefore will give lower yields.

(7) (a) Spivack, B.; Dori, Z. *J. Chem. Soc., Chem. Commun.* **1970,** 1716–1717. (b) Kay, A.; Mitchell, P. C. A. *J. Chem. Soc. A* **1970,** 2421–2428. (c) Armstrong, F. A.; Shibahara, T.; Sykes, A. G. *Inorg. Chem.* **1978,** *17,* 189–191.

(8) (a) Gheller, S. F.; Hambley, T. W.; Brownlee, R. T. C.; O'Connor, M. J.; Snow, M. R.; Wedd, A. G. *J. Am. Chem. Soc.* **1983,** *105,* 1527–1532. (b) Shibahara, T. *Abstracts of Papers, The 35th Okazaki Conference, Okazaki*; Institute for Molecular Science: Okazaki, Japan, 1989; pp 33–34.

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the solution became less than 300 mL. The solution was cooled in an ice bath and was filtered by suction. The precipitates (mainly boric acid) were washed with a small amount of 1 M HCl and the washings were joined to the filtrate and the total volume was reduced to ca. 100 mL by use of a rotary evaporator. The solution was filtered, and Sephadex G-10 column chromatography (diameter 4 cm, length 80 cm) was applied, the eluent being 1 M HCl.[9,10] The fourth eluate, which contains **1′** (blue-violet; λ_{max} = 570 nm in 1 M HCl), was collected (ca. 350 mL). Other eluates were as follows: first, $W_3(\mu_3\text{-}S)(\mu\text{-}O)_2(\mu\text{-}S)^{4+}$(aq) (red, 0.3%);[11a] second, $W_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2^{4+}$(aq) (red-purple, 5%);[11b] third, $W_2O_2S_2^{2+}$(aq) (yellow, 10%);[11c] fifth, reduced form of **1′** (brown, ca. 2 L). For concentration and purification, the solution obtained from the fourth band containing the aqua ion **1′** was diluted to five times its original volume with water and was absorbed on a short Dowex 50W-X2 cation exchanger column (diameter 2 cm, length 10 cm) and eluted with 2 M HCl slowly. A small amount of the tungsten(V) dimer $W_2O_2S_2^{2+}$(aq) was eluted first and then the aqua ion **1′** was collected. To purify further the solution (ca. 30 mL) from the cation exchanger, Sephadex G-10 column chromatography (diameter 2 cm, length 90 cm) was applied again, with the eluent being 1 M HCl. A small amount of $W_3OS_3^{4+}$(aq) was eluted first and the main band containing **1′** was collected; yield 25% based on $(NH_4)_2WS_4$. Typically 170 mL of a 0.013 M solution in 1 M HCl was obtained. The brown solution from the fifth band turned blue-violet over several hours, and the resulting blue-violet solution was purified similarly; yield ca. 5%.

In order to obtain the solid sample **1**, the aqua ion **1′** was absorbed on a Dowex 50W-X2 cation exchanger. The resin was washed with 0.1 M HPTS (p-toluenesulfonic acid) to remove Cl⁻ ion, and a purple solution was obtained by elution with 4 M HPTS. Cooling of the solution in a freezer (ca. −20 °C) for a few days gave purple plate crystals; yield 0.47 g, ca. 21% based on **1′** in 1 M HCl. Anal. Found (calcd): W, 31.7 (32.65); C, 20.21 (19.91); H, 3.84 (3.81).

Na₂[W₃S₄(Hnta)₃]·5H₂O (2a). H₃nta (0.22 g, H₃nta/W = 1.1) dissolved in a minimum amount of concentrated NaOH was added dropwise to a solution of the aqua trimer **1′** (20 mL, 0.0175 M per trimer) in 1 M HCl, and the pH was adjusted to 1.2 with concentrated NaOH. The resulting precipitates are dissolved by heating the mixture above 90 °C with stirring in a water bath (ca. 30 min). Blue-violet crystals were obtained after storage in a refrigerator for a week and were collected by filtration, washed with ethanol, and air-dried; yield 0.346 g (72%). Anal. Found (calcd): N, 2.90 (3.03); C, 15.38 (15.62); H, 2.13 (2.25).

K₂[W₃S₄(Hnta)₃]·10H₂O (2b). A procedure similar to that used for the sodium salt was employed except for the use of KOH instead of NaOH. Typically, 20 mL of the aqua ion **1′** (0.0136 M per trimer) in 1 M HCl and H₃nta (0.17 g) gave 0.27 g (66%) of **2b**. Anal. Found (calcd): N, 2.79 (2.79); C, 14.28 (14.36); H, 2.57 (2.74).

(bpyH)₅[W₃S₄(NCS)₉]·3H₂O (3). Excess KSCN (4.0 g, 0.041 mol) was added to the aqua ion **1′** (25 mL, 0.0018 M per trimer in 1 M HCl). The color of the solution turned immediately from blue-violet to green. The solution was heated at 50 °C for 90 min to promote the substitution reaction and allowed to stand overnight at room temperature. After filtration, several drops of a saturated solution of 2,2′-bipyridine in 2 M HCl were added to the solution. When this mixture was allowed to stand at room temperature for 2 weeks, deep green crystals were collected; yield 0.04 g (43%). Anal. Found (calcd): N, 13.01 (13.01); C, 33.92 (34.67); H, 2.35 (2.52). Standing for more than 2 weeks will give contamination with white precipitates.

[Mo₃(μ₃-S)(μ-S)₃(H₂O)₉]⁴⁺ Aqua Ion (4′). Method A. A procedure similar to that used for the synthesis of the tungsten trimer **1′** was applied. Sodium borohydride (9 g, 0.24 mol in 120 mL of H₂O) and 6 M HCl (120 mL) were pipetted alternately (ca. 4 mL each) into a red solution of $(NH_4)_2MoS_4$ (9.0 g, 0.0346 mol in 300 mL of H₂O) with vigorous stirring at room temperature. Another quantity of 6 M HCl (480 mL) was added to the resultant dark brown suspension, through which air was passed at a temperature above 90 °C for 20 h, which need not be continuous. During aeration the suspension turned to a solution and the color of the solution became dark green. Also, 1 M HCl was added to the solution during air oxidation, if the volume of the solution became less than ca. 300 mL. The solution was cooled in an ice bath and was filtered by means of suction. The precipitate (mainly boric acid) was washed with a small amount of 1 M HCl and the washings were joined

to the filtrate and the total volume was reduced to ca. 100 mL by use of a rotary evaporator. The solution was filtered and Sephadex G-10 column chromatography (diameter 4 cm, length 80 cm) was applied to the solution, the eluent being 1 M HCl. A small amount (ca. 1%) of $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2^{4+}$(aq) (green, λ_{max} = 605 nm in 1 M HCl)[12a] was followed by the aqua ion **4′** (green, λ_{max} = 620 nm in 1 M HCl), which was collected. For concentration and purification, the solution containing the aqua ion **4′** was diluted to five times its original volume with water and was absorbed on a short Dowex 50W-X2 cation exchanger column (diameter 2 cm, length 15 cm) and eluted with 2 M HCl slowly. Trace amount of a Mo(V) aqua dimer $Mo_2O_2S_2^{2+}$(aq) (yellow) was eluted first and then the aqua ion **4′** was collected; yield 50%. Typically 57 mL of a 0.1 M (per trimer) solution was obtained.

Method B. The cysteinato Mo(V) dimer $Na_2[Mo_2O_2S_2(cys)_2]\cdot4H_2O$ (10 g, 0.0155 mol) was dissolved in water (1 L) with stirring and 1 M HCl (30 mL) was added, which was followed by the slow addition of solid NaBH₄ (5 g). After the addition of Na₂S·9H₂O (5 g) to the solution, concentrated HCl (150 mL) was added very slowly. After 10 min, the resulting dark brown suspension was heated in a boiling water bath for 20 h, (which need not be continuous) with an air stream bubbling through the suspension to give a dark green solution. During heating in a water bath, a small amount of 1 M HCl was added occasionally if the volume of the solution became less than 200 mL. After being cooled to room temperature, the solution was filtered by means of suction and the precipitates (mainly boric acid) were washed with a small amount of 1 M HCl and the washings were joined to the filtrate. Then, the filtrate was subjected to Sephadex G-10 column chromatography (eluent 1 M HCl, diameter 4 cm, length 80 cm). The order of elution was as follows: $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_2(\mu\text{-}S)^{4+}$(aq) (grayish green, 2%),[12b] $Mo_3(\mu_3\text{-}S)(\mu\text{-}O)(\mu\text{-}S)_2^{4+}$(aq) (green, 27%),[12a] **4′** (green, 25%), and $Mo_2(\mu\text{-}S)_2O_2^{2+}$(aq) (orange, ca. 17%).[12c] For concentration and purification, Dowex 50W-X2 column chromatography (eluent 2 M HCl; diameter 2 cm, length 10 cm) was applied as described in method A.

Na₂[Mo₃S₄(Hnta)₃]·7H₂O (5a). A procedure similar to that used for the corresponding tungsten cluster **2a** was employed. Typically 10 mL of the aqua ion **4′** (0.067 M per trimer in 2 M HCl) and H₃nta (0.41 g) gave 0.60 g (78%) of **5a**. Anal. Found (calcd): N, 3.62 (3.63); C, 18.76 (18.70); H, 2.58 (3.05).

K₂[Mo₃S₄(Hnta)₃]·9H₂O (5b). A procedure similar to that used for the corresponding tungsten cluster **2b** was employed. Typically, 10 mL of the aqua ion **4′** (0.057 M per trimer in 2 M HCl) and H₃nta (0.345 g) gave 0.45 g (65%) of **5b**. Anal. Found (calcd): N, 3.47 (3.43); C, 17.83 (17.66); H, 3.00 (3.21).

Structural Determination of [W₃S₄(H₂O)₉](CH₃C₆H₄SO₃)₄·9H₂O (1), Na₂[W₃S₄(Hnta)₃]·5H₂O (2a), and (bpyH)₅[W₃S₄(NCS)₉]·3H₂O (3). A purple plate crystal (dimensions 0.25 × 0.17 × 0.15 mm) of **1** and a rhombic deep green crystal (dimensions 0.27 × 0.19 × 0.19 mm) of **3** were mounted in glass capillaries, respectively, and a black distorted cubic crystal (dimensions 0.20 × 0.18 × 0.15 mm) of **2a** was mounted on a glass fiber with an adhesive. The crystallographic and machine data for

Table I. Crystallographic Data for [W₃S₄(H₂O)₉](CH₃C₆H₄SO₃)₄·9H₂O, Na₂[W₃S₄(Hnta)₃]·5H₂O, and (bpyH)₅[W₃S₄(NCS)₉]·3H₂O

	$W_3S_8O_{30}C_{28}H_{64}$	$W_3S_4Na_2O_{23}N_3C_{18}H_{31}$	$W_3S_{13}O_3N_{19}C_{59}H_{51}$
fw	1688.83	1383.24	2042.59
space group	$P\bar{1}$	$P2_1/a$	$P\bar{1}$
syst absences		$h0l$: $h = 2n + 1$	
		$0k0$: $k = 2n + 1$	
a, Å	15.353 (7)	21.712 (6)	12.607 (5)
b, Å	16.733 (6)	12.711 (6)	24.893 (9)
c, Å	12.003 (5)	13.378 (4)	12.108 (4)
α, deg	95.49 (3)		92.98 (3)
β, deg	108.42 (3)	102.09 (3)	90.96 (3)
γ, deg	101.96 (4)		77.34 (3)
V, Å³	2818.7 (22)	3610.1 (23)	3702.4 (24)
Z	2	4	2
T, °C	18	18	19
λ(Mo Kα), Å	0.71073	0.71073	0.71073
d_{obsd}, g/cm³	2.00	2.52	1.84
d_{calcd}, g/cm³	1.990	2.545	1.825
μ, cm⁻¹	66.0	100.8	51.6
trans factors (max;min)	1.000; 0.807	1.000; 0.732	1.000; 0.827
$R(F_o)$, %	4.68	4.28	5.36
$R_w(F_o)$, %	5.96	7.25	7.37

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(10) The Sephadex column used can be refreshed by use of a small amount of diluted hydrogen peroxide (ca. 3%) followed by washing well with water.

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Table II. Atomic Coordinates in $[W_3S_4(H_2O)_9]^{4+}$

atom	x	y	z
W1	0.71208 (3)	0.10890 (3)	0.11596 (5)
W2	0.67965 (3)	−0.00598 (3)	−0.07696 (5)
W3	0.73617 (4)	−0.04499 (3)	0.14373 (5)
S1	0.8270 (2)	0.0536 (2)	0.0712 (3)
S2	0.5790 (2)	0.0717 (2)	−0.0513 (3)
S3	0.6100 (2)	−0.1196 (2)	−0.0164 (3)
S4	0.6543 (2)	0.0254 (2)	0.2297 (3)
O11	0.6478 (7)	0.2006 (6)	0.1801 (8)
O12	0.7662 (8)	0.2177 (6)	0.0496 (9)
O13	0.8280 (6)	0.1772 (6)	0.2726 (8)
O21	0.5767 (6)	−0.0602 (6)	−0.2547 (8)
O22	0.7560 (6)	−0.0734 (6)	−0.1554 (9)
O23	0.7248 (7)	0.0777 (6)	−0.1871 (9)
O31	0.6994 (9)	−0.1466 (8)	0.237 (1)
O32	0.8544 (8)	−0.0148 (8)	0.309 (1)
O33	0.8241 (7)	−0.1250 (7)	0.112 (1)

Table III. Atomic Coordinates in $[W_3S_4(Hnta)_3]^{2-}$

atom	x	y	z
W1	0.09949 (3)	0.50154 (4)	0.29193 (4)
W2	0.08037 (3)	0.70892 (4)	0.24254 (4)
W3	0.17294 (2)	0.59671 (4)	0.17609 (4)
S1	0.1714 (2)	0.6380 (3)	0.3468 (3)
S2	0.0043 (2)	0.5809 (3)	0.2241 (3)
S3	0.0995 (2)	0.7049 (3)	0.0794 (3)
S4	0.1181 (2)	0.4412 (3)	0.1376 (3)
O11	0.0867 (6)	0.5039 (8)	0.4417 (8)
O12	0.1721 (4)	0.4009 (8)	0.3665 (8)
O13	0.0607 (6)	0.414 (1)	0.5691 (9)
O14	0.2088 (6)	0.239 (1)	0.370 (1)
O15	−0.0262 (6)	0.154 (1)	0.291 (1)
O16	−0.0880 (7)	0.213 (1)	0.149 (1)
O21	0.1281 (5)	0.8556 (8)	0.2669 (9)
O22	0.0532 (5)	0.7681 (9)	0.3729 (8)
O23	0.1305 (5)	1.0251 (8)	0.224 (1)
O24	−0.0126 (9)	0.864 (2)	0.440 (1)
O25	−0.0918 (6)	0.960 (1)	0.048 (1)
O26	−0.0980 (7)	0.841 (1)	−0.075 (1)
O31	0.2550 (5)	0.5088 (9)	0.2333 (8)
O32	0.2438 (5)	0.7106 (8)	0.1897 (8)
O33	0.3325 (7)	0.411 (1)	0.200 (1)
O34	0.3173 (6)	0.786 (1)	0.119 (1)
O35	0.2382 (5)	0.549 (1)	−0.1731 (9)
O36	0.1362 (6)	0.545 (1)	−0.2350 (9)
N1	0.0488 (5)	0.3431 (9)	0.3068 (9)
N2	0.0029 (5)	0.830 (1)	0.1774 (9)
N3	0.2138 (5)	0.567 (1)	0.0334 (8)
C11	0.0590 (7)	0.427 (1)	0.478 (1)
C12	0.1643 (8)	0.299 (1)	0.351 (1)
C13	0.0200 (8)	0.355 (1)	0.397 (1)
C14	0.0975 (8)	0.259 (1)	0.321 (2)
C15	−0.0011 (7)	0.317 (1)	0.216 (1)
C16	−0.0382 (7)	0.219 (1)	0.224 (1)
C21	0.1041 (7)	0.937 (1)	0.221 (1)
C22	0.004 (1)	0.830 (2)	0.365 (1)
C23	0.0359 (7)	0.927 (1)	0.155 (1)
C24	−0.0314 (8)	0.853 (1)	0.262 (1)
C25	−0.0404 (8)	0.790 (1)	0.083 (1)
C26	−0.0793 (7)	0.874 (1)	0.019 (1)
C31	0.2846 (8)	0.466 (1)	0.171 (1)
C32	0.2720 (7)	0.729 (1)	0.114 (1)
C33	0.2613 (8)	0.479 (1)	0.057 (1)
C34	0.2464 (8)	0.670 (1)	0.014 (1)
C35	0.1649 (7)	0.543 (1)	−0.059 (1)
C36	0.1863 (8)	0.547 (1)	−0.161 (1)

Table IV. Atomic Coordinates in $[W_3S_4(NCS)_9]^{5-}$

atom	x	y	z
W1	0.20567 (7)	0.76905 (3)	0.40335 (6)
W2	0.06308 (7)	0.79471 (3)	0.22881 (6)
W3	0.07405 (7)	0.69799 (3)	0.33510 (6)
S1	0.2139 (4)	0.7205 (2)	0.2315 (4)
S2	0.0812 (4)	0.8502 (2)	0.3817 (4)
S3	−0.0815 (4)	0.7623 (2)	0.2929 (4)
S4	0.0975 (4)	0.7299 (2)	0.5143 (4)
S11	0.3073 (7)	0.8849 (4)	0.7046 (6)
S12	0.4851 (7)	0.8665 (4)	0.3098 (7)
S13	0.4985 (9)	0.6217 (5)	0.5267 (9)
S21	−0.206 (1)	0.9621 (4)	0.154 (1)
S22	0.0175 (7)	0.7223 (4)	−0.1506 (5)
S23	0.2523 (7)	0.9045 (3)	0.0124 (6)
S31	−0.2067 (6)	0.6129 (4)	0.4812 (6)
S32	0.3195 (7)	0.5177 (3)	0.3805 (8)
S33	0.0106 (6)	0.5655 (3)	0.0427 (6)
N11	0.248 (1)	0.8109 (7)	0.551 (1)
N12	0.332 (1)	0.8047 (7)	0.341 (1)
N13	0.342 (2)	0.7081 (8)	0.447 (1)
N21	−0.060 (2)	0.8646 (7)	0.179 (1)
N22	0.037 (1)	0.7634 (7)	0.063 (1)
N23	0.162 (2)	0.8370 (6)	0.135 (1)
N31	−0.040 (1)	0.6558 (7)	0.407 (1)
N32	0.189 (1)	0.6214 (7)	0.363 (1)
N33	0.046 (1)	0.6476 (6)	0.192 (1)
C11	0.273 (2)	0.8423 (9)	0.614 (2)
C12	0.397 (2)	0.830 (1)	0.328 (1)
C13	0.410 (2)	0.674 (1)	0.479 (2)
C21	−0.121 (2)	0.904 (1)	0.168 (2)
C22	0.029 (2)	0.7463 (9)	−0.024 (2)
C23	0.201 (2)	0.8652 (9)	0.085 (1)
C31	−0.108 (2)	0.6377 (8)	0.438 (2)
C32	0.244 (2)	0.578 (1)	0.370 (2)
C33	0.033 (2)	0.6134 (8)	0.131 (2)

factors. The corrections for absorption were applied to each crystal with the program CRYSTAN.[13]

The coordinates of W and S atoms that composed the cores were determined by means of SHELXS-86[14a] for **1** and **2a** and by MULTAN[14b] for **3**, and the remaining non-hydrogen atoms were located from difference maps. No attempt was made to locate hydrogen atoms for each structural determination. The refinement of the structures was performed at initial stage by the block-diagonal least-squares method using the programs in the UNICS system[15] and at later stage by the full-matrix least-squares program CRYSTAN.[13] The program ORTEP[16] were used to draw perspective views. Atomic scattering factors for W^0, S^0, Na^0, O^0, N^0, and C^0 were taken from ref 17. Computations were performed on a FA-COM M380 computer at the Okayama University of Science. Coordinates of cluster atoms for **1**, **2a**, and **3** are listed in Tables II–IV, respectively: Coordinates of noncluster atoms for **1**, **2a**, and **3** are listed in the Supplementary materials (Tables SIV–SVI).

Electrochemistry. Electrochemical Measurements. Current-sampled dc polarography and cyclic voltammetry of the molybdenum and tungsten clusters **2b** and **5b** were performed with a Yanaco P-1000 voltammetric analyzer equipped with a Riken Denshi F-43 x-y recorder. The working electrode for cyclic voltammetry was a Metrohm EA-290 hanging-mercury-drop electrode (HMDE) or a Bioanalytical Systems glassy-carbon electrode (GCE). The reference and the counter electrodes were an Ag/AgCl (3 M NaCl) electrode and a platinum wire, respectively.

Bulk controlled-potential electrolysis and coulometric experiments were carried out with a Nichia Keisoku NP-IR1000 potentiostat combined with a Fuso Electrochemical System HECS-343B digital coulometer. The working electrode was a reticulated vitreous carbon electrode (RVC 80-S) and the apparent volume was ca. 0.7 mL. The working

1, **2a**, and **3** are given in Table I and in the supplementary material (Table SI for **1**, Table SII for **2a**, and Table SIII for **3**). Systematic absences uniquely identified the space group as $P2_1/a$ for compound **2a**. Cell constants and orientation matrixes for the crystals were obtained from least-squares refinement, by using setting angles of 20 reflections for **1** and 25 reflections for **2a** and **3** in the range $20° < 2\theta < 30°$ measured on a Rigaku AFC-6A diffractometer by use of Mo Kα radiation ($\lambda = 0.71073$ Å). The intensities of standard reflections monitored after every 150 reflections did not show any appreciable decay for the three crystals. Intensities were corrected for polarization and Lorentz

(13) Katayama, C. *Acta Crystallogr.* **1986**, *A42*, 19–23.
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(15) *The Universal Crystallographic Computation Program System*; The Crystallographic Society of Japan: Tokyo, 1969.
(16) Johnson, C. K. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.
(17) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

Table V. Electronic Spectral Data for Trimers with M_3S_4 Cores (M = Mo, W)[a,b]

expt no.	compound	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	ref
1	$[W_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4 \cdot 9H_2O$ (1)	314 (7040), 430 sh (330), 560 (490)	c
2	$Na_2[W_3S_4(Hnta)_3] \cdot 5H_2O$ (2a)	270 sh (7720), 320 (7090), 440 sh (440), 580 (730)	c
3	$(bpyH)_5[W_3S_4(NCS)_9] \cdot 3H_2O$ (3)	490 sh (500), 640 (730)	c
4	$[Mo_3S_4(H_2O)_9](CH_3C_6H_4SO_3)_4 \cdot 9H_2O$ (4)	367 (5190), 500 sh (290), 602 (351)	21
5	$K_2[Mo_3S_4(Hnta)_3] \cdot 9H_2O$ (5b)	245 (21 600), 379 (5900), 616 (463)	c
6	$[W_3S_4(H_2O)_9]^{4+}$ (1')	221 (15 000), 317 (6100), 430 sh (310), 570 (480)	c
7	$[Mo_3S_4(H_2O)_9]^{4+}$ (4')	256 (10 350), 327 (5510), 620 (315)	c

[a] Data for experiments 1 and 4 in 2 M HPTS, for experiments 2 and 5 in water, for experiment 3 in 1 M HCl containing 1 M KSCN, and for experiments 6 and 7 in 1 M HCl. [b] ϵ values per trimer. [c] This work.

compartment (5 mL) was separated from the counter compartment by a sintered-glass disk. Electronic spectra of the electrolyzed solution were recorded on a Hitachi 330 spectrophotometer, a 10-mm cell being used.

The pH of the sample solution (ca. 0.5 mM) containing 0.1 M KCl or 0.1 M tetraethylammonium chloride as supporting electrolyte was adjusted with 0.025 M borate buffer (pH 8.0–10.0), 0.025 M phosphate buffer (pH 10.9–11.5), or tetraethylammonium hydroxide (pH 11.0–12.0). All the solutions were deoxygenated with a stream of argon for at least 10 min prior to recording electrochemical data. During polarographic and voltammetric experiments, an argon atmosphere was maintained above the solution. In controlled-potential electrolysis experiments, argon was bubbled continuously through the solution. After complete electrolysis (ca. 30 min) the solution was transferred to a spectrometric cell through a Teflon tubing and argon pressure.

Electrochemical measurements were performed at 25 ± 1 °C. HMDE was renewed before recording voltammetric scans.
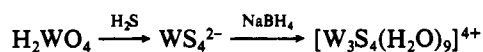
Other Physical Measurements. UV, visible, and near-infrared spectra were recorded on a Hitachi 330, 320, or U2000 spectrophotometer, ICP spectrometry was applied for the analysis of tungsten using a Shimadzu ICPS-500 analyzer. Carbon, hydrogen, and nitrogen were determined by standard microanalytical procedures.
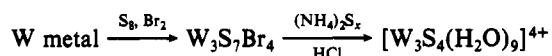
Results and Discussion

Syntheses and Properties of Tungsten(IV) Compounds with W_3S_4 Cores. In the early stage of this research the yield of the aqua ion 1' was 17%,[1] and the yield has now been improved up to 30% by the adjustment of synthetic conditions. Main alteration points are the use of a smaller amount of water and heating at a higher temperature. Heating for more than 5 h did not increase the yield.

There are two main routes to the aqua ion 1'. One route is shown in Scheme I and another is shown in Scheme II. The former method uses water as solvent throughout the procedures and the latter one uses techniques of solid-state chemistry in the first step while water is used in the second step.[18] Both methods have their own merits and the merit of the former method is as follows: (1) a large amount (for example 100 g) of the intermediate, $(NH_4)_2WS_4$, is prepared without special apparatuses, which enabled us to obtain the aqua ion 1' easily; (2) no air-free technique is required; (3) the method described here can be scaled up.

Scheme I

$$H_2WO_4 \xrightarrow{H_2S} WS_4^{2-} \xrightarrow{NaBH_4} [W_3S_4(H_2O)_9]^{4+}$$

Scheme II

$$W\ metal \xrightarrow{S_8,\ Br_2} W_3S_7Br_4 \xrightarrow[HCl]{(NH_4)_2S_x} [W_3S_4(H_2O)_9]^{4+}$$

The aqua ion 1' is stable against air oxidation in dilute HCl and in freshly prepared HPTS solutions, however, the aqua ion decomposes to give precipitate in a stale HPTS solution. A dark violet powder is obtained by evaporation of the aqua ion 1' in 1 M HCl to dryness by use of a rotary evaporator above 90 °C. Solidification of 1' is very convenient for storage or transportation. The solid cluster 1 and the dark violet powder dissolve in some organic solvents (for example, methanol, acetone, tetrahydrofuran).

The reactivity of the aqua ion 1' toward metals is very different from that of the corresponding molybdenum(IV) aqua ion 4'. The incomplete cubane-type molybdenum aqua ion reacts with metals
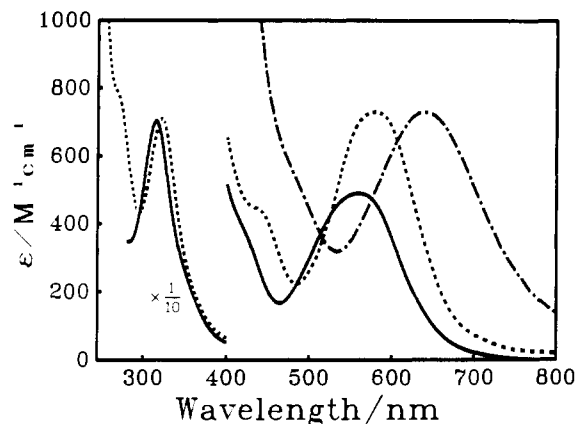

Figure 1. Electronic spectra (ϵ values per trimer): (—) $[W_3S_4(H_2O)_9]^{4+}$ in 2 M HPTS; (- -) $[W_3S_4(Hnta)_3]^{2-}$ in water; (- - -) $[W_3S_4(NCS)_9]^{5-}$ in 1 M HCl containing 1 M KSCN.

M (M = Fe, Co, Ni, Cu, Sn, Hg) or metal ions (Sn^{2+} and Hg^{2+}) to give mixed-metal cubane-type aqua ions with Mo_3MS_4 cores,[19] while the reactivity of the tungsten aqua ion toward these metals is very low, and no formation of mixed-metal cubane-type aqua ions has so far been observed except for the cases of Sn, Sn^{2+}, and Hg.[20a,b] Since the dimensions of the aqua cluster are very similar to those of **4** (see the section discussing the X-ray structure), the reactivity difference must stem from the chemical difference between molybdenum and tungsten. That molybdenum is more easily reduced than tungsten is may be one reason.

The compounds **2a** and **2b** can be synthesized from the corresponding aqua ion 1'. When a more concentrated solution was used that was obtained by use of a short Dowex 50W-X2 column using 2 M HCl as eluent, a slightly higher yield was obtained in a shorter time: e.g., 20 mL of 0.0283 M (per trimer in 2 M HCl) solution gave 0.581 g (75%) of solid **2a** in 3 days. Contrary to the case of $Na_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(Hnta)_3] \cdot 10H_2O$,[21] a precipitate appeared during the addition of concentrated NaOH solution to solution of 1'. The precipitate was easily dissolved by heating.

Crystals of **3** were obtained by the addition of a small amount of a saturated solution of 2,2'-bipyridine. Further addition of 2,2'-bipyridine solution to get a larger sample of **3** gave unidentified yellow precipitates.

Electronic spectra of **1–3** are shown in Figure 1. The peak positions (nm) and ϵ values are shown in Table V. The ϵ values of **1** and **1'** are determined by use of the ICP method, which seems to give more reliable values than the thiocyanato method does.[1]

Syntheses and Properties of Molybdenum(IV) Compounds with Mo_3S_4 Cores. Two methods are described here for the synthesis of the aqua ion 4'. Methods A and B use $(NH_4)_2MoS_4$ and

(18) WS_3 can also be used for the synthesis of $W_3S_7Br_4$.[2f]

(19) For example: (a) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc.* **1986**, *108*, 1342–1343. (b) Aikoh, H.; Shibahara, T. *Physiol. Chem. Phys. Med. NMR* **1990**, *22*, 187–192. (c) Shibahara, T.; Yamasaki, M.; Akashi, H.; Katayama, T. *Inorg. Chem.* **1991**, *30*, 2693–2699.

(20) (a) For Sn, Sn^{2+}, cluster compounds with W_3SnS_4 cores obtained from the aqua cluster 1' and Sn (or Sn^{2+}) have been isolated: Shibahara, T.; Yamasaki, M.; Kubota, R. Unpublished result. (b) For Hg, see the Electrochemistry Section.

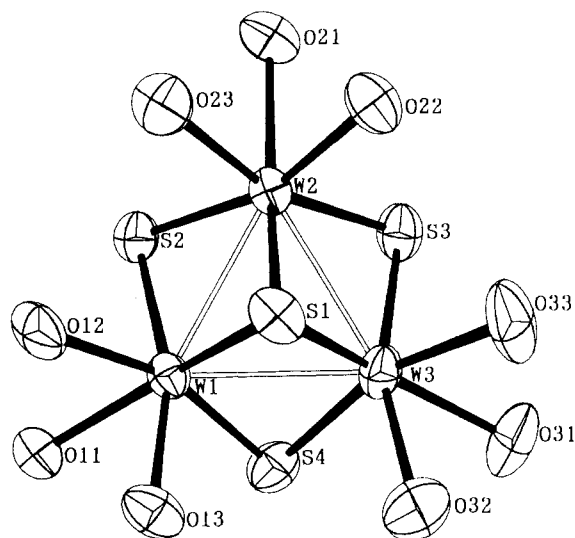(21) Shibahara, T.; Akashi, H.; Nagahata, S.; Hattori, H.; Kuroya, H. *Inorg. Chem.* **1989**, *28*, 362–370.

Figure 2. Perspective view of $[W_3S_4(H_2O)_9]^{4+}$ (the cation of **1**) showing the atom-labeling scheme. In Figures 2–4 the 50% probability vibrational ellipsoids are shown.

Na$_2$[Mo$_2$O$_2$S$_2$(cys)$_2$]·4H$_2$O, respectively, as starting materials. Both methods do not require any air-free techniques and use the techniques of Sephadex G-10 and Dowex 50W-X2 column chromatography. Larger scale syntheses than those described in the Experimental Section can be carried out easily.

We had reported briefly the NaBH$_4$ reduction of Na$_2$-[Mo$_2$O$_2$S$_2$(cys)$_2$]·4H$_2$O, where we had used a dinitrogen atmosphere,[22] and now we described here the revised procedure, method B, in detail. Sykes and co-workers reported the NaBH$_4$ reduction of Mo$_2$O$_2$S$_2^{2+}$(aq) to give 3% of the aqua ion **4'** using a dinitrogen atmosphere.[23] When they used the cysteinato complex, Na$_2$-[Mo$_2$O$_2$S$_2$(cys)$_2$]·4H$_2$O instead of Mo$_2$O$_2$S$_2^{2+}$(aq), they observed some unwanted black solid material during the reduction. We also noticed black solid material, which, however, disappeared under longer air-oxidation (20 h) at high temperature (>90 °C) to give **4'** in a higher yield according to our procedure: the black solid material seems to contain the intermediate to **4'**.

Other methods so far reported for the syntheses of the aqua ion **4'** are as follows: (a) reaction of Mo(CO)$_6$ with Na$_2$S;[24] (b) electrolysis of [Mo$_2$O$_2$S$_2$(cys)$_2$]$^{2-}$;[23] (c) reaction of Mo$_2$O$_2$S$_2^{2+}$(aq) with [MoCl$_6$]$^{3-}$.[23] These methods have their own merits; however, we think that it is worthwhile to try methods A and B described here.

The aqua ion **4'** is very stable toward air oxidation and does not require a dinitrogen atmosphere for storage. A dark green powder is obtained by evaporation of the aqua ion **4'** in 2 M HCl to dryness by use of a rotary evaporator at a temperature above 90 °C. Solidification of **4'** is very convenient for storage or transportation. The solid cluster [Mo$_3$S$_4$(H$_2$O)$_9$](CH$_3$C$_6$H$_4$S-O$_3$)$_4$·9H$_2$O (**4**) can be obtained by a procedure similar to the synthesis of the tungsten analogue **1**. The X-ray structure of **4** has been determined.[25] The cluster **4** dissolves in some organic solvents (for example, methanol, acetone, tetrahydrofuran), and the dark green powder dissolves in methanol.

The (nitrilotriacetato)molybdenum clusters **5a** and **5b** were synthesized in relatively high yields from the corresponding aqua cluster **4'** by methods similar to those used for **2a** and **2b**. The anion [Mo$_3$S$_4$(Hnta)$_2$(nta)]$^{3-}$ has already been synthesized and its X-ray structure determined as calcium[22a] and ammonium[26]

Table VI. Selected Interatomic Distances (Å) and Angles (deg) in $[W_3S_4(H_2O)_9]^{4+}$

| W1–W2	2.707 (1)	W1–O11	2.192 (11)
W1–W3	2.713 (1)	W2–O21	2.186 (8)
W2–W3	2.704 (1)	W3–O31	2.195 (14)
mean	2.708 [5]	mean	2.191 [5]
W1–S1	2.331 (4)	W1–O12	2.169 (11)
W2–S1	2.336 (3)	W1–O13	2.153 (8)
W3–S1	2.347 (4)	W2–O22	2.139 (11)
mean	2.338 [8]	W2–O23	2.172 (12)
W1–S2	2.288 (3)	W3–O32	2.156 (10)
W1–S4	2.286 (4)	W3–O33	2.177 (13)
W2–S2	2.287 (4)	mean	2.161 [14]
W2–S3	2.280 (4)		
W3–S3	2.278 (3)		
W3–S4	2.287 (4)		
mean	2.284 [4]		
W2–W1–W3	59.84 (3)	O12–W1–O13	78.8 (4)
W1–W2–W3	60.19 (3)	O22–W2–O23	77.9 (4)
W1–W3–W2	59.97 (2)	O32–W3–O33	77.4 (5)
mean	60.00 [18]	mean	78.0 [7]
S1–W1–S2	106.9 (1)	W1–S1–W2	70.9 (1)
S1–W1–S4	106.7 (1)	W1–S1–W3	70.9 (1)
S1–W2–S2	106.8 (1)	W2–S1–W3	70.5 (1)
S1–W2–S3	107.2 (1)	mean	70.8 [2]
S1–W3–S3	106.8 (1)		
S1–W3–S4	106.1 (1)	W1–S2–W2	72.6 (1)
mean	106.8 [4]	W2–S3–W3	72.7 (1)
S2–W1–S4	96.9 (1)	W1–S4–W3	72.8 (1)
S2–W2–S3	95.4 (1)	mean	72.7 [1]
S3–W3–S4	97.3 (1)		
mean	96.5 [10]		
O11–W1–O12	77.9 (4)		
O11–W1–O13	78.9 (4)		
O21–W2–O22	77.2 (4)		
O21–W2–O23	77.6 (4)		
O31–W3–O32	77.6 (5)		
O31–W3–O33	78.6 (5)		
mean	78.0 [7]		
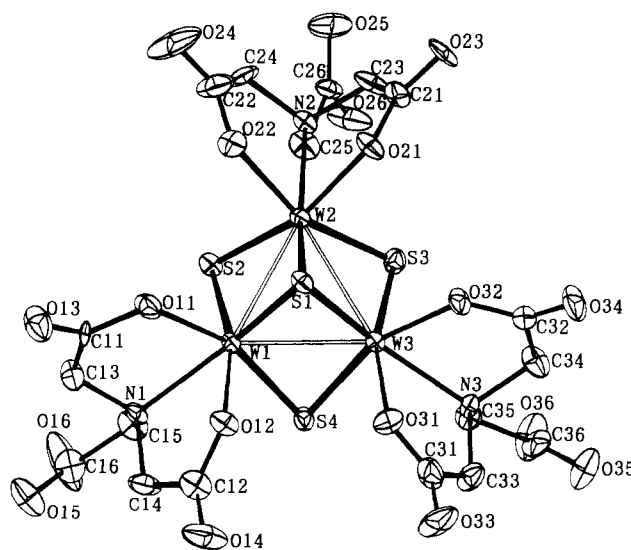
Figure 3. Perspective view of $[W_3S_4(Hnta)_3]^{2-}$ (the anion of **2a**) showing the atom-labeling scheme.

salts. The calcium salt was synthesized at pH 2.0, while **5a** and **5b** were done at pH 1.2. At pH 2.0 one of the three COOH groups seems to dissociate. The peak positions (nm) and ε values of the electronic spectra of **4** and **5b** are shown in Table V.

Structures of [W$_3$S$_4$(H$_2$O)$_9$](CH$_3$C$_6$H$_4$SO$_3$)$_4$·9H$_2$O (1), Na$_2$-[W$_3$S$_4$(Hnta)$_3$]·5H$_2$O (2a), and (bpyH)$_5$[W$_3$S$_4$(NCS)$_9$]·3H$_2$O (3).
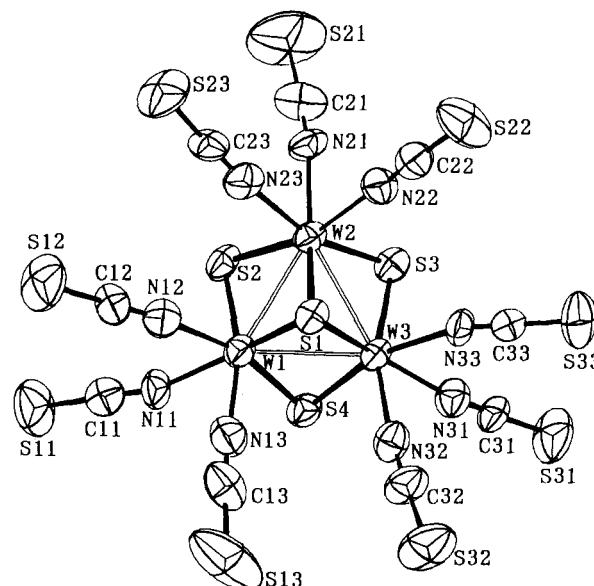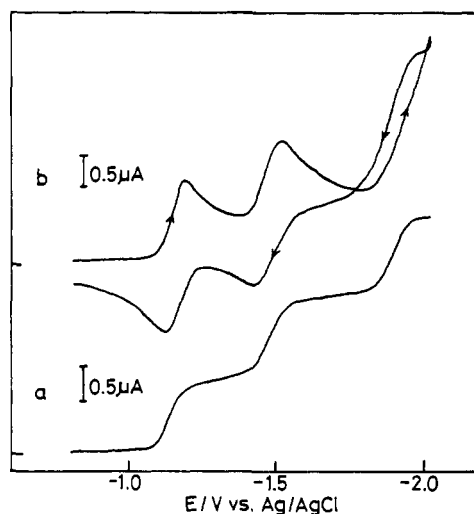
(22) (a) Shibahara, T.; Kuroya, H. *Abstracts of Papers*, 5th International Conference on the Chemistry and Uses of Molybdenum, Newcastle upon Tyne, England, July 1985; p 59. (b) Shibahara, T.; Kuroya, H. *Polyhedron* **1986**, *5*, 357–361.

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Table VII. Selected Interatomic Distances (Å) and Angles (deg) in $[W_3S_4(Hnta)_3]^{2-}$

W1–W2	2.728 (1)	O11–C11	1.300 (20)
W1–W3	2.728 (1)	O12–C12	1.317 (20)
W2–W3	2.759 (1)	O21–C21	1.263 (18)
mean	2.738 [18]	O22–C22	1.310 (23)
W1–S1	2.347 (4)	O31–C31	1.278 (23)
W2–S1	2.348 (3)	O32–C32	1.304 (21)
W3–S1	2.351 (4)	mean	1.295 [21]
mean	2.349 [2]	O13–C11	1.216 (20)
W1–S2	2.308 (4)	O14–C12	1.217 (21)
W1–S4	2.316 (4)	O23–C21	1.251 (19)
W2–S2	2.296 (4)	O24–C22	1.217 (26)
W2–S3	2.306 (4)	O33–C31	1.249 (23)
W3–S3	2.291 (4)	O34–C32	1.208 (20)
W3–S4	2.310 (4)	mean	1.226 [19]
mean	2.305 [9]	O15–C16	1.207 (22)
W1–O11	2.080 (12)	O25–C26	1.206 (21)
W1–O12	2.111 (9)	O35–C36	1.174 (22)
W2–O21	2.125 (11)	mean	1.196 [19]
W2–O22	2.095 (11)	O16–C16	1.309 (20)
W3–O31	2.106 (10)	O26–C26	1.308 (20)
W3–O32	2.094 (11)	O36–C36	1.313 (18)
mean	2.102 [16]	mean	1.310 [3]
W1–N1	2.323 (12)		
W2–N2	2.312 (11)		
W3–N3	2.297 (12)		
mean	2.311 [13]		
W2–W1–W3	60.75 (2)	O11–W1–N1	76.6 (4)
W1–W2–W3	59.63 (3)	O12–W1–N1	75.8 (4)
W1–W3–W2	59.62 (3)	O21–W2–N2	76.5 (4)
mean	60.00 [65]	O22–W2–N2	76.4 (4)
S1–W1–S2	106.4 (1)	O31–W3–N3	76.8 (4)
S1–W1–S4	107.2 (1)	O32–W3–N3	77.3 (4)
S1–W2–S2	106.8 (1)	mean	76.6 [5]
S1–W2–S3	105.0 (1)	W1–S1–W2	71.1 (1)
S1–W3–S3	105.4 (1)	W1–S1–W3	71.0 (1)
S1–W3–S4	107.2 (1)	W2–S1–W3	71.9 (1)
mean	106.3 [9]	mean	71.3 [5]
S2–W1–S4	95.9 (1)	W1–S2–W2	72.7 (1)
S2–W2–S3	98.7 (1)	W2–S3–W3	73.8 (1)
S3–W3–S4	97.0 (1)	W1–S4–W3	72.3 (1)
mean	97.2 [14]	mean	72.9 [8]
O11–W1–O12	77.9 (4)		
O21–W2–O22	76.8 (5)		
O31–W3–O32	77.6 (4)		
mean	77.4 [6]		

Figure 4. Perspective view of $[W_3S_4(NCS)_9]^{5-}$ (the anion of **3**) showing the atom-labeling scheme.

Figure 5. Electrochemical behavior of 0.50 mM $[W_3S_4(Hnta)_3]^{2-}$ in 0.1 M tetraethylammonium chloride at pH 12.0 with tetraethylammonium hydroxide: (a) current-sampled dc polarogram; (b) cyclic voltammogram at a HMDE with a scan rate of 100 mV/s.

The cluster **1** is isomorphous with the corresponding molybdenum cluster **4**.[25] The structure of the cation of **1** is shown in Figure 2, and the selected interatomic distances and angles are collected in Table VI. The cell constants and the number of water of crystallization of **1** described here are different from those of the preliminary results, where the number of crystallization is 7.[2a] Several crystals obtained from independent experiments under different conditions gave the same cell constants as the present ones and the crystals obtained earlier seem to have been collected in a quasi-stable state. The structures of the anion parts of **2a** and **3** are shown in Figures 3 and 4, and the selected interatomic distances and angles are collected in Tables VII and VIII, respectively. The cluster cation and anions have an approximate symmetry of C_{3v} and contain the same incomplete cubane-type core as W_3S_4. The W–W distances of clusters containing W_3S_4 cores so far reported are in the range 2.6728 (6)–2.784 (1) Å. The W–W distances of the aqua cluster **1** is the shortest of the distances in the clusters except for the case in $[W_3S_4-(O_2CCH_3)(dtp)_3(py)]$ where acetato ligands bridge between two W's.[28] It is interesting that the corresponding molybdenum aqua cluster **4** also has the shortest Mo–Mo distances of clusters with Mo_3S_4 cores.[25] One uncoordinated CO_2 group in each $Hnta^{2-}$ ligand has a long (average 1.310 [3] Å) and a short (1.196 [19] Å) distance, indicating the existence of three –COOH groups in the whole cluster anion as shown in Table VII.

Electrochemistry. Both of the clusters $[W_3S_4(Hnta)_3]^{2-}$ (**2'**) and $[Mo_3S_4(Hnta)_3]^{2-}$ (**5'**) exhibit three reduction processes. Figure 5a shows a current-sampled dc polarogram of **2'** in 0.1 M tetraethylammonium chloride solution adjusted to pH 12.0 with tetraethylammonium hydroxide. Three consecutive reduction waves with the equal wave height were observed only at this solution, because **2'** decomposed at a higher pH and the wave due to the hydrogen evolution covered the third wave at lower pH. The use of KCl and/or the buffer also hindered the appearance of the third wave because of the reduction wave of the alkali-metal ion. The half-wave potentials ($E_{1/2}$) of the first and second waves are respectively −1.12 and −1.41 V and are independent of the nature of supporting electrolytes and buffers used (see Table IX). The first and second waves have log-plot slopes[27] of 59.3 and 55.3 mV, respectively, which are consistent with the theoretical value for a reversible one-electron process. The third wave, though complicated, has the same wave height as the first and second ones, and we concluded that three one-electron processes exist. Therefore, the three electrochemical processes are one-electron reductions of W^{IV}_3 to $W^{IV}_2W^{III}$, $W^{IV}_2W^{III}$ to $W^{IV}W^{III}_2$, and

(27) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; p 160.

Table VIII. Selected Interatomic Distances (Å) and Angles (deg) in $[W_3S_4(NCS)_9]^{5-}$

W1–W2	2.760 (1)	S11–C11	1.601 (23)
W1–W3	2.767 (1)	S12–C12	1.605 (28)
W2–W3	2.764 (1)	S13–C13	1.641 (26)
mean	2.764 [4]	S21–C21	1.617 (28)
		S22–C22	1.632 (23)
W1–S1	2.343 (4)	S23–C23	1.587 (24)
W2–S1	2.344 (4)	S31–C31	1.614 (24)
W3–S1	2.362 (5)	S32–C32	1.614 (23)
mean	2.350 [11]	S33–C33	1.630 (22)
		mean	1.616 [17]
W1–S2	2.295 (5)		
W1–S4	2.322 (6)	N11–C11	1.155 (27)
W2–S2	2.291 (5)	N12–C12	1.151 (33)
W2–S3	2.309 (6)	N13–C13	1.141 (30)
W3–S3	2.312 (5)	N21–C21	1.115 (30)
W3–S4	2.309 (5)	N22–C22	1.130 (27)
mean	2.306 [11]	N23–C23	1.152 (29)
		N31–C31	1.128 (29)
W1–N11	2.145 (16)	N32–C32	1.140 (27)
W1–N12	2.156 (20)	N33–C33	1.137 (26)
W1–N13	2.111 (18)	mean	1.139 [13]
W2–N21	2.169 (16)		
W2–N22	2.157 (16)		
W2–N23	2.163 (19)		
W3–N31	2.173 (19)		
W3–N32	2.168 (16)		
W3–N33	2.152 (16)		
mean	2.155 [19]		
W2–W1–W3	60.03 (3)	S2–W1–N12	90.4 (5)
W1–W2–W3	60.11 (3)	S4–W1–N13	89.6 (6)
W1–W3–W2	59.86 (3)	S2–W2–N23	89.8 (5)
mean	60.00 [13]	S3–W2–N22	90.7 (5)
		S3–W3–N33	89.7 (4)
S1–W1–S2	105.6 (2)	S4–W3–N32	90.9 (5)
S1–W1–S4	105.9 (2)	mean	90.2 [6]
S1–W2–S2	105.8 (2)		
S1–W2–S3	106.1 (2)	N11–W1–N12	80.0 (6)
S1–W3–S3	105.4 (2)	N11–W1–N13	82.9 (7)
S1–W3–S4	105.8 (2)	N12–W1–N13	80.8 (7)
mean	105.8 [2]	N21–W2–N22	82.5 (6)
		N21–W2–N23	80.0 (7)
S2–W1–S4	96.2 (2)	N22–W2–N23	79.5 (7)
S2–W2–S3	96.7 (2)	N31–W3–N32	83.1 (6)
S3–W3–S4	97.9 (2)	N31–W3–N33	81.1 (7)
mean	96.9 [9]	N32–W3–N33	78.4 (6)
		mean	80.9 [16]
S1–W1–N11	163.1 (5)		
S1–W2–N21	163.7 (5)	W1–S1–W2	72.1 (1)
S1–W3–N31	164.5 (4)	W1–S1–W3	72.0 (1)
mean	163.8 [7]	W2–S1–W3	72.0 (1)
		mean	72.0 [1]
S1–W1–N12	85.7 (4)		
S1–W1–N13	86.0 (5)	W1–S2–W2	74.0 (1)
S1–W2–N22	85.2 (4)	W2–S3–W3	73.5 (2)
S1–W2–N23	87.3 (4)	W1–S4–W3	73.4 (1)
S1–W3–N32	85.6 (5)	mean	73.6 [3]
S1–W3–N33	86.3 (5)		
mean	86.0 [7]	W1–N11–C11	164.4 (17)
		W1–N12–C12	165.4 (15)
S2–W1–N13	164.9 (6)	W1–N13–C13	173.3 (20)
S4–W1–N12	164.4 (4)	W2–N21–C21	169.7 (18)
S2–W2–N22	164.4 (5)	W2–N22–C22	176.0 (17)
S3–W2–N23	162.8 (5)	W2–N23–C23	170.6 (15)
S3–W3–N32	163.4 (5)	W3–N31–C31	172.7 (15)
S4–W3–N33	163.3 (5)	W3–N32–C32	172.8 (19)
mean	163.9 [8]	W3–N33–C33	166.8 (16)
		mean	170.2 [40]
S2–W1–N11	83.6 (4)		
S4–W1–N11	86.7 (5)		
S2–W2–N21	84.5 (4)		
S3–W2–N21	84.8 (5)		
S3–W3–N31	83.6 (4)		
S4–W3–N31	85.0 (5)		
mean	84.7 [11]		

$W^{IV}W^{III}_2$ to W^{III}_3, respectively.

Figure 5b illustrates a cyclic voltammogram of **2′** at HMDE in the same solution. A negative potential scan initiated at −0.8 V and the following positive scan reversed at −2.0 V with a scan rate of 100 mV/s reveal two chemically reversible redox couples and one irreversible reduction process. For the first and second

Table IX. Comparison of $E_{1/2}$ for the Reductions of Clusters with M_3S_4 Cores (M = Mo, W)

	$E_{1/2}$/V vs Ag/AgCl			
cluster	IV,IV,IV/ IV,IV,III	IV,IV,III/ IV,III,III	IV,III,III/ III,III,III	ref
$[W_3S_4(Hnta)_3]^{2-}$ (**2′**)	−1.12	−1.41	−1.88[a]	c
$[W_3S_4Cl_3(dmpe)_3]^+$	−1.11[b]			2c
$[W_3S_4Cl_3(depe)_3]^+$	−1.12[b]			2c
$[Mo_3S_4(Hnta)_3]^{2-}$ (**5′**)	−0.64	−1.08	−1.39[a]	c
$[Mo_3S_4(ida)_3]^{2-}$	−0.64	−0.98	−1.33[a]	22b
$[Mo_3S_4Cl_3(dmpe)_3]^+$	−0.64	−0.85		2c

[a] Accompanied with the catalytic hydrogen wave. [b] One-electron reduction has not been claimed. [c] This work.

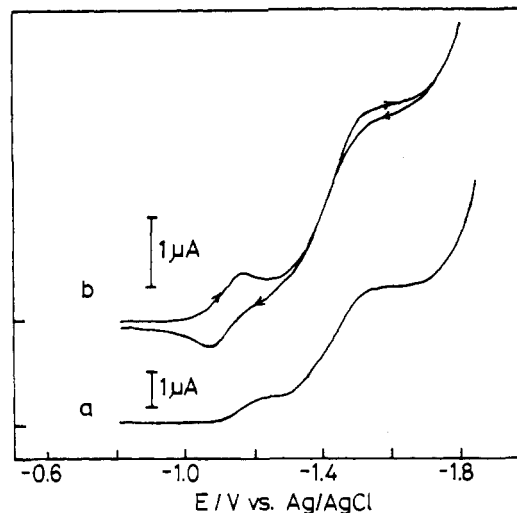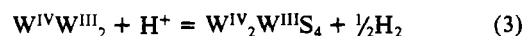**Figure 6.** Electrochemical behavior of $[W_3S_4(Hnta)_3]^{2-}$ (0.55 mM) in 0.1 M KCl at pH 8.0 with 0.025 M borate buffer: (a) current-sampled dc polarogram; (b) cyclic voltammogram at a HMDE with a scan rate of 100 mV/s.

redox couples the peak currents are proportional to the square root of the scan rate in the range from 50 to 500 mV/s, and the peak separations are 70 and 91 mV, respectively. These observations indicate that both redox couples are diffusion-controlled, electrochemically quasi-reversible one-electron processes; the first reduction process being more reversible than the second one. The voltammogram for the third reduction step looks like a polarographic wave and gives no reoxidation peak. This voltammetric behavior can be explained by a catalytic reaction scheme.[28]

Although the $E_{1/2}$ value of the first and second waves in the polarography does not change with the solution pH, the limiting current of the second wave increases with the decrease in pH while that of the first wave is still the same as at pH 12.0. Figure 6 shows a current-sampled dc polarogram and a cyclic voltammogram of **2′** at pH 8.0. The limiting current of the second wave is 6.1 times that of the first wave. The analysis of the cyclic voltammogram suggests that the first reduction process (eq 1) is a chemically reversible and electrochemically quasi-reversible one-electron process and the second reduction process (eq 2) is accompanied with a catalytic reaction (eq 3)[28] involving H_2 evolution.

$$W^{IV}_3 + e^- = W^{IV}_2W^{III} \tag{1}$$

$$W^{IV}_2W^{III} + e^- = W^{IV}W^{III}_2 \tag{2}$$

$$W^{IV}W^{III}_2 + H^+ = W^{IV}_2W^{III}S_4 + \tfrac{1}{2}H_2 \tag{3}$$

Bulk controlled-potential coulometry of **2′** with a reticulated vitreous carbon electrode at −1.35 V, which corresponds to the plateau part of the first reduction wave in the polarogram, further confirms that the reduction is a one-electron process. Thus, the electrolysis yields the one-electron reduction product [W₃S₄-

(28) Reference 27, p 455.
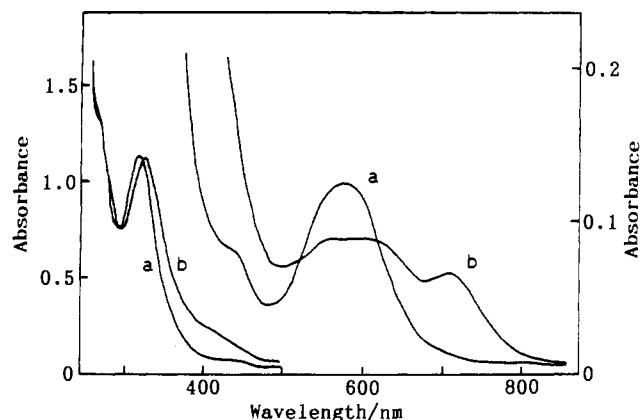
Figure 7. UV–visible spectra in 0.1 M KCl at pH 11.4: (a) [W$_3$S$_4$-(Hnta)$_3$]$^{2-}$ (0.209 mM); (b) the reduction product [W$_3$S$_4$(Hnta)$_3$]$^{3-}$.

Figure 9. UV–visible spectra in 0.1 M KCl at pH 11.4: (a) [Mo$_3$S$_4$-(Hnta)$_3$]$^{2-}$ (0.198 mM); (b) the reduction product [Mo$_3$S$_4$(Hnta)$_3$]$^{3-}$.

Figure 8. Electrochemical behavior of [Mo$_3$S$_4$(Hnta)$_3$]$^{2-}$ (0.58 mM) in 0.1 M KCl at pH 11.4 with 0.025 M phosphate buffer: (a) current-sampled dc polarogram; (b) cyclic voltammogram at HMDE with a scan rate of 50 mV/s.

(Hnta)$_3$]$^{3-}$, which is stable in an inert atmosphere but is readily reoxidized to **2′** when exposed to air. The UV–visible spectra of the solution before and after the bulk electrolysis are shown in Figure 7. After the complete electrolysis of **2′**, the absorption maximum splits into two maxima at 557 and 597 nm, and the new absorption maximum appears at 708 nm. The spectrum with these absorption maxima is characteristic of the W^{IV}$_2$W^{III} cluster complex.

The molybdenum(IV) cluster complex **5′** exhibits, as does **2′**, three consecutive one-electron reduction processes in the polarography and the voltammetry measurements (Figure 8), data of which are listed in Table IX. The similar three one-electron reduction processes have already been observed for [Mo$_3$S$_4$-(ida)$_3$]$^{2-}$ [22b] (see Table IX). The first reduction process of **5′** at the dropping and hanging mercury electrodes is accompanied with an adsorption redox couple (−0.7 V), which is not observed at a glassy-carbon electrode. At the same potential an adsorption wave appeared in the CV of **2′**, when the potential scan was initiated at −0.5 V. The adsorption is characteristic of clusters with M$_3$S$_4$
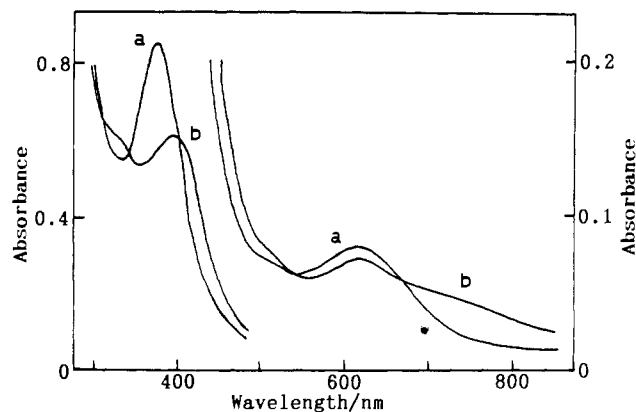
cores (M = Mo, W) due to the strong interaction of mercury with sulfur. The third reduction is also accompanied with the catalytic hydrogen reaction in the pH range of 8.0 to 11.1. At higher pH (ca. 12) decomposition of **5′** is too fast to get well-defined electrochemical information. The $E_{1/2}$ for the reductions of **5′** is more positive than that for the corresponding reduction of the tungsten analogue **2′**. In other words, the Mo^{IV}$_3$, Mo^{IV}$_2$Mo^{III}, and Mo^{IV}-Mo^{III}$_2$ clusters are more easily reduced by 0.48, 0.33, 0.49 V, respectively, than the corresponding tungsten analogues. Cotton et al. reported the electrochemistry of [Mo$_3$S$_4$Cl$_3$(dmpe)$_3$]$^+$ and [W$_3$S$_4$Cl$_3$(dmpe)$_3$]$^+$ in an organic solvent.[2c] Since the medium used is different from that used here, a direct comparison can not be made. It is interesting, however, that the difference of the reduction potentials of **5′** and **2′** (0.48 V) is almost the same as that of [Mo$_3$S$_4$Cl$_3$(dmpe)$_3$]$^+$ and [W$_3$S$_4$Cl$_3$(dmpe)$_3$]$^+$ (0.47 V). Wiegardt et al. deduced the existence of one-electron oxidation and one-electron reduction species of [Mo$_3$S$_4$(CN)$_9$]$^{5-}$ from the studies of cyclic voltammetry in DMSO.[29]

Figure 9 shows UV–visible spectra of the solutions before and after the controlled potential electrolysis of **5′** at −0.90 V. The electrolysis was coulometrically confirmed to be one-electron reduction process. Therefore, the reduction product is [Mo^{IV}$_2$Mo^{III}S$_4$(Hnta)$_3$]$^{3-}$ that has absorption maxima at 400, 620, and 720 (sh) nm. Both of the one-electron reduction products [W^{IV}$_2$W^{III}S$_4$(Hnta)$_3$]$^{3-}$ and [Mo^{IV}$_2$Mo^{III}S$_4$(Hnta)$_3$]$^{3-}$ are mixed-valence compounds.[30] Although several compounds with W$_3$S$_4$ cores and many compounds with Mo$_3$S$_4$ cores are known, the spectra shown in Figures 7 and 9 are the first examples of mixed-valence compounds with M$_3$S$_4$ cores (M = Mo, W).

Supplementary Material Available: Listings of crystallographic and machine parameters, coordinates of noncluster atoms, thermal parameters, bond distances and angles, and short contacts for compounds **1, 2a,** and **3** (Tables SI–SXV) (27 pages); tables of F_o and F_c for compounds **1, 2a,** and **3** (49 pages). Ordering information is given on any current masthead page.

(29) Wieghardt, K.; Herrmann, W.; Muller, A.; Eltzner, W.; Zimmermann, M. *Z. Naturforsch.* **1984,** *39B,* 876–879.
(30) Review: Young, C. G. *Coord. Chem. Rev.* **1989,** *96,* 89–251.