

## Preparation and Properties of the Full Series of Cuboidal Clusters $[\text{Mo}_x\text{W}_{4-x}\text{Se}_4(\text{H}_2\text{O})_{12}]^{n+}$ ( $n = 4-6$ ) and Their Derivatives

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Hydrothermal reactions between incomplete cuboidal cluster aqua complexes  $[\text{M}_3\text{Q}_4(\text{H}_2\text{O})_9]^{4+}$  and  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Q} = \text{S}, \text{Se}$ ) offer easy access to the corresponding cuboidal clusters  $\text{M}_4\text{Q}_4$ . The complete series of homometal and mixed Mo/W clusters  $[\text{Mo}_x\text{W}_{4-x}\text{Q}_4(\text{H}_2\text{O})_{12}]^{n+}$  ( $x = 0-4$ ,  $n = 4-6$ ) has been prepared. Upon oxidation of the mixed-metal clusters, it is the W atom which is lost, allowing selective preparation of new trinuclear clusters  $[\text{Mo}_2\text{WSe}_4(\text{H}_2\text{O})_9]^{4+}$  and  $[\text{MoW}_2\text{Se}_4(\text{H}_2\text{O})_9]^{4+}$ . The aqua complexes were converted by ligand exchange reactions into dithiophosphato and thiocyanato complexes, and crystal structures of  $[\text{W}_4\text{S}_4((\text{EtO})_2\text{PS}_2)_6]$ ,  $[\text{MoW}_3\text{S}_4((\text{EtO})_2\text{PS}_2)_6]$ ,  $[\text{Mo}_4\text{Se}_4((\text{EtO})_2\text{PS}_2)_6]$ ,  $[\text{W}_4\text{Se}_4((i\text{-PrO})_2\text{PS}_2)_6]$ , and  $(\text{NH}_4)_6[\text{W}_4\text{Se}_4(\text{NCS})_{12}] \cdot 4\text{H}_2\text{O}$  were determined. Cyclic voltammetry was performed on  $[\text{Mo}_x\text{W}_{4-x}\text{Q}_4(\text{H}_2\text{O})_{12}]^{n+}$ , showing reversible redox waves  $6+/5+$  and  $5+/4+$ . The lower oxidation states are more difficult to access as the number of W atoms increases. The  $[\text{Mo}_2\text{WSe}_4(\text{H}_2\text{O})_9]^{4+}$  and  $[\text{MoW}_2\text{Se}_4(\text{H}_2\text{O})_9]^{4+}$  species were derivatized into  $[\text{Mo}_2\text{WSe}_4(\text{acac})_3(\text{py})_3]^+$  and  $[\text{MoW}_2\text{Se}_4(\text{acac})_3(\text{py})_3]^+$ , which were also studied by CV. When appropriate, the products were also characterized by FAB-MS and NMR ( $^{31}\text{P}$ ,  $^1\text{H}$ ) data.

### Introduction

Notwithstanding the pronounced tendency of the third-row transition metals to form stronger metal–metal bonds as compared to their second-row congeners, tungsten clusters have received less attention than those of molybdenum. However, recent work on low valent W halides has unraveled a wealth of new structures which are unknown for Mo.<sup>1</sup> The contrast between the amount of data published for Mo and for W is especially striking in the field of the chalcogen-bridged cuboidal clusters. While the Cp derivatives of the

type  $[\text{Cp}_4\text{Mo}_4\text{S}_4]$  were made as early as the 1960s, and various other derivatives of the  $\text{Mo}_4\text{S}_4^{n+}$  ( $n = 4-6$ ) were prepared later (including the aqua ions  $[\text{Mo}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{n+}$  ( $n = 4, 5, 6$ )), the first  $\text{W}_4\text{S}_4$  cluster was reported only in 1990 (as  $[\text{W}_4\text{S}_4((\text{EtO})_2\text{PS}_2)_6]$ ).<sup>2</sup> The cyanides  $[\text{W}_4\text{Q}_4(\text{CN})_{12}]^{6-}$  ( $\text{Q} = \text{S}, \text{Se}, \text{Te}$ ) were added to the list later.<sup>3</sup> Recently, useful starting compounds, the aqua ion  $[\text{W}_4\text{S}_4(\text{H}_2\text{O})_{12}]^{6+}$  and its NCS<sup>-</sup> derivative,  $(\text{Me}_2\text{NH}_2)_6[\text{W}_4\text{S}_4(\text{NCS})_{12}]$ , were prepared. Mixed-metal cuboidal aqua complexes  $[\text{Mo}_x\text{W}_{4-x}\text{S}_4(\text{H}_2\text{O})_{12}]^{5+}$  ( $x = 1-3$ ) and  $[\text{MoW}_3\text{Se}_4(\text{H}_2\text{O})_{12}]^{5+}$  are also known.<sup>5</sup>

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**Table 1.** Hydrothermal Reactions of  $M(CO)_6$  with Triangular Cluster Aqua Ions

reactants	$Mo(CO)_6$	$W(CO)_6$
$[Mo_3S_4(H_2O)_9]^{4+}$	$[Mo_4S_4(H_2O)_{12}]^{4+}$ ( <b>1a''</b> ) 36 h, 43%	$[Mo_4S_4(H_2O)_{12}]^{5+}$ ( <b>1a</b> ) 36 h, 40%
$[W_3S_4(H_2O)_9]^{4+}$	$[MoW_3S_4(H_2O)_{12}]^{5+}$ ( <b>1g</b> ) 48 h, 67%	$[W_4S_4(H_2O)_{12}]^{5+/6+}$ ( <b>1i</b> , <b>1i'</b> ) 48 h, 85%
$[Mo_3Se_4(H_2O)_9]^{4+}$	$[Mo_4Se_4(H_2O)_{12}]^{5+}$ ( <b>1b</b> ) 48 h, 45%	$[Mo_3WSe_4(H_2O)_{12}]^{5+}$ ( <b>1d</b> ) 60 h, 40%
$[W_3Se_4(H_2O)_9]^{4+}$	$[MoW_3Se_4(H_2O)_{12}]^{5+}$ ( <b>1h</b> ) 36 h, 70%	$[W_4Se_4(H_2O)_{12}]^{6+}$ ( <b>1j'</b> ) 60 h, 65%
$[MoW_2Se_4(H_2O)_9]^{4+}$	$[Mo_2W_2Se_4(H_2O)_{12}]^{4+}$ ( <b>1f</b> ) 48 h, 55%	not done

An additional stimulus for the development of aqueous W cluster chemistry is added by the quest for new classes of soluble X-ray contrast agents based on heavy metal ( $Z > 53$ ) clusters. The triangular W clusters with the cores  $W_3S_4^{4+}$  and  $W_3O_3S^{4+}$  have been already put forward as entry points for such agents. As cuboidal clusters of the type  $W_4Q_4$  ( $Q = S, Se, Te$ ) have even more heavy atoms per formula unit, they are attractive candidates for these studies.<sup>6</sup>

In the present work we report designed synthesis, solution studies, and electrochemistry of the whole series of  $[Mo_xW_{4-x}Se_4(H_2O)_{12}]^{n+}$  ( $x = 0-4$ ) aqua complexes. Preparation and X-ray characterization of some of their derivatives are also reported, as well as related studies on their sulfido-bridged analogues. Triangular mixed-metal clusters with  $Mo_2WSe_4^{4+}$  and  $MoW_2Se_4^{4+}$  cores are reported here for the first time.

## Experimental Section

**Materials and Procedures.** Hydrothermal syntheses were performed under  $N_2$ , while all the further workup, including column purification, ligand exchange, and crystallizations, was done in air. All reagents were of commercial purity. The triangular aqua complexes  $[M_3Q_4(H_2O)_9]^{4+}$  were prepared by the published procedures and purified using Dowex cation exchange chromatography, elution being with 2 M HCl.<sup>7</sup> Dithiophosphates  $(RO)_2PS_2K$  ( $R = i\text{-Pr, Et}$ ) were made by dissolving  $P_4S_{10}$  in excess alcohol and subsequently neutralizing with KOH and recrystallizing from acetone/ether. Chromatographic separation and purification of the reaction products were done on a Dowex 50WX-2 cation-exchange resin.

Molybdenum, tungsten, and selenium were determined by atomic absorption (AAS) spectroscopy by the analytical service of the University of La Laguna. Elemental analyses for C, H, N, S were performed on a Carlo Erba 1106 (University of La Laguna). UV-vis spectra (300–900 nm) were recorded on a Shimadzu UV-1202 spectrophotometer.

**Electrochemical Studies.** These were carried out at room temperature with an AMEL 5000 potentiostat–galvanostat system controlled by a Pentium PC. The electrochemical cell was a conventional one with three electrodes. The reference was a standard

calomel electrode, the counter electrode was a platinum sheetwire (Radiometer), and a glassy carbon working electrode (Metrohm) was used. For the cuboidal clusters, aqueous 4 M Hpts, deoxygenated by bubbling nitrogen through the solution, was used. The  $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$  couple in 0.1 M HCl (410 mV vs NHE) was chosen as an internal reference. Reduction potentials are ( $E_{1/2}$ 's) defined as  $(1/2)(E_a + E_c)$ , where  $E_a$  and  $E_c$  are anodic and cathodic peak potentials, respectively. Potentials were converted versus NHE. CV experiments on  $[Mo_{3-x}W_xSe_4(acac)_3(py)_3]PF_6$  were run in acetonitrile with 0.1 M  $Bu_4NClO_4$  as supporting electrolyte, scan rate 100 mV/s. Under these conditions, the potential of the  $Fc^+/Fc$  standard couple was 440 mV versus NHE.

Bulk electrolysis experiments of roughly 5 mM solutions of a cluster in 4 M Hpts were performed under  $N_2$ . These required about 2 h, with both working and counter electrodes made up of Pt wire spirals (10 cm length; 0.5 mm in diameter). Cathodic and anodic compartments were separated by a liquid junction, with the reference electrode in the cathodic compartment alongside the working electrode. In the cathodic compartment, full reduction was achieved, and UV-vis spectra were then immediately recorded in an optical cell flushed with nitrogen.

**Reaction of  $[M_3Q_4(H_2O)_9]^{4+}$  with  $M(CO)_6$ . General Procedure for Preparation of **1a–j**.** A stainless steel high-pressure reactor lined with Teflon ( $V = 100$  mL) was filled with 30 mL of 20 mM solution of a triangular cluster aqua complex  $[M_3Q_4(H_2O)_9]^{4+}$  ( $M = Mo, W; Q = S, Se$ ) in 2 M HCl. Then, 200 mg of solid  $M(CO)_6$  ( $M = Mo, W$ ) was added. The reactor was filled with nitrogen, closed, and kept at 130–140 °C for 48–72 h. After cooling, it was opened, and the resulting solution was filtered from solid particles, diluted to  $[H^+] = 0.2$  M, and loaded onto a Dowex cation exchanger. After washing with 50 mL of 0.5 M HCl, unreacted  $[M_3Q_4(H_2O)_9]^{4+}$  were eluted first with 1 M HCl, followed by the cuboidal products. The 5+  $Mo_4$  and  $Mo_xW_{4-x}$  ( $x = 1-3$ ) (**1a–h**) species were eluted satisfactorily with 2 M HCl, while in order to obtain reasonably concentrated solutions of  $[W_4Q_4(H_2O)_{12}]^{6+}$  (**1i'**, **1j'**) the use of 3–4 M HCl is advisable. Alternatively, the elution was with 4 M Hpts. The details of individual reactions are given in Table 1.

The previously reported sulfur-bridged clusters, as well as  $[Mo_4Se_4(H_2O)_{12}]^{5+}$  (**1b**) and  $[W_3MoSe_4(H_2O)_{12}]^{5+}$  (**1h**), were identified by their UV-vis spectra. The peak positions for the newly prepared  $[Mo_3WSe_4(H_2O)_{12}]^{5+}$  (**1d**),  $[Mo_2W_2Se_4(H_2O)_{12}]^{5+}$  (**1f**), and  $[W_4Se_4(H_2O)_{12}]^{6+}$  (**1j'**) were quantified in terms of  $\epsilon$  values using AAS (which gave the required Mo/W/Se ratios). The spectral data are listed in Table 2.

**Preparation of  $[MoW_2Se_4(H_2O)_9]^{4+}$  (**2a**).** A 50 mL portion of a 10 mM solution of  $[MoW_3Se_4(H_2O)_{12}]^{5+}$  (**1h**) in 4 M HCl was heated in air (90 °C) for 10 h until the color change from red-brown into greenish-brown was complete. The resulting solution was filtered from a minor amount of an unidentified precipitate, diluted to  $[H^+] = 0.2$  M and loaded onto a Dowex cation exchanger. After washing with 50 mL of 0.5 M HCl, the greenish-brown product was eluted with 1 M HCl. More concentrated solutions were made after repeated columning and elution with 4 M HCl. Yield 60%.

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**Table 2.** Peak Positions  $\lambda/\text{nm}$  ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$  per Cube) in the UV–Vis Spectra of the Cuboidal Cluster Aqua Ions in 2 M HCl unless Otherwise Stated

	color	peaks	ref
5+ Cube			
[Mo <sub>4</sub> S <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>5+</sup> ( <b>1a</b> )	green	635(435), 1100(122) <sup>a</sup>	10
[Mo <sub>4</sub> Se <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>5+</sup> ( <b>1b</b> )	green	425(sh)(669), 662(407), 1188(117) <sup>a</sup>	12
[Mo <sub>3</sub> WS <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>5+</sup> ( <b>1c</b> )	green(-blue)	606(457), 1040(150)	5
[Mo <sub>3</sub> WSe <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>5+</sup> ( <b>1d</b> )	green(-brown)	664 <sup>b</sup>	this work
[Mo <sub>2</sub> W <sub>2</sub> S <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>5+</sup> ( <b>1e</b> )	pink-grey	563(502), 1000(201)	5
[Mo <sub>2</sub> W <sub>2</sub> Se <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>5+</sup> ( <b>1f</b> )	red-brown	543(sh) <sup>b</sup>	this work
[MoW <sub>3</sub> S <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>5+</sup> ( <b>1g</b> )	orange-brown	522(694), 857(284)	5
[MoW <sub>3</sub> Se <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>5+</sup> ( <b>1h</b> )	brown-orange	524(769), 882(172)	5
[W <sub>4</sub> S <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>5+</sup> ( <b>1i</b> )	red	493(230), 830(90) <sup>a,b</sup>	4
[W <sub>4</sub> Se <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>5+</sup> ( <b>1j</b> )	brown	829 <sup>b</sup>	this work
6+ Cube			
[Mo <sub>4</sub> S <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>6+</sup> ( <b>1a'</b> )	red	575(460), 990(150)	18
[W <sub>4</sub> S <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>6+</sup> ( <b>1i'</b> )	red-brown	452(460), 770(180) <sup>b</sup>	4
[W <sub>4</sub> Se <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>6+</sup> ( <b>1j'</b> )	brown	839(310) <sup>b</sup>	this work
4+ Cube			
[Mo <sub>4</sub> S <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>4+</sup> ( <b>1a''</b> )	orange	375(1120)	22
[Mo <sub>4</sub> Se <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>4+</sup> ( <b>1b''</b> )	yellowish-brown	403(1172), 450(sh)	12
[Mo <sub>3</sub> WSe <sub>4</sub> (H <sub>2</sub> O) <sub>12</sub> ] <sup>4+</sup> ( <b>1d''</b> )	orange	395(sh) <sup>b</sup>	this work

<sup>a</sup> In 2 M Hpts. <sup>b</sup> Not recorded at  $\lambda \geq 900$  nm.

**Table 3.** Peak Positions  $\lambda/\text{nm}$  ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$  per Cube) in the UV–Vis Spectra of the [Mo<sub>x</sub>W<sub>3-x</sub>Se<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> in 2 M HCl

cluster	color	peaks	ref
[Mo <sub>3</sub> Se <sub>4</sub> (H <sub>2</sub> O) <sub>9</sub> ] <sup>4+</sup>	brown	433(5250), 681(580)	20
[Mo <sub>2</sub> WSe <sub>4</sub> (H <sub>2</sub> O) <sub>9</sub> ] <sup>4+</sup> ( <b>2a</b> )	brown	405, 655	this work
[MoW <sub>2</sub> Se <sub>4</sub> (H <sub>2</sub> O) <sub>9</sub> ] <sup>4+</sup> ( <b>2b</b> )	greenish-brown	378(5980), 635(501)	this work
[W <sub>3</sub> Se <sub>4</sub> (H <sub>2</sub> O) <sub>9</sub> ] <sup>4+</sup>	green	360(6950), 625(500)	20

Similarly, from [Mo<sub>2</sub>W<sub>2</sub>Se<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup> (**1f**) brown [Mo<sub>2</sub>WSe<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> (**2b**) was obtained in a 55% yield. Identification of both compounds was by UV–vis quantified in terms of  $\epsilon$  values using AAS. The spectral data are listed in Table 3.

**Preparation of (Me<sub>2</sub>NH<sub>2</sub>)<sub>6</sub>[M<sub>4</sub>Se<sub>4</sub>(NCS)<sub>12</sub>] (3a, M = Mo; 3b, M = W).** To a solution of corresponding cuboidal aqua cluster in 4 M HCl (typically 20 mL of 5 mM solution) was added an excess of solid KNCS (ca. 1 g) followed by 1 g of dimethylammonium chloride. The resulting solution was left in an open beaker for 2–3 days. The crystalline thiocyanato complex was then filtered off and dried in air. Yields were quantitative. The analytical data are given in Table 4.

Crystals of brown (NH<sub>4</sub>)<sub>6</sub>[W<sub>4</sub>Se<sub>4</sub>(NCS)<sub>12</sub>]·4H<sub>2</sub>O (**3c**) were prepared in a similar way with NH<sub>4</sub>NCS instead of KNCS and without dimethylammonium chloride.

**Preparation of [M<sub>4</sub>Q<sub>4</sub>((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>6</sub>] (4a–h).** To a solution of corresponding cuboidal cluster in 4 M HCl (typically 20 mL of 5 mM solution) was added an excess of potassium diethyldithiophosphate (ca. 1 g). The precipitation of the complexes is complete in 1 day. The precipitate was filtered off and dissolved in 5 mL of CHCl<sub>3</sub>, and then 10 mL of ethanol was added and slow evaporation of this solution produces well-shaped crystals of title complexes. The analytical data are given in Table 4.

**Preparation of [W<sub>4</sub>Se<sub>4</sub>((i-PrO)<sub>2</sub>PS<sub>2</sub>)<sub>6</sub>] (5a).** This complex was prepared as indicated above using (i-PrO)<sub>2</sub>PS<sub>2</sub>K instead of (EtO)<sub>2</sub>PS<sub>2</sub>K. Crystallization was from ethanol, giving single crystals of X-ray quality.

**Preparation of [W<sub>4</sub>S<sub>4</sub>((MeO)<sub>2</sub>PS<sub>2</sub>)<sub>6</sub>] (5b).** This complex was prepared as indicated above using (MeO)<sub>2</sub>PS<sub>2</sub>K instead of (EtO)<sub>2</sub>PS<sub>2</sub>K. Crystallization was from ethanol, giving single crystals of X-ray quality.

**Preparation of [Mo<sub>2</sub>WSe<sub>4</sub>(acac)<sub>3</sub>(py)<sub>3</sub>]PF<sub>6</sub> (**6a**) and [MoW<sub>2</sub>Se<sub>4</sub>(acac)<sub>3</sub>(py)<sub>3</sub>]PF<sub>6</sub> (**6b**).** To a solution of corresponding triangular

aqua complex in HCl, 1 mL of acetylacetone (Hacac) was added. The mixture was then neutralized with solid NaHCO<sub>3</sub> until no more CO<sub>2</sub> evolved, and then 1 mL of pyridine (py) was added, quickly followed by 0.5 g of NH<sub>4</sub>PF<sub>6</sub>. The resulting slurry was stirred for 1 h, and the precipitate was collected, washed with water, and dissolved in CHCl<sub>3</sub>. Analytically pure crystalline samples were obtained by slow evaporation from hot CHCl<sub>3</sub>/EtOH (50:50 v/v) mixtures. Yields about 80%.

**[MoW<sub>2</sub>Se<sub>4</sub>(acac)<sub>3</sub>(py)<sub>3</sub>]PF<sub>6</sub> (**6a**).** This compound forms as brown crystals. FAB-MS: 1318 (12%, M<sup>+</sup>), 1239 (11%, [M – py]<sup>+</sup>), 1160 (21%, [M – 2py]<sup>+</sup>), 1081 (100%, [MoW<sub>2</sub>Se<sub>4</sub>(acac)<sub>3</sub>]<sup>+</sup>), 995 (28%), 914 (11%), 829 (8%). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 1.98 (s, 6H, CH<sub>3</sub>), 2.02 (s, 6H, CH<sub>3</sub>), 2.07 (6H, CH<sub>3</sub>), 5.38 (1H,  $\gamma$ -CH), 5.49 (2H,  $\gamma$ -CH), 7.63, 7.61, 7.58, 7.57, 7.55, 7.53 (multiplets, 3H,  $\gamma$ -py), 8.09, 8.07, 8.05, 8.00 (multiplets, 6H,  $\beta$ -py), 9.56, 9.58 (d, 2H,  $\alpha$ -py), 9.83, 9.85 (d, 4H,  $\alpha$ -py).

**[Mo<sub>2</sub>WSe<sub>4</sub>(acac)<sub>3</sub>(py)<sub>3</sub>]PF<sub>6</sub> (**6b**).** This compound forms as brown crystals. FAB-MS: 1226 (30%, M<sup>+</sup>), 1126 (30%, [M – Hacac]<sup>+</sup>), 1085 (25%), 1047 (40%, [M – py – Hacac]<sup>+</sup>), 989 (45%, [MoW<sub>2</sub>Se<sub>4</sub>(acac)<sub>3</sub>]<sup>+</sup>). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$  ppm): 1.94 (s, 6H, CH<sub>3</sub>), 1.98 (s, 6H, CH<sub>3</sub>), 2.02 (6H, CH<sub>3</sub>), 5.37 (2H,  $\gamma$ -CH), 5.49 (1H,  $\gamma$ -CH), 7.53, 7.56, 7.58, 7.60, 7.64, 7.66, 7.70 (multiplets, 3H,  $\gamma$ -py), 7.96, 7.99, 8.02, 8.05 (multiplets, 6H,  $\beta$ -py), 9.61, 9.63 (d, 4H,  $\alpha$ -py), 9.86, 9.88 (d, 2H,  $\alpha$ -py).

**Crystallographic Studies.** X-ray crystallography was done in an essentially routine manner. The crystals are air stable and were mounted on the tip of a glass fiber with the use of epoxy cement. All X-ray data except for [Mo<sub>4</sub>Se<sub>4</sub>((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>6</sub>] (**4h**) were collected on a Bruker Smart CCD diffractometer using graphite monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) with a nominal crystal-to-detector distance of 4.0 cm. A hemisphere of data was collected on the basis of three  $\omega$ -scan runs (starting  $\omega = -28^\circ$ ) at values  $\phi = 0, 90, \text{ and } 180^\circ$  with the detector at  $2\theta = 28^\circ$ . At each of these runs, frames (606, 435, and 230, respectively) were collected at  $0.3^\circ$  intervals and 30, 20, 25, and 15 s per frame for compounds **3c**, **4a**, **4b**, and **5a**, respectively. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.<sup>8</sup> The positions of the heavy atoms were determined by direct methods, and successive difference electron density maps

(8) (a) SAINT 5.0; B.A.X.R. Systems: Madison, WI, 1996. (b) Sheldrick, G. M. SADABS empirical absorption program; Bruker: Madison, WI, 1996.

**Table 4.** Analytical and Spectroscopic Data for Thiocyanate and Dithiophosphate Complexes Prepared in This Work

formula	found, %	calcd, %	UV-vis, $^{31}P$ NMR, and FAB-MS data
$(Me_2NH_2)_6[Mo_4Se_4(NCS)_{12}]$ ( <b>3a</b> )	C, 17.9; H, 2.9; N, 15.5; S, 23.5	C, 17.2; H, 2.9; N, 15.1; S, 23.0	FAB-MS: 1974 ( $M^+$ , 75%), 1788 ( $[M - dtp]^+$ , 100%), 1236 ( $[W_3S_4(dtp)_3]^+$ , 15%); $^{31}P$ NMR: 112.1 ppm (2P), 195.6 ppm (4P) ( $\beta$ -isomer), 116.2 ppm (3P); 219.1 ppm (3P) ( $\alpha$ -isomer); UV-vis 725(305), 434(3950)
$(Me_2NH_2)_6[W_4Se_4(NCS)_{12}]$ ( <b>3b</b> )	C, 13.9; H, 2.2; N, 12.1; S, 20.2	C, 14.2; H, 2.4; N, 12.4; S, 19.0	
$[W_4S_4((EtO)_2PS_2)_6]$ ( <b>4a</b> )	C, 14.5; H, 3.0	C, 14.6; H, 3.1	
$[MoW_3S_4((EtO)_2PS_2)_6]$ ( <b>4b</b> )	C, 15.4; H, 3.2	C, 15.3; H, 3.2	FAB-MS: 1885 ( $M^+$ , 30%), 1702 ( $[M - dtp]^+$ , 100%), 1516 ( $[M - 2dtp]^+$ , 18%), 1360 ( $[M - 3dtp]^+ + S]^+$ , 20%), 1148 ( $[W_2MoS_4(dtp)_3]^+$ , 22%) $^{31}P$ NMR: 101.2 ppm (2P); 138.1 ppm (4P) ( $\beta$ -isomer)
$[Mo_4S_4((EtO)_2PS_2)_6]$ ( <b>4c</b> )	C 18.8; H 3.9	C, 17.8; H, 3.7	FAB-MS: 2162 ( $M^+$ , 35%); $^{31}P$ NMR ( $\beta$ -isomer): 112.1 ppm (2P); 195.6 ppm (4P)
$[W_4Se_4((EtO)_2PS_2)_6]$ ( <b>4d</b> )	C, 13.3; H, 2.8; S, 17.8	C, 13.3; H, 2.8; S, 17.1	FAB-MS: 2074 ( $M^+$ , 100%) FAB-MS: 1987 ( $M^+$ , 40%) FAB-MS: 1899 ( $M^+$ , 30%) $^{31}P$ NMR: 106.7 ppm (2P), 140.6 ppm (4P) ( $\beta$ -isomer)
$[MoW_3Se_4((EtO)_2PS_2)_6]$ ( <b>4e</b> )	C, 13.1; H, 2.7; S, 18.0	C, 13.9; H, 2.9; S, 18.5	FAB-MS: 1904 ( $M^+ - 2dtp$ , 48%), 1690 ( $M^+ - 3dtp$ , 28%), 1509 ( $[W_3Se_4(i-PrO)_2PS_2)_3]^+$ , 68%); $^{31}P$ NMR: 112.2 ppm (2P); 195.6 ppm (4P) ( $\beta$ -isomer)
$[Mo_2W_2Se_4((EtO)_2PS_2)_6]$ ( <b>4f</b> )	C, 15.0; H, 3.0	C, 14.5; H, 3.0	
$[Mo_3WSe_4((EtO)_2PS_2)_6]$ ( <b>4g</b> )	C, 15.5; H, 3.5	C, 15.2; H, 3.2	
$[Mo_4Se_4((EtO)_2PS_2)_6]$ ( <b>4h</b> )	C, 16.3; H, 3.5	C, 15.9; H, 3.3	
$[W_4Se_4((i-PrO)_2PS_2)_6]$ ( <b>5a</b> )	C, 19.1; H, 3.6; S, 17.3	C, 18.6; H, 3.6; S, 16.5	$^{31}P$ NMR: 117.0 (2P), 207.3 (4P) ( $\beta$ -isomer)
$[W_4S_4((MeO)_2PS_2)_6]$ ( <b>5b</b> )	C, 8.4; H, 2.0; S, 28.7	C, 8.0; H, 2.0; S, 28.4	

using the SHELXTL 5.10 software package were done to locate the remaining atoms. Refinement was performed by the full-matrix least-squares method based on  $F^2$ .<sup>9</sup> X-ray data for **4h** were collected on a Bruker-Nonius KappaCCD diffractometer using graphite monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), with  $\varphi$  and  $\omega$  scans chosen to give a complete asymmetric unit using the COLLECT program, indexed and processed using Denzo SMN, and scaled together using the HKL2000 program. The absorption correction was applied using a semiempirical method based on multiple scanned reflections on the PLATON program. The structure solution was obtained by direct methods, using the SIR2002 program, and refined using the SHELXTL-97 program.<sup>9</sup>

Crystal parameters and basic information relating data collection and structure refinement are summarized in Table 5.

## Results and Discussion

**Syntheses of the Cuboidal Clusters.**  $Mo(CO)_6$  and  $W(CO)_6$  react with triangular cluster aqua complexes  $[M_3Q_4(H_2O)_9]^{4+}$  ( $M = Mo, W$ ;  $Q = S, Se$ ) to give cuboidal cluster aqua complexes as the result of formal addition of " $M(H_2O)_3$ " groups to the cluster. Topological similarity between the  $M_3Q_4$  and  $M_4Q_4$  cores makes this pathway viable. Under

these conditions, all the CO groups are lost; no carbonyl intermediates were detected. In the case of the reaction of  $[Mo_3S_4(H_2O)_9]^{4+}$  with  $Mo(CO)_6$ , the orange  $[Mo_4S_4(H_2O)_{12}]^{4+}$  (**1a''**) forms first which is then rapidly oxidized in air into the green 5+ cation, in agreement with the reported low potential for the 5+/4+ couple of 210 mV (vs NHE, in 2 M Hpts).<sup>10</sup> As the potentials for the corresponding couples in the case of mixed Mo/W clusters are even lower, no 4+ cube could be detected, and the only products were  $[Mo_2W_2S_4(H_2O)_{12}]^{5+}$  (**1e**) and  $[MoW_3S_4(H_2O)_{12}]^{5+}$  (**1g**). A mixture of  $[W_4S_4(H_2O)_{12}]^{n+}$  with  $n = 5$  (**1i**) and 6 (**1i'**) forms from  $W(CO)_6$  and  $[W_3S_4(H_2O)_9]^{4+}$ . Surprisingly enough,  $W(CO)_6$  with  $[Mo_3S_4(H_2O)_9]^{4+}$  gave  $[Mo_4S_4(H_2O)_{12}]^{5+}$  (**1a**) and not the expected mixed metal  $[Mo_3WS_4(H_2O)_{12}]^{5+}$  (**1c**), thus acting merely as reducing agent. In the case of  $Q = Se$ , the reactions follow a more uniform pattern to give the 5+ species in the case of  $Mo_xW_{4-x}Se_4$  cores when  $x = 1-4$ , but the  $W_4Se_4$  cuboidal cluster is obtained as  $[W_4Se_4(H_2O)_{12}]^{6+}$  (**1j'**). In an earlier work we reported the preparation of  $[Mo_xW_{4-x}S_4(H_2O)_{12}]^{5+}$  from  $K_4[Mo_2Cl_8]$  and corresponding triangular clusters, by formal addition of a " $Mo(H_2O)_3$ " group;  $[W_3MoSe_4(H_2O)_{12}]^{5+}$  was made in the same way from  $[W_3Se_4(H_2O)_9]^{4+}$  and  $[Mo_2Cl_8]^{4-}$ .<sup>5</sup> As  $K_4[Mo_2Cl_8]$  is usually made in a two-step procedure starting from  $Mo(CO)_6$ ,<sup>11</sup> the direct hydrothermal synthesis of the cuboidal clusters from  $Mo(CO)_6$  and triangular aqua ions offers an obvious advantage. Since  $[Mo_4Se_4(H_2O)_{12}]^{5+}$  is

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**Table 5.** Crystallographic Data for (NH<sub>4</sub>)<sub>6</sub>[W<sub>4</sub>Se<sub>4</sub>(NCS)<sub>12</sub>]·4H<sub>2</sub>O (**3c**), [W<sub>4</sub>S<sub>4</sub>(μ<sub>2</sub>-(EtO)<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>4</sub>] (**4a**), [W<sub>3</sub>MoS<sub>4</sub>(μ<sub>2</sub>-(EtO)<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>] (**4b**), [Mo<sub>4</sub>Se<sub>4</sub>(μ<sub>2</sub>-(EtO)<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>] (**4h**), and [W<sub>4</sub>Se<sub>4</sub>(μ<sub>2</sub>-(i-PrO)<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>((i-PrO)<sub>2</sub>PS<sub>2</sub>)<sub>4</sub>] (**5a**)

	<b>3c</b>	<b>4a</b>	<b>4b</b>	<b>4h</b>	<b>5a</b>
empirical formula	C <sub>12</sub> H <sub>32</sub> N <sub>18</sub> O <sub>4</sub> - S <sub>12</sub> Se <sub>4</sub> W <sub>4</sub>	C <sub>24</sub> H <sub>60</sub> O <sub>12</sub> - P <sub>6</sub> S <sub>16</sub> W <sub>4</sub>	C <sub>24</sub> H <sub>60</sub> MoO <sub>12</sub> - P <sub>6</sub> S <sub>16</sub> W <sub>3</sub>	C <sub>24</sub> H <sub>60</sub> Mo <sub>4</sub> O <sub>12</sub> - P <sub>6</sub> S <sub>12</sub> Se <sub>4</sub>	C <sub>36</sub> H <sub>84</sub> O <sub>12</sub> P <sub>6</sub> - S <sub>12</sub> Se <sub>4</sub> W <sub>4</sub>
fw	1928.52	1974.90	1886.99	1810.86	2330.81
cryst syst	hexagonal	monoclinic	triclinic	triclinic	triclinic
<i>a</i> , Å	17.340(3)	12.842(4)	14.102(4)	13.3753(10)	13.4014(13)
<i>b</i> , Å		17.336(5)	16.345(4)	13.899(2)	13.6570(14)
<i>c</i> , Å	10.541(3)	13.594(4)	13.409(3)	16.467(3)	21.563(2)
α, deg			91.982(6)	72.204(5)	97.737(2)
β, deg		98.135(6)	95.291(6)	87.584(5)	90.214(2)
γ, deg			73.292(6)	84.193(5)	106.734(2)
<i>V</i> , Å <sup>3</sup>	2744.6(10)	2996.1(14)	2947.8(13)	2899.5(7)	3758.3(6)
<i>T</i> , K	293(2)	293(2)	293(2) K	150(2)	293(2)
space group	<i>P</i> 6 <sub>3</sub> <i>mc</i>	<i>P</i> 2/ <i>n</i>	<i>P</i> 1	<i>P</i> 1	<i>P</i> 1
<i>Z</i>	2	2	2	2	2
μ(Mo Kα), mm <sup>-1</sup>	11.504	8.416	6.817	4.000	8.543
reflns collected	12148	24696	16952	56936	23945
unique reflns/ <i>R</i> <sub>int</sub>	1289 [ <i>R</i> (int) = 0.1729]	8963 [ <i>R</i> (int) = 0.0780]	10376 [ <i>R</i> (int) = 0.0444]	13331 [ <i>R</i> (int) = 0.0599]	15337 [ <i>R</i> (int) = 0.0522]
<i>R</i> <sup>1</sup> / <i>wR</i> <sup>2</sup> <sup>b</sup>	<i>R</i> 1 = 0.0672, <i>wR</i> 2 = 0.1604	<i>R</i> 1 = 0.0765, <i>wR</i> 2 = 0.2266	<i>R</i> 1 = 0.0502, <i>wR</i> 2 = 0.1137	<i>R</i> 1 = 0.0407, <i>wR</i> 2 = 0.1035	<i>R</i> 1 = 0.0651, <i>wR</i> 2 = 0.1220
<i>R</i> <sup>1</sup> / <i>wR</i> <sup>2</sup> <sup>b</sup> (all data)	<i>R</i> 1 = 0.0973, <i>wR</i> 2 = 0.1885	<i>R</i> 1 = 0.1941, <i>wR</i> 2 = 0.2541	<i>R</i> 1 = 0.0873, <i>wR</i> 2 = 0.1279	<i>R</i> 1 = 0.0639, <i>wR</i> 2 = 0.1315	<i>R</i> 1 = 0.1176, <i>wR</i> 2 = 0.1377

$${}^a R1 = \sum ||F_o| - |F_c|| / \sum F_o, {}^b wR2 = [\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]]^{1/2}.$$

made by this way in a 45% yield instead of a much lower yield ( $\leq 10\%$ ) by the only reported procedure (which employs reduction of [Mo<sub>2</sub>O<sub>2</sub>Se<sub>2</sub>(cys)<sub>2</sub>]<sup>2-</sup> with NaBH<sub>4</sub><sup>12</sup>), the hydrothermal reaction is the best access route to this cluster. And reaction of W(CO)<sub>6</sub> with [W<sub>3</sub>Q<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> is the only way to the cuboidal aqua complexes [W<sub>4</sub>Q<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup>.<sup>4</sup>

Some Mo/W mixed-metal cuboidal clusters with external ligands other than water were reported before. These include [Mo<sub>3</sub>WS<sub>4</sub>(μ-R<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>(R<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>] and [Mo<sub>2</sub>W<sub>2</sub>S<sub>4</sub>(μ-R<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>(R<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>] (R = Et, i-Pr).<sup>13</sup> Mo(CO)<sub>6</sub> as a source of metal to convert a Mo<sub>3</sub>S<sub>4</sub> cluster core into Mo<sub>4</sub>S<sub>4</sub> was used to make [Mo<sub>4</sub>S<sub>4</sub>(n-Pr<sub>2</sub>NCS<sub>2</sub>)<sub>6</sub>] from [Mo<sub>3</sub>S<sub>4</sub>(n-Pr<sub>2</sub>NCS<sub>2</sub>)<sub>4</sub>], Mo(CO)<sub>6</sub>, and (n-Pr<sub>2</sub>NCS<sub>2</sub>)<sub>2</sub>,<sup>14</sup> [Mo<sub>4</sub>S<sub>4</sub>(R<sub>2</sub>PS<sub>2</sub>)<sub>6</sub>] from [Mo<sub>3</sub>S<sub>4</sub>(R<sub>2</sub>PS<sub>2</sub>)<sub>4</sub>], Mo(CO)<sub>6</sub>, and (R<sub>2</sub>PS<sub>2</sub>)<sub>2</sub> (R = Et, i-Pr),<sup>13</sup> and H[Mo<sub>4</sub>S<sub>4</sub>(μ-OAc)<sub>2</sub>(dtp)<sub>4</sub>] from Mo(CO)<sub>6</sub>, [Mo<sub>3</sub>S<sub>4</sub>(μ-dtp)(dtp)<sub>3</sub>], and acetic acid.<sup>15</sup> In our case, H<sup>+</sup> might serve as external oxidant for M(0) in the carbonyls.

Other reported W<sub>4</sub>Q<sub>4</sub> (Q = S, Se) clusters are made by (i) a self-assembly reaction between W(CO)<sub>6</sub>, Na<sub>2</sub>WO<sub>4</sub>, and P<sub>4</sub>S<sub>10</sub> in EtOH or from unspecified “H<sub>3</sub>W<sub>2</sub>Cl<sub>9</sub>” and P<sub>4</sub>S<sub>10</sub> in EtOH, to give either [W<sub>4</sub>S<sub>4</sub>(μ-(EtO)<sub>2</sub>PS<sub>2</sub>)<sub>2</sub>((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>4</sub>] or [W<sub>4</sub>S<sub>4</sub>(μ-(EtO)<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>((EtO)<sub>2</sub>PS<sub>2</sub>)<sub>3</sub>];<sup>15</sup> (ii) high-temperature (ca. 430–450 °C) synthesis from KCN and W<sub>3</sub>S<sub>7</sub>Br<sub>4</sub> or KNCS and WTe<sub>2</sub> (gives [W<sub>4</sub>S<sub>4</sub>(CN)<sub>12</sub>]<sup>6-</sup>), or from KCN and W<sub>3</sub>Se<sub>7</sub>Br<sub>4</sub> (gives [W<sub>4</sub>Se<sub>4</sub>(CN)<sub>12</sub>]<sup>6-</sup>).<sup>3</sup>

**Stability and Reactivity.** Air oxidation of the cuboidal aqua complexes is slow at room temperature, but at 90 °C they decay into triangular clusters [M<sub>3</sub>Q<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> in a few hours. When both Mo and W are present in the cluster core, it is invariably the W atom which is lost. The reason for this may be a stronger preference of W for higher oxidation states: low-valence tungsten compounds are more easily to oxidize both kinetically and thermodynamically. This selective degradation opens a way to mixed-metal triangular clusters starting from easily accessible [W<sub>3</sub>Q<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup>. Using this approach, we have prepared the first seleno bridged mixed-metal triangular clusters [Mo<sub>2</sub>WSe<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> (**2a**) and [MoW<sub>2</sub>Se<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> (**2b**). Their sulfur analogues were prepared by reducing a mixture of WS<sub>4</sub><sup>2-</sup> and [Mo<sub>2</sub>O<sub>2</sub>S<sub>2</sub>(cys)<sub>2</sub>]<sup>2-</sup> with NaBH<sub>4</sub> in HCl.<sup>16</sup> This procedure always gives a mixture of both [Mo<sub>2</sub>WS<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> and [MoW<sub>2</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> which must then be separated by a tedious chromatographical procedure.<sup>16,17</sup> Selective degradation of mixed metal cuboidal clusters [Mo<sub>2</sub>W<sub>2</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup> (**1c**) and [MoW<sub>3</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup> (**1g**) is thus a better alternative. The cuboidal cluster/incomplete cuboidal cluster interconversions are shown in the Chart 1.

This degradation of the 5+ charged species must proceed through the 6+ state. [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> (**1a'**) was indeed reported but seems to be rather unstable and will decay spontaneously even at 0 °C in a few days to give a mixture of [Mo<sub>3</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]<sup>4+</sup> and [Mo<sub>4</sub>S<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>5+</sup> (**1a**). As it is a strong oxidant (*E*<sup>0</sup> for the 6+/5+ couple is 860 mV vs NHE), the decay may be the result of self-oxidation.<sup>18</sup> [Mo<sub>4</sub>Se<sub>4</sub>(H<sub>2</sub>O)<sub>12</sub>]<sup>6+</sup> has not been isolated. Taking into account its high reduction potential (792 mV vs NHE) determined from CV,

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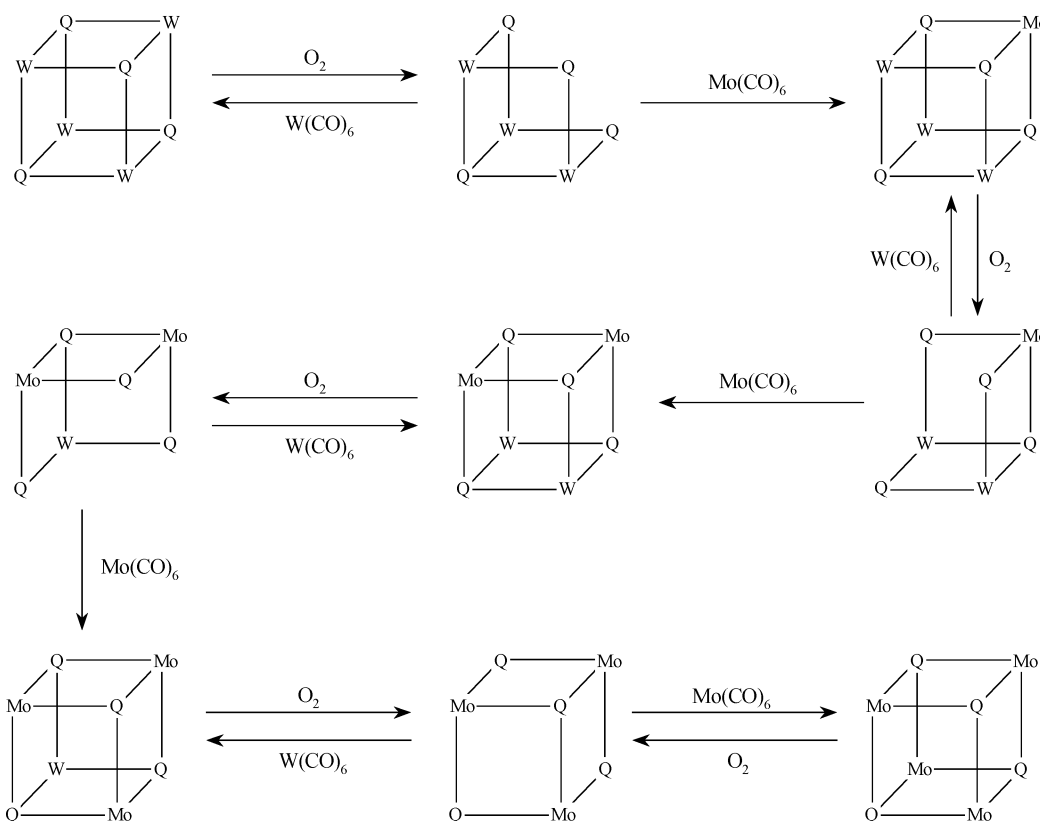
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Chart 1



it is expected to be unstable.<sup>12</sup> In contrast, both W clusters  $[W_4Q_4(H_2O)_{12}]^{6+}$  (Q = S, **1i'**; Se, **1j'**) are stable at least for months if kept at 0 °C. The reason may be much lower reduction potentials of the corresponding 6+/5+ couples: 35 mV for Q = S and -28 mV for Q = Se, which make self-oxidation improbable. In turn, the 5+ species  $[W_4Q_4(H_2O)_{12}]^{5+}$ , which are quantitatively generated in an electrolysis cell, are oxidized in air into the 5+ species within a few hours (Q = S)<sup>4</sup> or even minutes (Q = Se). Bulk electrolysis was also used to generate  $[Mo_3WSe_4(H_2O)_{12}]^{4+}$  (**1d''**) from **1d**. Attempts to obtain the mixed-metal 6+ species by controlled potential electrolytic oxidation of **1d**, **1f**, and **1h** led only to decomposition into trinuclear  $[Mo_3S_4(H_2O)_9]^{4+}$ , **2a** and **2b**, respectively. Similar decomposition was reported for electrolytic oxidation of  $[Mo_4S_4(H_2O)_{12}]^{5+}$ .<sup>10</sup>

Coordination of dithiophosphate or  $NCS^-$  seems to favor the 6+ state of the cluster core, leading to dithiophosphates  $[M_4Q_4(dtp)_6]$  (**4a–h**, **5a–b**) and thiocyanates  $[M_4Se_4(NCS)_{12}]^{6-}$  (**3a–c**). The dithiophosphates are made by simply adding a solution of the ligand to a solution of 5+ (in our case,  $[Mo_4Se_4(H_2O)_{12}]^{5+}$  (**1b**) or mixed Mo/W species), or 6+ charged ( $[W_4Q_4(H_2O)_{12}]^{6+}$  (**1i'**, **1j'**)) aqua ions. They give the required molecular peaks in FAB-MS (Table 4), thus confirming the individuality of a given  $Mo_xW_{4-x}Q_4$  cluster and the absence of metal exchange in the reactions with carbonyles. That the thiocyanate coordination favors the 6+ state was noted in the preparation of  $[Mo_4S_4(NCS)_{12}]^{6-}$  and  $[MoW_3Q_4(NCS)_{12}]^{6-}$  (Q = S, Se) from the 5+ charged aqua complexes and  $NCS^-$  in air.<sup>5,19</sup> Reaction with bidentate dithiophosphate always gives a mixture of so-called  $\beta$  and  $\alpha$  isomers with a strong predominance of the former, as can

**Table 6.** Electrochemical Data (mV) for  $[Mo_{4-x}W_xSe_4(H_2O)_{12}]^{n+}$  Complexes in 4 M Hpts

complex	$E^2_{1/2}$ (6+/5+)	$E^2_{1/2}$ (5+/4+)
$[Mo_4Se_4(H_2O)_{12}]^{n+}$	792	193
$[Mo_3WSe_4(H_2O)_{12}]^{n+}$	500	10
$[Mo_2W_2Se_4(H_2O)_{12}]^{n+}$	364	-205
$[MoW_3Se_4(H_2O)_{12}]^{n+}$	214	-410
$[W_4Se_4(H_2O)_{12}]^{n+}$	-28	-600 <sup>a</sup>

<sup>a</sup> Extrapolated value.

be seen from  $^1H$  and  $^{31}P$  NMR data (Table 4). The isomers differ by the ratio of bridging and terminal dithiophosphate ligands, which is 2:4 in  $\beta$  isomers, and 3:3 in  $\alpha$ . The  $\beta$  isomers form preferentially ( $\beta/\alpha$  ratio about 10:1) in all cases, for  $[M_4Q_4((EtO)_2PS_2)_6]$  (M = Mo, W; Q = S, Se, **4a–h**),  $[W_4Se_4((i\text{-}PrO)_2PS_2)_6]$  (**5a**), and  $[W_4S_4((MeO)_2PS_2)_6]$  (**5b**). As in the case of  $[Mo_4S_4(R_2PS_2)_6]$  (where only  $\beta$  isomers were detected),<sup>13a</sup> the lower chemical shifts at  $^{31}P$  correspond to the bridging ligands. Though no separation of the isomers has been achieved yet, in two cases crystals of  $\alpha$ -isomers were picked up from the reaction mixture.

**Electrochemistry.** As in the case of  $[Mo_xW_{4-x}S_4(H_2O)_{12}]^{5+}$  ( $x = 0–4$ ),<sup>5</sup> reversible one-electron oxidation and reduction processes were observed for their Se analogues (Table 6). For both S and Se clusters when  $x = 0$ , the 4+ species were not detected in the CVA experiments, because they must be too reducing to exist in the strongly acidic solution used in the experiments (reduction of  $H^+$ ). Reduction potentials  $E_{1/2}$  versus NHE for the 6+/5+ and 5+/4+ couples were

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**Table 7.** Electrochemical Data (V) for  $[\text{Mo}_{3-x}\text{W}_x\text{Se}_4(\text{acac})_3(\text{py})_3]\text{PF}_6$ 

compd	$E^{1/2}$	$\Delta E$	$E^{2/2}$	$\Delta E$
$[\text{Mo}_3\text{Se}_4(\text{acac})_3(\text{py})_3]\text{PF}_6^{21}$	-0.85	0.084	-0.98	0.084
$[\text{Mo}_2\text{WSe}_4(\text{acac})_3(\text{py})_3]\text{PF}_6$ ( <b>6a</b> )	-0.81	0.071	-0.95	0.072
$[\text{MoW}_2\text{Se}_4(\text{acac})_3(\text{py})_3]\text{PF}_6$ ( <b>6b</b> )	-1.09	0.099	-1.34	0.088
$[\text{W}_3\text{Se}_4(\text{acac})_3(\text{py})_3]\text{PF}_6^{21}$	-1.05	0.058	-1.18	0.087

determined, and they follow the systematic trend to more negative values as more W is incorporated, established earlier for the S-bridged clusters.<sup>5</sup> This again reflects the greater difficulty in generating the lower oxidation states of W. The average increment is about 200 mV per one W atom. The influence of chalcogen is less dramatic: the substitution of Se for S (all four atoms) lowers the reduction potential by less than 100 mV. This effect is more pronounced for the 6+/5+ than for the 5+/4+ couples. The molecular orbital involved in these redox processes is predominantly a metal-d-AO-based  $t_2$  orbital with only small participation of chalcogen-based orbitals. A similar trend is observed for  $[\text{W}_4\text{Q}_4(\text{CN})_{12}]^{n-}$  (Q = S, Se, Te),<sup>3</sup> whereas for  $[\text{Mo}_4\text{Q}_4(\text{edta})_2]^{n-}$  the difference between Q = S and Q = Se is almost negligible (no more than 5 mV).<sup>20</sup> In the case of cyanides, the 6+ state is less oxidizing and the 4+ state less reducing, with less influence of metal nature upon the potential, which can be explained by participation of  $\pi$ -orbitals of the CN-ligand in the electronic delocalization.<sup>3</sup>

**Derivatization of  $[\text{Mo}_2\text{WSe}_4(\text{H}_2\text{O})_9]^{4+}$  and  $[\text{MoW}_2\text{Se}_4(\text{H}_2\text{O})_9]^{4+}$ .** To isolate solid complexes of  $\text{Mo}_2\text{WSe}_4^{4+}$  and  $\text{MoW}_2\text{Se}_4^{4+}$ , the aqua ions were treated with acetylacetonate and pyridine in the procedure used to prepare  $[\text{M}_3\text{Q}_4(\text{acac})_3(\text{py})_3]\text{PF}_6$ .<sup>21</sup> Accordingly, the products were  $[\text{Mo}_2\text{WSe}_4(\text{acac})_3(\text{py})_3]\text{PF}_6$  (**6a**) and  $[\text{MoW}_2\text{Se}_4(\text{acac})_3(\text{py})_3]\text{PF}_6$  (**6b**). Their FAB MS data show the required molecular peaks  $[\text{Mo}_2\text{WSe}_4(\text{acac})_3(\text{py})_3]^+$  and  $[\text{MoW}_2\text{Se}_4(\text{acac})_3(\text{py})_3]^+$  with the characteristic pattern of pyridine loss, so that the most intense peaks were those of  $[\text{Mo}_2\text{WSe}_4(\text{acac})_3]^+$  (for **6a**) and  $[\text{MoW}_2\text{Se}_4(\text{acac})_3]^+$  (for **6b**). From X-ray analysis of isostructural  $[\text{M}_3\text{Q}_4(\text{acac})_3(\text{py})_3]\text{PF}_6$  (Q = S, Se) and  $[\text{W}_3\text{Se}_4(\text{acac})_3(\text{py})_3]\text{PF}_6$ , coordination of pyridine *trans* to the  $\mu_3$ -Q atom has been established. The <sup>1</sup>NMR data show that this coordination is preserved in solution.<sup>21</sup> In the present case, the NMR spectra look more complicated due to the presence of two different sorts of metal atom. However, they are easily interpreted within the same geometry. There are three singlets of CH<sub>3</sub> groups from acac in a 1:1:1 ratio, due to three types of methyls, two signals from  $\gamma$ -CH in the acac (in the expected 1:2 ratio), and groups of signals from protons in  $\alpha$ -,  $\beta$ -, and  $\gamma$ -positions of coordinated pyridines. The chemical shifts from acac and py bound to W are at lower field than at the Mo. Cyclic voltammetry reveals two waves due to consecutive one-electron reductions, as in  $[\text{Mo}_3\text{Se}_4(\text{acac})_3(\text{py})_3]\text{PF}_6$  and  $[\text{W}_3\text{Se}_4(\text{acac})_3(\text{py})_3]\text{PF}_6$  (Table 7). Whether the reduction is primarily Mo centered, or the extra

electrons are delocalized all over the cluster, remains to be seen.

**Structure of the Cuboidal Clusters.** Compound **3c** crystallizes in the noncentrosymmetric space group  $P6_3mc$ , and its structure was solved applying a racemic twin law, with a final BASF factor 0.14(7). All tungsten, selenium, and sulfur atoms were refined anisotropically whereas nitrogen and carbon atoms of the NCS ligands, the nitrogen atoms of the  $\text{NH}_4^+$ , and oxygen atoms of water molecules had to be refined isotropically. Water molecules of crystallization and ammonium cations could not be distinguished in the structure and were modeled as follows: the two highest peaks O(100) and O(103) in the difference Fourier map, both on a mirror plane, were assigned to oxygen atoms from water of crystallization. Due to solvent disorder, these oxygen atoms had to be refined over three positions, namely O(100), O(101), and O(102), while the remaining oxygen atom was refined as disordered (50:50) over two positions, O(103) and O(104). At this moment, the two highest peaks in the difference Fourier map were assigned to ammonium cations N(100) (special position, mirror plane) and N(101) (general position). The N(101) position was refined as half-occupied in order to balance the overall charge of the cluster. Hydrogen atoms were not included in the refinement. In spite of the poor quality of the data due to the crystal twinning and solvent disorder reflected in the high  $R_{\text{int}}$  value, a valid model could be found for the structure that allows a bond distance discussion and the analysis of the supramolecular arrangement. The cluster ion  $[\text{W}_4\text{Se}_4(\text{NCS})_{12}]^{6-}$  is shown in Figure 1a.

Monoclinic  $[\text{W}_4\text{S}_4(\mu_2((\text{EtO})_2\text{PS}_2)_2)((\text{EtO})_2\text{PS}_2)_4]$  (**4a**) is isostructural with  $\beta$ - $[\text{M}_4\text{S}_4((\text{EtO})_2\text{PS}_2)_6]$  (M = Mo, W).<sup>15</sup> For the latter, the structure has been already reported, although only a partial structure solution in the space group  $P2/n$  is given in CSDB. The successful solution in this space group required a model in which the phosphorous atoms of the bridging  $(\text{EtO})_2\text{PS}_2$  ligand are disordered over two positions resulting in two nonplanar five-membered rings  $\text{W}_2\text{S}_2\text{P}$ . The rings have the conformation of an envelope with two W and two S fixing the plane, thus allowing the P atom to be out-of-plane from either side. This sort of disorder, which we attribute to the presence of different conformers in the structure, is accompanied by a disorder of the atomic positions of the EtO groups. All non-hydrogen atoms were refined anisotropically except for those of the EtO groups which were refined isotropically as rigid groups. Attempts to solve the structure in space groups with lower symmetry led to a large correlation of the atomic positions during refinement so that no ordered model could be found. The constraints applied to model the ligand disorder result in high but acceptable residual values with a goodness of fit parameter of 1.22.

$[\text{MoW}_3\text{S}_4(\mu_2((\text{EtO})_2\text{PS}_2)_3((\text{EtO})_2\text{PS}_2)_3)]$  (**4b**) is isostructural with triclinic  $\alpha$ - $[\text{W}_4\text{S}_4((\text{EtO})_2\text{PS}_2)_6]$  and  $\alpha$ - $[\text{Mo}_4\text{OS}_3((\text{EtO})_2\text{PS}_2)_6]$ .<sup>15</sup> The Mo and W atomic positions are disordered over the four metal sites. All non-hydrogen atoms except carbons were refined anisotropically. The positions of the ethyl

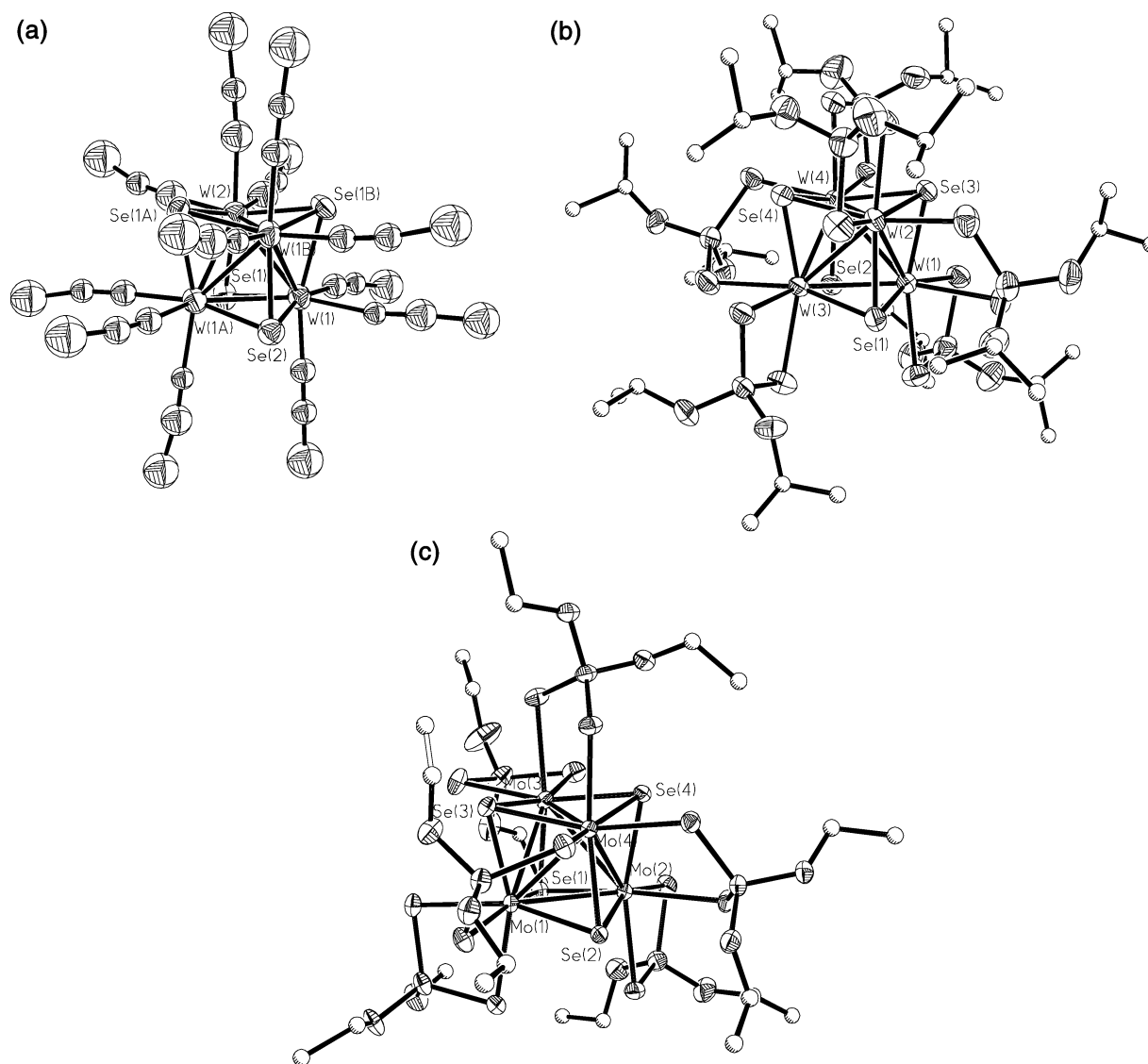
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**Table 8.** Selected Average Bond Distances (Å) for  $[M_4Q_4((RO)_2PS_2)_6]$  and  $[M_4Q_4(NCS)_{12}]^{6-}$ <sup>a</sup>

formula	M–M <sub>(br)</sub>			M–M			M–μ <sub>3</sub> -Q av	ref
	min	max	av	min	max	av		
α-[W <sub>4</sub> S <sub>4</sub> ((EtO) <sub>3</sub> PS <sub>2</sub> ) <sub>6</sub> ] <sup>b</sup>	2.742	2.749	2.746[3]	2.872	2.896	2.88[1]	2.35[2]	15
β-[W <sub>4</sub> S <sub>4</sub> ((EtO) <sub>2</sub> PS <sub>2</sub> ) <sub>6</sub> ]	2.762(1)	2.799(2)	2.78[3]	2.857(1)	2.866(1)	2.861[6]	2.37[1]	this work <b>4a</b>
β-[W <sub>4</sub> S <sub>4</sub> ((EtO) <sub>2</sub> PS <sub>2</sub> ) <sub>6</sub> ]	2.756(5)	2.773(4)	2.77[1]	2.834(3)	2.846(3)	2.840[8]	2.35[2]	15
α-[MoW <sub>3</sub> S <sub>4</sub> ((EtO) <sub>2</sub> PS <sub>2</sub> ) <sub>6</sub> ]	2.7542(9)	2.771(1)	2.762[9]	2.900(1)	2.925(1)	2.91[1]	2.36[2]	this work <b>4b</b>
β-[Mo <sub>4</sub> S <sub>4</sub> ((EtO) <sub>2</sub> PS <sub>2</sub> ) <sub>6</sub> ] <sup>c</sup>	2.746(4)	2.808(5)	2.77[4]	2.856(3)	2.865(3)	2.860[6]		15
β-[W <sub>4</sub> Se <sub>4</sub> ((i-PrO) <sub>2</sub> PS <sub>2</sub> ) <sub>6</sub> ]	2.7857(7)	2.8447(8)	2.81[4]	2.9060(8)	2.9186(7)	2.92[1]	2.49[1]	this work <b>5a</b>
α-[Mo <sub>4</sub> Se <sub>4</sub> ((EtO) <sub>2</sub> PS <sub>2</sub> ) <sub>6</sub> ]	2.7536(7)	2.7814(7)	2.76[1]	3.0020(8)	3.0247(6)	3.01[1]	2.47[2]	this work <b>4h</b>
(NH <sub>4</sub> ) <sub>6</sub> [Mo <sub>4</sub> S <sub>4</sub> (NCS) <sub>12</sub> ]·10H <sub>2</sub> O				2.791(1)	2.869(1)	2.83[5]	2.355[8]	19a
(NH <sub>4</sub> ) <sub>6</sub> [W <sub>4</sub> Se <sub>4</sub> (NCS) <sub>12</sub> ]·4H <sub>2</sub> O				2.818(3)	2.897(3)	2.85[5]	2.468[7]	this work <b>3c</b>
(Me <sub>2</sub> NH <sub>2</sub> ) <sub>6</sub> [W <sub>4</sub> S <sub>4</sub> (NCS) <sub>12</sub> ]·0.5H <sub>2</sub> O				2.835(1)	2.851(1)	2.84[1]	2.378[1]	4
(Me <sub>2</sub> NH <sub>2</sub> ) <sub>6</sub> [MoW <sub>3</sub> S <sub>4</sub> (NCS) <sub>12</sub> ]·0.5H <sub>2</sub> O				2.831(1)	2.849(1)	2.84[1]	2.35[1]	5

<sup>a</sup> Standard deviations for averaged values are given in square brackets. <sup>b</sup> Standard deviations for W–W bond distances are not reported. <sup>c</sup> Mo–S bond distances are not reported.



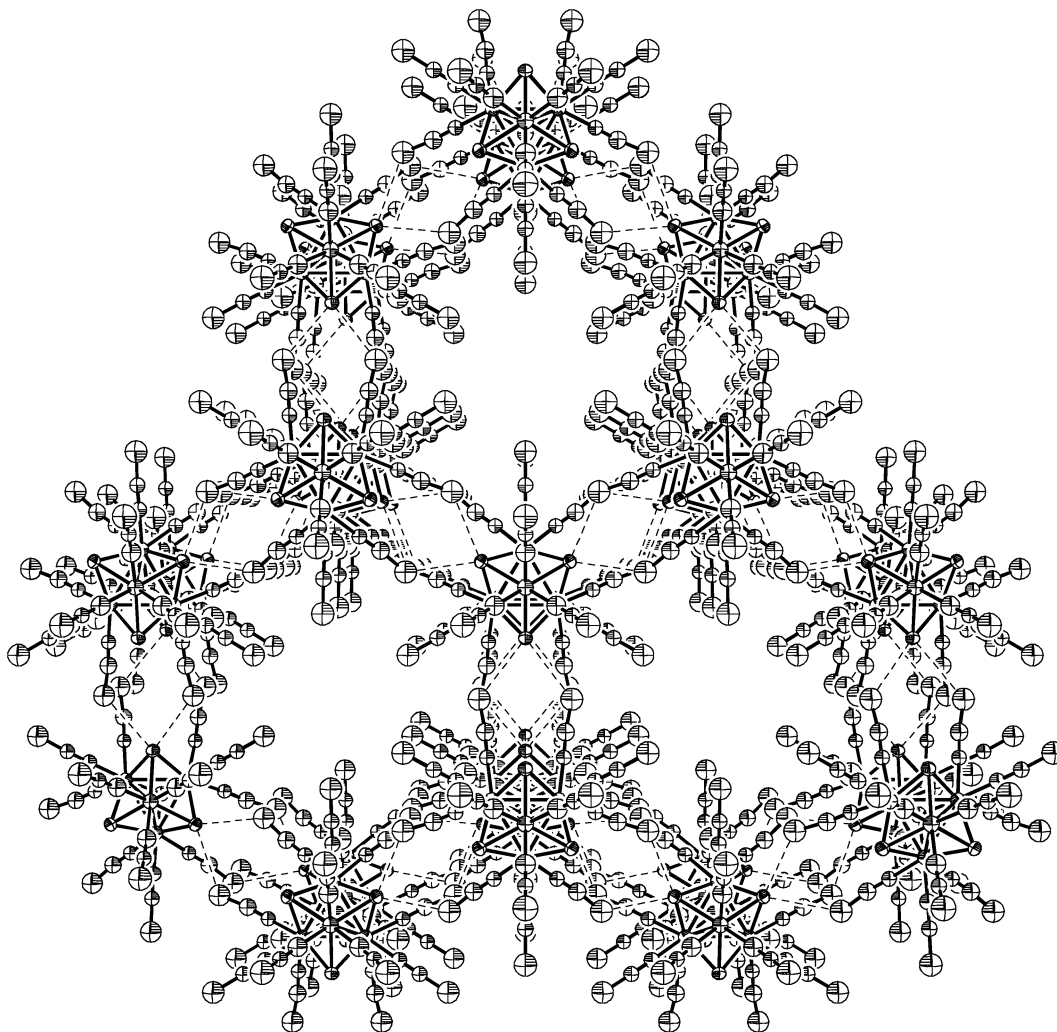
**Figure 1.** Only the atoms within the cuboidal core are labeled. (a) ORTEP representation (50% thermal ellipsoids) for anionic cuboidal cluster  $[W_4Se_4(NCS)_{12}]^{6-}$  (**3c**). Symmetry transformations used to generate equivalent atoms: A  $-y + 1, x - y + 1, z$ ; B  $-x + y, -x + 1, z$ . (b) ORTEP representation (50% thermal ellipsoids) for neutral cuboidal cluster  $[W_4Se_4(\mu_2-(i-PrO)_2PS_2)_2((i-PrO)_2PS_2)_4]$  (**5a**). Carbon atoms are drawn as spheres for clarity. (c) ORTEP representation (50% thermal ellipsoids) for neutral cuboidal cluster  $[Mo_4Se_4(\mu_2-(EtO)_2PS_2)_3((EtO)_2PS_2)_3]$  (**4h**). Only C23(A) is shown. Carbon atoms are drawn as spheres for clarity.

hydrogen atoms were generated geometrically and allowed to ride on their parent carbon atoms.

Crystallization of  $[Mo_4Se_4((EtO)_2PS_2)_6]$  (**4h**) gave a mixture of crystals in which both the monoclinic form (the

β-isomer, isostructural with  $[W_4S_4(\mu_2-(EtO)_2PS_2)_2((EtO)_2PS_2)_4]$  and the triclinic form (the α-isomer, isostructural with  $[MoW_3S_4(\mu_2-(EtO)_2PS_2)_3((EtO)_2PS_2)_3]$ ) were present. Only cell parameters were determined for the β-form ( $a =$





**Figure 2.** Supramolecular arrangement of the anionic cluster  $[W_4Se_4(NCS)_{12}]^{6-}$  showing the hexagonal packing and the channels formed along the  $c$ -axis.

12.855(1) Å,  $b = 17.491(1)$  Å,  $c = 13.542(1)$  Å,  $\beta = 97.48^\circ$ ,  $V = 3018.9$  Å<sup>3</sup>), but complete structure determination was done for the  $\alpha$ -form (Figure 1c). All non-hydrogen atoms were refined anisotropically. One terminal methyl group is disordered

(50:50) over two positions C23(a) and C23(b). The methyl-H atoms were refined as rigid groups, which were allowed to rotate but not to tip, with  $U_{iso}(H) = 1.5U_{eq}(C)$ . All other hydrogen atoms were allowed to ride on their parent atoms with  $U_{iso}(H) = 1.2U_{eq}(C)$ . The positions of hydrogen atoms of the ethylic groups were generated geometrically and allowed to ride on their parent carbon atoms.

Complex **5a** crystallizes in space group  $P\bar{1}$ . All its non-hydrogen atoms were refined isotropically. The positions of hydrogen atoms of the isopropyl groups were generated geometrically and allowed to ride on their parent carbon atoms. The molecule is shown in Figure 1b.

Table 8 summarizes relevant bond distances for these compounds and their known analogues. A comparison between the M–M bond distances in **4a** and **5a** shows a 0.04 Å increase on the bridged W–W bond distance and a 0.06 Å increase on the remaining W–W bond length on proceeding from the sulfide to the selenide. As expected, the dtp-bridged intermetallic distances are by 0.08, 0.15, 0.25,

and 0.11 Å shorter than the nonbridged ones in **4a**, **4b**, **4h**, and **5a**, respectively. This is in agreement with the known “pulling together” effect of bridging ligands ((RO)<sub>2</sub>PS<sub>2</sub>, R<sub>2</sub>NCS<sub>2</sub>, R<sub>2</sub>PS<sub>2</sub>, CH<sub>3</sub>COO) regularly encountered in their complexes with Mo<sub>4</sub>S<sub>4</sub>.<sup>13–15</sup> The ability of M<sub>4</sub>Q<sub>4</sub> clusters to undergo considerable distortions to adapt even to crystal packing requirements has been amply demonstrated for [M<sub>4</sub>Q<sub>4</sub>(CN)<sub>6</sub>]<sup>6–</sup>.<sup>3</sup> M–μ<sub>3</sub>-Q and M–L distances are more rigid, on the contrary.

The most significant structural feature associated with complex **3c** has to do with the formation of supramolecular structures through interaction of the inner capping cluster selenide ligands and the sulfur atoms of the thiocyanate ligands with Se⋯S contacts of 3.704 Å. Such interactions result in hexagonal channels of 6.68 Å in diameter filled with ammonium cations and water molecules as shown in Figure 2. The complex (NH<sub>4</sub>)<sub>6</sub>[Mo<sub>4</sub>S<sub>4</sub>(NCS)<sub>12</sub>]·10H<sub>2</sub>O crystallizes in the same space group and has close cell parameters, the only difference being the amount of water molecules in the channels.<sup>19a</sup>

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**Supporting Information Available:** X-ray crystallographic data for the structures reported in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>. The PMR spectra can be obtained from the author M.S. upon request.

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