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Selenium as a Structural Surrogate of Sulfur: Template-Assisted Assembly of Five Types of Tungsten-Iron-Sulfur/Selenium Clusters and the Structural Fate of Chalcogenide Reactants

Bo Zheng, Xu-Dong Chen, Shao-Liang Zheng, and R. H. Holm*

Department of Chemistry and Chemical Biology, Harvard University, Cambridge, Massachusetts 02138, United States

Abstract

Syntheses of five types of tungsten-iron-sulfur/selenium clusters—incomplete cubanes, single cubanes, edge-bridged double cubanes (EBDCs), P^N-type clusters, and double-cuboidal clusters—have been devised based on the concept of template-assisted assembly. The template reactant is six-coordinate [(Tp*)W^{VI}S₃]^{1−}, which in the assembly systems organizes Fe^{II,III} and sulfide/selenide into cuboidal [(Tp*)WFe₂S₃] or cubane [(Tp*)WFe₃S₃Q] units. With appropriate terminal iron ligation, these units are capable of independent existence or may be transformed into higher nuclearity species. Selenide is used as a surrogate for sulfide in cluster assembly in order to determine by X-ray structures the position occupied by an external chalcogenide nucleophile or an internal chalcogenide atom in product clusters. Specific incorporation of selenide is demonstrated by formation of [WFe₃S₃Se]^{2+,3+} cubane cores. Reductive dimerization of the cubane leads to the EBDC core [W₂Fe₆S₆Se₂]²⁺ containing μ_4 -Se sites. Reaction of these species with HSe[−] affords the P^N-type cores [W₂Fe₆S₆Se₃]¹⁺ in which selenide occupies μ_6 -Se and μ_2 -Se sites. Reaction of [(Tp*)WS₃]^{1−}, FeCl₂, and Na₂Se results in the double cuboidal [W₂Fe₄S₆Se₃]^{2+,0} core with μ_2 -Se and μ_4 -Se bridges. It is highly probable that in analogous sulfide-only assembly systems, external and internal sulfide reactants occupy corresponding positions in cluster products. The results further demonstrate the viability of template-assisted cluster synthesis inasmuch as the reduced (Tp*)WS₃ unit is present in all clusters. Structures, zero-field Mössbauer data, and redox potentials are presented for all cluster types. (Tp* = tris(pyrazolyl)hydroborate(1−))

INTRODUCTION

Metal cluster self-assembly proceeds by self-organizing reactions between mononuclear precursors and ligand reactants in the initial step.¹ Recently, we have demonstrated a new method of cluster assembly leading to weak-field heterometal cubane-type core units [MFe₃S₃Q]^{2+/3+} (M = Mo, W; Q = S, Se). Compared to earlier assembly procedures,^{1–3} this method has two distinguishing features. (i) The system contains a template reactant of the general type [L₃M^{VI}S₃]^{0,1−} in which L₃ is a facial tridentate ligand that blocks three coordination sites and provides a discrete coordination unit. Reduction to the M^{III,IV} level in the assembly reaction system facilitates binding of three Fe^{II,III} atoms in cluster product formation. (ii) Because the template reactant supplies three sulfur atoms, a fourth chalcogenide atom as a separate reactant can be specifically incorporated in cubane clusters as μ_3 -Q. The first template ligand employed for this purpose is the cyclic triamine Bu^t₃tach⁴

Corresponding Author: holm@chemistry.harvard.edu.

Supporting Information. X-ray crystallographic files in CIF form for all compounds in Table S1, the ¹H NMR spectrum of **9**, representative Mössbauer spectra, and isomers of edge-bridged double cubanes. This material is available free of charge via the Internet at <http://pubs.acs.org>.

which supports formation of the cubane clusters $[(\text{Bu}^t\text{tach})\text{MFe}_3\text{S}_3\text{QL}_3]^{0/1-}$ ($\text{L} = \text{Cl}^-$, RS^-).⁵

Single cubanes are precursors to higher nuclearity clusters that are participants in attempts to achieve synthetic representations of large biological clusters such as the P^{N} and FeMo -cofactor clusters of nitrogenase^{6–10} and the C-cluster of nickel-containing carbon monoxide dehydrogenase.^{11–13} Clusters elaborated from single cubanes are primarily edge-bridged double cubanes $[\text{M}_2\text{Fe}_6(\mu_3\text{-S})_6(\mu_4\text{-S})_2]$ and P^{N} -type clusters $[\text{M}_2\text{Fe}_6(\mu_2\text{-S})_2(\mu_3\text{-S})_6(\mu_6\text{-S})]$ ($\text{M} = \text{Mo}$,^{14–18} V ^{19,20}) with the indicated bridge connectivities (see below).

To examine the scope of template-based assembly, we have utilized $[(\text{Tp}^*)\text{WS}_3]^{1-}$, readily obtained from $[(\text{Tp}^*)\text{W}(\text{CO})_3]^{1-}$ and elemental sulfur.^{21a} Earlier we showed that this reactant will assemble certain $[\text{WFe}_3\text{S}_4]$ clusters.²² The complex has also been shown to form dinuclear complexes with other metal species.²¹ This report provides a much more extensive examination of reactivity, including conversion of single cubanes to higher nuclearity clusters, among which is a new type not previously obtained in this way. Additionally, we utilize, as a surrogate marker for sulfide, selenide as an added reactant in cluster synthesis or present in the core of a precursor cluster. The fate of selenide in the product cluster implies a corresponding role for sulfide. As will be seen, this approach supports the template interpretation of single cubane assembly systems and provides additional insight into cluster formation.

EXPERIMENTAL SECTION

Preparation of Compounds

All reactions and manipulations were performed under a dinitrogen atmosphere. Volume reduction and drying steps were carried out in vacuo; filtrations were through Celite. Commercial grade chemicals were used without further purification. Unless otherwise indicated, FeCl_2 , NaSEt , and Na_2Se were used as suspensions in the indicated solvents. THF and diethyl ether were purified by an Innovative Technology or MBraun solvent purification system. DMF was dried over molecular sieves for 24 h. Compounds were identified by combinations of elemental analyses (Midwest Microlab, LLC, Indianapolis, IN 46250), ^1H NMR spectra, and in nearly all cases, X-ray structure determinations. Chemical shifts of counterions are not included in the ^1H NMR data below. In some cases, not all proton signals were located because of paramagnetic broadening or overlap with cation or solvent signals; certain very broad (vbr) signals that are not easily assigned are noted. Analytical results indicate that some compounds crystallized as solvates; solvate components were detected in ^1H NMR spectra. Because of the tendency of some compounds to desolvate, yields are calculated for unsolvated compounds.

The compounds $(\text{Et}_4\text{N})[(\text{Tp}^*)\text{WFe}_3\text{S}_4\text{Cl}_3]$ (δ –1.53 (3), 4.65 (1), 17.7 (br, 3)) and $(\text{Et}_4\text{N})[(\text{Tp}^*)\text{WFe}_3\text{S}_4(\text{SEt})_3]$ (δ –0.53 (9), 4.91 (3), 5.36 (9), 16.7 (br, 9), 47.4 (br, 6) were prepared as described.²²

A. Incomplete Cubanes

$(\text{Et}_4\text{N})[(\text{Tp}^*)\text{WFeS}_3\text{Cl}_2]$: To a solution of 1.00 g (1.41 mmol) of $(\text{Et}_4\text{N})[(\text{Tp}^*)\text{WS}_3]^{21}$ in 65 mL of acetonitrile was added a slurry of 179 mg (1.41 mmol) of FeCl_2 in 5 mL of acetonitrile. The dark red reaction mixture was stirred for 48 h and filtered. The filtrate was reduced to dryness and the residue was recrystallized from acetonitrile/ether to give the product as 990 mg (84%) of dark red crystals. ^1H NMR (CD_3CN): δ 0.29 (br, 3), 3.79 (br, 3). *Anal.* Calcd. for $\text{C}_{23}\text{H}_{42}\text{BCl}_2\text{FeN}_7\text{S}_3\text{W}\cdot\text{CH}_3\text{CN}$: C, 34.31; H, 5.18; N, 12.80. Found: C, 34.43; H, 5.00; N, 12.72.

(Et₄N)[(Tp*)WFe₂S₃Cl₂(SEt)]: To a solution of 80 mg (0.11 mmol) of (Et₄N)[(Tp*)WS₃] in 3 mL of acetonitrile was added a solution of 28 mg (0.23 mmol) of FeCl₂ in 0.5 mL of methanol. After 1 min, a solution of 19 mg (0.23 mmol) of NaSEt in 0.5 mL of methanol was added. The mixture was stirred for 2 h and filtered. Slow diffusion of ether into the filtrate resulted in formation of a solid, which was washed with ether to yield the product as 67 mg (64%) of black platelike crystals. ¹H NMR: δ -30.5 (br, ~3), -11.57 (3), -7.76 (6), -1.93 (2), 0.10 (1), 1.17 (2), 5.09 (1). Additional signals were observed at δ 62 (vbr) and 106 (vbr). *Anal.* Calcd. for C₂₅H₄₇BCl₂Fe₂N₇S₄W: C, 31.57; H, 4.98; N, 10.31. Found: C, 31.74; H, 5.03; N, 10.07. This procedure affords a purer product than that reported earlier.²²

(Et₄N)[(Tp*)WFe₂S₃(SEt)₃]: To a solution of 100 mg (0.10 mmol) of (Et₄N)[WFe₂S₃Cl₂(SEt)] in 4 mL of acetonitrile was added 18 mg (0.21 mmol) of NaSEt in 2 mL of acetonitrile. The mixture was stirred for 2 h, filtered, and ether was diffused into the filtrate. The product was obtained as 49 mg (49%) of black crystals. ¹H NMR (CD₃CN, anion): δ -32.1 (br, 3), -8.75 (3), -7.18 (6), -2.95 (2), 0.27 (1), 3.49 (1), 5.17 (br, 2), 29.0 (br, ~6). Additional signals were observed at δ 58 and 100.

B. Single Cubanes

(Et₄N)[(Tp*)WFe₃S₃SeCl₃]

Method 1: To a solution of 900 mg (1.27 mmol) of (Et₄N)[(Tp*)WS₃] in 150 mL of acetonitrile was added a slurry of 518 mg (4.07 mmol) of FeCl₂ in 30 mL of THF. After 3 min, a suspension of 322 mg (2.54 mmol) of Na₂Se in 30 mL of THF was introduced. The black reaction mixture was stirred for 30 h and filtered. The filtrate was reduced to dryness. The residue was recrystallized from acetonitrile/ether to give the product as 875 mg (64%) of black needlelike crystals. ¹H NMR (CD₃CN, anion): δ -1.53 (3), 4.58 (1), 17.4 (br, 3). *Anal.* Calcd. for C₂₃H₄₂BCl₃Fe₃N₇S₃SeW: C, 26.05; H, 3.99; N, 9.25. Found: C, 26.37; H, 4.06; N, 9.16.

Method 2: To a solution of 100 mg (0.12 mmol) of (Et₄N)[(Tp*)WFe₃S₃Cl₂] in 40 mL of acetonitrile was added 49 mg (0.38 mmol) of FeCl₂ in 20 mL of THF. After 2 min, 32 mg (0.24 mmol) of Na₂Se in 20 mL of THF was introduced. The black reaction mixture was stirred for 36 h and filtered, and the dark filtrate was reduced to dryness. The black residue was recrystallized from acetonitrile/ether to give the product as 97 mg (77%) of black needle-like crystals whose ¹H NMR spectrum is identical to the product of method 1.

(Et₄N)[(Tp*)WFe₃S₃Se(SEt)₃]: To a solution of 64 mg (0.06 mmol) of (Et₄N)[(Tp*)WFe₃S₃SeCl₃] in 1 mL of acetonitrile was added 18 mg (0.21 mmol) of NaSEt in 2.5 mL of acetonitrile. The reaction mixture was stirred for 2 h and filtered. Diffusion of ether into the filtrate caused separation of a solid, which was washed with ether to afford the product as 42 mg (61%) of black crystals. ¹H NMR (CD₃CN, anion): δ -0.64 (9), 2.77 (3), 4.81 (3), 5.47 (6), 15.34 (2), 16.7 (br, 9), 48.5 (br, 4).

[(Tp*)WFe₃S₄(PEt₃)₃](BPh₄): To a solution of 608 mg (0.60 mmol) of (Et₄N)[(Tp*)WFe₃S₄Cl₃] in 40 mL of acetonitrile was added 352 mg (2.98 mmol) of PEt₃. After 1 min, a solution of 1.19 g (3.48 mmol) of NaBPh₄ in 6 mL of acetonitrile was introduced. The black solution was stirred for 24 h and 130 mL of ether was added. The mixture was stirred for 5 h, filtered, and the filtrate was reduced to dryness. The residue was extracted with dichloromethane and benzene. Solvent removal followed by crystallization of the residue from dichloromethane/ether afforded the product as 345 mg (38%) of black crystals. ¹H NMR (CD₃CN, anion): δ -2.85 (9), 3.84 (27), 7.52 (3), 11.63 (18), 26.8 (br, 9). *Anal.* Calcd. for C₅₇H₈₇B₂Fe₃N₆P₃S₄W·CH₂Cl₂: C, 45.37; H, 5.84; N, 5.47. Found: C, 45.89; H, 5.84; N, 5.79.

[(Tp*)WFe₃S₃Se(PEt₃)₃](BPh₄): To a stirred solution of 837 mg (0.79 mmol) of (Et₄N) [(Tp*)WFe₃S₃SeCl₃] in 50 mL of acetonitrile was added 465 mg (3.94 mmol) of PEt₃. After 1 min, a solution of 1.57 g (4.60 mmol) of NaBPh₄ in 8 mL of acetonitrile was introduced. The black solution was stirred for 24 h and 170 mL of ether was added. The mixture was stirred for 5 h and filtered. The filtrate was reduced to dryness, and the residue was extracted with dichloromethane and benzene. Solvent removal followed by crystallization of the residue from acetonitrile/ether gave the product as 550 mg (47%) of black crystals. ¹H NMR (CD₃CN): δ -3.37 (9), 5.41 (27), 6.36 (3), 11.76 (18), 24.5 (br, 9). *Anal.* Calcd. for C₅₇H₈₇B₂Fe₃N₆P₃S₃SeW: C, 45.72; H, 5.86; N, 5.61. Found: C, 45.81; H, 5.81; N, 5.43.

C. Edge-Bridged Double Cubanes

[(Tp*)₂W₂Fe₆S₈(PEt₃)₄]: A solution of 317 mg (0.22 mmol) of [(Tp*)WFe₃S₄(PEt₃)₃](BPh₄) in 1.5 mL of acetonitrile was added to a solution of 67 mg (0.26 mmol) of (Bu₄N)(BH₄) in 0.3 mL of acetonitrile. The reaction mixture was allowed to stand for 48 h. The solid that separated was collected and washed with acetonitrile to afford the product as 156 mg (70%) of a sparingly soluble black crystalline solid. This method leads to much higher yields than that reported earlier whose product has been shown to be an edge-bridged double cubane by a structure determination.²²

[(Tp*)₂W₂Fe₆S₆Se₂(PEt₃)₄]: A solution of 300 mg (0.20 mmol) of [(Tp*)WFe₃S₃Se(PEt₃)₃](BPh₄) in 1 mL of acetonitrile was added to a solution of 62 mg (0.24 mmol) of

(Bu₄N)(BH₄) in 0.3 mL of acetonitrile. The preceding method gave the product as 140 mg (65%) of a sparingly soluble black crystalline solid suitable for X-ray crystallography.

D. P^N-Type Clusters

(Et₄N)₃[(Tp*)₂W₂Fe₆S₇Se₂(SH)₂]: To a suspension of 50 mg (0.024 mmol) of [(Tp*)₂W₂Fe₆S₆Se₂(PEt₃)₄] in 20 mL of acetonitrile was added 13 mg (0.083 mmol) of (Et₄N)(SH). The black solution was stirred for 48 h and filtered. Slow diffusion of ether into the filtrate resulted in the separation of a crystalline solid, which was recrystallized from acetonitrile/ether to give the product as 32 mg (64%) of black blocklike crystals. ¹H NMR (CD₃CN): δ -1.22 (3), -0.18 (3), -0.08 (3), 0.22 (3), 1.89 (3), 4.47 (1), 4.68 (1), 5.85 (br, 1), 7.07 (1), 28.3 (br, 3). *Anal.* Calcd. for C₅₄H₁₀₆B₂Fe₆N₁₅S₉Se₂W₂·2CH₃CN·(C₂H₅)₂O: C, 32.48; H, 5.36; N, 10.39. Found: C, 32.71; H, 5.25; N, 10.30.

(Et₄N)₃[(Tp*)₂W₂Fe₆S₆Se₃(SeH)₂]: [(Tp*)₂W₂Fe₆S₆Se₂(PEt₃)₄] (30 mg, 0.014 mmol) was suspended in 20 mL of acetonitrile, and a solution of 13 mg (0.062 mmol) of (Et₄N)(SeH) was added, causing the solid to dissolve over 8 h. The dark brown reaction mixture was stirred for 30 h and filtered. Slow diffusion of ether into the filtrate resulted in the separation of crystalline solid, which was recrystallized from acetonitrile/ether to afford the product as 19 mg (59%) of black blocklike crystals. *Anal.* Calcd. for C₅₄H₁₀₆B₂Fe₆N₁₅S₆Se₅W₂·CH₃CN·(C₂H₅)₂O: C, 30.12; H, 5.01; N, 9.37. Found: C, 29.88; H, 4.86; N, 9.09. ¹H NMR (CD₃CN): δ -0.10 (6), 0.74 (6), 1.77 (3), 4.76 (2), 5.8 (br), 6.66 (1), 23.4 (3).

(Et₄N)₃[(Tp*)₂W₂Fe₆S₆Se₂(SMe)₃]: A mixture of 4.0 mg (0.060 mmol) of NaSMe and 9.0 mg (0.060 mmol) of Et₄NCl in 2 mL of acetonitrile was stirred for 24 h, and was transferred into a suspension of 32 mg (0.015 mmol) of [(Tp*)₂W₂Fe₆S₆Se₂(PEt₃)₄] in 1 mL of acetonitrile. The reaction mixture was stirred for 24 h and filtered. Diffusion of ether into the filtrate led to give the product as 17 mg (51%) of black blocklike crystals. ¹H NMR (CD₃CN): δ 0.45 (6), 0.52 (6), 0.73 (6), 4.73 (2), 4.89 (2), 5.29 (2), 34.6–35.5 (vbr, ~9).

Anal. Calcd. for $C_{57}H_{113}B_2Fe_6N_{15}S_9Se_2W_2 \cdot CH_3CN$: C, 31.91; H, 5.27; N, 10.09. Found: C, 32.09; H, 5.23; N, 10.19.

E. Double Cuboidal Clusters

(Et₄N)[(Tp*)₂W₂Fe₄S₉]: To a solution of 320 mg (2.0 mmol) of (Et₄N)(SH) in 10 mL of acetonitrile was added a solution of 250 mg (2.0 mmol) of FeCl₂ in methanol, producing a black precipitate. This material was added to a solution of 710 mg (1.0 mmol) of (Et₄N)[(Tp*)WS₃] in 50 mL of acetonitrile. To the reaction mixture was added 1.6 g (16 mmol) of neat Et₃N under vigorous stirring, which was continued for 24 h. The black precipitate was washed with ether, dried, and recrystallized from DMF/ether to give 420 mg (52%) of black crystalline product. ¹H NMR (Me₂SO-*d*₆): δ 0.33 (3), 2.01 (3), 2.10 (6), 4.51 (6), 5.50 (2), 5.85 (1), 6.71 (1). *Anal.* Calcd. for $C_{38}H_{64}B_2Fe_4N_{13}S_9W_2 \cdot 2C_3H_7NO$ (DMF solvate): C, 30.19; H, 4.49; N, 12.00. Found: C, 30.12; H, 4.42; N, 11.83.

(Et₄N)₂[(Tp*)₂W₂Fe₄S₉]: (Et₄N)[(Tp*)₂W₂Fe₄S₉] (400 mg, 0.25 mmol) and 73 mg (0.50 mmol) of (Et₄N)(BH₄) were stirred in 50 mL of acetonitrile for 12 h. The reaction mixture was filtered, the filtrate was reduced to 30 mL, and was layered over 150 mL of THF. A black crystalline material was collected, washed with THF and ether, and dried, giving 338 mg (78%) of product. Crystalline product was obtained by ether diffusion into a DMF solution. ¹H NMR (CD₃CN): δ 1.2 (vbr, sh), 2.14 (3), 2.16 (6), 3.2 (vbr), 5.08 (vbr), 5.33 (2), 6.26 (1). *Anal.* Calcd. for $C_{46}H_{84}B_2Fe_4N_{14}S_9W_2 \cdot 2.5C_3H_7NO$ (DMF solvate): C, 33.52; H, 5.34; N, 12.05. Found: C, 33.92; H, 5.41; N, 12.37.

[(Tp*)₂W₂Fe₄S₆Se₃]: To a solution of 900 mg (1.27 mmol) of (Et₄N)[(Tp*)WS₃] in 150 mL of acetonitrile was added 518 mg (4.07 mmol) of FeCl₂ in 30 mL of THF. After 3 min, 322 mg (2.54 mmol) of Na₂Se in 30 mL of THF was introduced. The black reaction mixture was stirred for 30 h, and a dark brown solid was collected. This material was recrystallized from DMF/ether to give the product as 329 mg (32%) of black blocklike crystals. ¹H NMR (Me₂SO-*d*₆): δ -0.46 (3), 1.68 (3), 1.85 (6), 5.34 (2), 5.90 (vbr), 6.60 (1). *Anal.* Calcd. for $C_{30}H_{44}B_2Fe_4N_{12}S_6Se_3W_2C_3H_7NO \cdot (C_2H_5)_2O$: C, 25.22; H, 3.49; N, 10.33. Found: C, 25.05; H, 3.64; N, 10.69.

(Et₄N)₂[(Tp*)₂W₂Fe₄S₆Se₃]: To a solution of 100 mg (0.12 mmol) of (Et₄N)[(Tp*)WFeS₃Cl₂] in 5 mL of acetonitrile was added a slurry of 15 mg (0.12 mmol) of FeCl₂ in 5 mL of THF. After 2 min, a suspension of 30 mg (0.24 mmol) of Na₂Se in 5 mL of THF was introduced. The black reaction mixture was stirred for 1 d. A dark brown precipitate was collected and crystallized from DMF/ether to afford the product as 48 mg (43%) of black blocklike crystals. ¹H NMR (Me₂SO-*d*₆): δ 0.85 (vbr), 5.02 (br), 5.34 (2), 6.35 (1).

In the sections that follow, clusters are designated numerically according to Chart 1. For simplicity in the X-ray section, compounds are referred to by their cluster number.

X-ray Structure Determinations

Structures of the 14 compounds in Table S1 were determined. Diffraction-quality crystals of **2–4**, **5b**, and **7b** were obtained by ether diffusion into acetonitrile solutions. Crystalline **6b** was acquired by ether diffusion into a THF solution, and crystals of **9–15** were grown by ether diffusion into DMF solutions. Data were collected on a Bruker APEX II CCD diffractometer equipped with an Oxford Cryostream 700 series low-temperature apparatus operating at 100 K. Raw data were integrated and corrected for Lorentz and polarization effects using the Bruker APEX II program suite. Absorption corrections were applied using SADABS. Space groups were assigned by analysis of symmetry and systematic absences (determined by XPREP) and were further checked by PLATON. Structures were solved by

direct methods and refined against all data in the 2θ ranges by full-matrix least-squares on F^2 with the SHELXL program suite using the OLEX 2 interface. Hydrogen atoms at idealized positions were included in the final refinements. The OLEX 2 interface was also used for structure visualization and drawing ORTEP figures.

For selenium-containing compounds, all non-hydrogen atoms were located in difference Fourier maps. Careful refinement results clearly show the varying S/Se populations at μ_2 sites in **9** and **11**, indicating that other sites assigned to selenium in these and other clusters are fully occupied. Refined bond lengths at these sites further support selenium occupation. Constraints of both the positions and displacement parameters (EXYZ and EADP instructions of SHELXL-97) as well as constraints of the S–CH₃ bond length in **11** (SADI instructions of SHELXL-97) have been applied to the disorder refinements. The occupancy ratios of both μ_2 -S/Se sites of **9** derived from the refinements are 0.481(5)/0.519(5) and 0.567(4)/0.433(4). In the final refinement a 1:1 ratio was used. A similar procedure has been applied to both μ_2 -S/Se sites of **11**.

Other Physical Measurements

¹H NMR spectra were obtained with a Varian M400 spectrometer. ⁵⁷Fe Mössbauer spectra were measured with a constant acceleration spectrometer. Data were analyzed with Igor Pro 6 software (Wavemetrics, Portland, OR); isomer shifts are referenced to iron metal at room temperature. Cyclic voltammetry measurements were made with a BioAnalytical Systems Epsilon potentiostat/galvanostat in DMF or acetonitrile solutions at 100 mV/s using a glassy carbon working electrode, 0.1 M (Bu₄N)(PF₆) supporting electrolyte, and an SCE reference electrode.

RESULTS AND DISCUSSION

This research has two primary goals: (i) exploration of the concept of template-assisted cluster assembly, and (ii) determination of the structural fate of sulfide or selenide, introduced as free reactants (external) or bound in cluster precursors (internal), in cluster formation. In (i) we employ as the template [(Tp*)W^{VI}S₃]¹⁻, the entirety of which in a reduced form is intended as a component of the final product. Summarized in Figure 1 is the only previous attempt to address (ii). Cluster conversion reaction 1²³ proceeds by reaction of hydrosulfide with an edge-bridged double cubane to yield a P^N-type cluster (Q = S) whose most distinctive feature is a μ_6 -S atom with one large external angle Fe– μ_6 -S–Fe present in a core topologically equivalent to that of the P^N cluster of nitrogenase (see below).^{15,24,25} The structural fate of the attacking nucleophile was decided by the use of hydroselenide, which affords a product (Q = Se) containing selenide in a doubly bridging position only as determined by an X-ray structure.¹⁷

In the present context, selenide as a surrogate for sulfide is predicated on the small differences in ionic radii $r(\text{Se}^{2-}) - r(\text{S}^{2-}) = 1.91 - 1.84 = 0.07 \text{ \AA}$ and covalent radii $r(\text{Se}) - r(\text{S}) = 1.17 - 1.04 = 0.13 \text{ \AA}$,²⁶ and slightly smaller bond angles at selenium always found in comparative Q = S/Se molecules in which only the chalcogenide atom is varied. Also, replacement of sulfide by selenide in general produces only a small positive shift (often 50 mV) in redox potentials. These factors contribute to the existence of a sizable body of analogous stable clusters with selenide or sulfide core atoms,²⁷ and clusters with sulfur and selenium in the same cubane core $[\text{Fe}_4\text{S}_{4-n}\text{Se}_n]^{2+,1+}$ ($n = 1-3$).²⁸ Prominent examples of the latter type are found with the cubane pair $[\text{Fe}_4\text{Q}_4(\text{SPh})_4]^{2-}$ (Q = S, Se)²⁹ whose members are isostructural but not exactly isometric. Further, iron-selenide clusters comparable to native

clusters have been reconstituted in ferredoxin-type proteins.³⁰ As will be seen, S/Se substitution is possible in the core units of five clusters of different structures.

Cluster Synthesis and Structure

The syntheses of five types of W-Fe-S/Se clusters are described in the sections that follow. Feasible reaction stoichiometries are indicated; non-cluster reaction products were not identified. Cluster yields refer to isolated Et_4N^+ salts. Synthetic schemes are set out in Figures 2, 5, and 8 and X-ray structures in Figures 3, 4, 6, 7, and 10. Detailed structural descriptions of clusters are not required for the purpose of this work; metric data are available elsewhere.³¹ Mössbauer spectra usually consist of a single quadrupole doublet or less frequently two overlapping doublets. Oxidation states (*s*) are interpreted from ^{57}Fe isomer shifts (δ) with use of the empirical relationship $\delta = 1.43 - 0.40s$ best applied at and above 77 K³² to tetrahedral FeS_4 sites with anionic ligands. Values of 0.63 mm/s and 0.23 mm/s are estimated for Fe^{2+} and Fe^{3+} , respectively. This relationship can also be applied, although less accurately, to sites FeS_3L with one non-sulfur ligand. At constant oxidation state, isomer shifts generally tend to decrease in the order $\text{Cl}^- > \text{RS}^- > \text{R}_3\text{P}$.³³ Mössbauer parameters from zero-field spectra are collected in Table 1. Iron oxidation states are written as Fe^{2+} , Fe^{3+} but, as for nearly all Fe-S and M-Fe-S weak field clusters, electronic structures are actually delocalized. Tungsten oxidation states are obtained by difference and are confined to $\text{W}^{3+,4+}$ because of limits on iron oxidation states and experimental cluster charges. Oxidation state formalisms are useful in following redox changes in synthetic reactions. Stated values are sensibly consistent with isomer shift data but cannot be considered as demonstrated. Also collected in Table 1 are redox potentials for chemically reversible processes ($i_{\text{pc}}/i_{\text{pa}} \approx 1$).

(1) Incomplete Cubane Clusters—The syntheses of clusters of all types originate with the mononuclear W^{VI} template complex **1**. Relatively simple products are derivable from it with one or two equiv of FeCl_2 by reactions 2–4 in Figure 2; product structures are shown in Figure 3. Reaction 2 is not a redox process. One equiv of FeCl_2 affords binuclear **2** (84%) with six-coordinate W^{VI} and tetrahedral Fe^{II} . The η^2 binding mode of the WS_3 group has been previously observed with the heavier Group 8–10 metals.²¹ The dimensions of the WS_2Fe rhomb are nearly the same as in related molecules such as $[\text{S}_2\text{WS}_2\text{FeX}_2]^{2-}$ (*X* = anion)^{34–36} and $[(\text{Me}_2\text{PCH}_2\text{CH}_2\text{S})\text{W}(\text{S})\text{S}_2\text{FeCl}_2]^{1-}$.³⁷ The product is best considered as $\text{W}^{6+}\text{Fe}^{2+}$ with the isomer shift of 0.52 mm/s, relative to an FeS_4 site, apparently decreased by some extent of electron delocalization to the fully oxidized tungsten site. Reaction with two equiv each of FeCl_2 and NaSEt produces trinuclear **3**³⁸ (61%) which undergoes ligand substitution reaction 4 to yield isostructural **4** (49%) whose isomer shift of 0.45 mm/s suggests the description $\text{W}^{4+}\text{Fe}^{3+}\text{Fe}^{2+}$. Consequently, Fe^{2+} and EtS^- are reductants of W^{6+} in reaction 3. Cluster **4** sustains a three-membered electron transfer series; if the charge distribution is correct, the first reduction is likely to be iron-based and the second reduction at tungsten. The incomplete cubane description of **3** and **4** is evident from a vacancy at the site where an iron atom might be bound and by inclusion of a bridging ethanethiolate at a sulfide site. These clusters are apparently trapped intermediates in cluster assembly. Thiolate bridge formation positions an ethyl group in front of the iron site (Fe-S-C angles of 106 and 109 in **4**), a possible impediment to completion of the cubane core. As will be seen, the WFe_2S_3 portions of **3** and **4** are present in higher nuclearity clusters.

(2) Single Cubane Clusters—Synthetic methods are summarized in Figure 2. Cluster **5a** has previously been prepared in the assembly system $1/3\text{FeCl}_2/3\text{NaSEt}$ utilizing a four-electron reduction of **1** and sulfur; the cubane **6a** was prepared by ligand substitution.²² Cluster **5b** (64%) was obtained by related reaction 5, but with use of selenide as a ligand and probable reductant. It was also prepared in the system $2/3\text{FeCl}_2/2\text{Na}_2\text{Se}$ in 77% yield.

Reaction 6 yields the thiolate cluster **6b** (61%). Isomer shifts of the pairs **5ab** and **6ab** follow the order $\text{Cl}^- > \text{EtS}^-$ (Table 1) as do $[(\text{Tp})\text{MoFe}_3\text{S}_4\text{L}_3]^{1-}$ ($\text{L} = \text{Cl}^-$ (0.49 mm/s), EtS^- (0.39 mm/s))³⁹ with very similar shifts. For **6ab**, the shifts of 0.42 and 0.44 mm/s are intermediate between estimates of 0.36 mm/s ($\text{W}^{3+}\text{Fe}^{2+}\text{Fe}^{3+}_2$) and 0.50 mm/s ($\text{W}^{4+}\text{Fe}^{2+}_2\text{Fe}^{3+}$). We favor the former description for **5ab** and **6ab** based on our analysis of $[(\text{Tp})\text{MoFe}_3\text{S}_4\text{Cl}_3]^{1-}$ and the likelihood that core charge distribution with chloride and thiolate terminal ligands will not change appreciably. In this case, reduction steps (Table 1) would be iron-based and Fe^{II} and selenide are reductants of W^{VI} in reaction 5. Clusters **7a** (38%) and **7b** (47%) are accessible by chloride substitution of **5a** and **5b**, respectively, with excess phosphine. One-electron cluster reduction by phosphine to the $[\text{MoFe}_3\text{S}_4]^{2+}$ oxidation level is preceded.^{15,40} Mössbauer spectra consist of two overlapping quadrupole doublets. Mean isomer shifts are suggestive of the description $\text{W}^{3+}\text{Fe}^{2+}_2\text{Fe}^{3+}$. An analogous description has been deduced for $[\text{MoFe}_3\text{S}_4]^{2+}$ clusters.^{40,41}

The structures of **5b** and **6b** (Figure 4) and **7b** (Figure 6) demonstrate the specific incorporation of selenide in the cluster cores whose structures respond to the incorporation of that atom. In selenide cluster **6b**, for example, the mean Fe-Se bond length and Fe-Se-Fe bond angle are 2.37(2) Å and 68.8° respectively, whereas in **6a**²² the corresponding values at the same site are 2.25(3) Å and 72.6°. As seen in Table 2, the same trend in bond lengths and angles holds for corresponding S/Se sites in all other clusters. Note also that the recent isolation of the cluster $[\text{Fe}_4\text{S}_3(\text{NBu}^t)\text{Cl}_3]^{2-}$ (Fe-N 1.95 Å)⁴² is a further indication of the structural flexibility of weak-field cubane clusters to accommodate bridging atoms of very different radii.

(3) Edge-Bridged Double Cubanes—Borohydride reduction of **7a** and **7b** in reaction 7 affords the sparingly soluble EBDCs **8a** ($\text{Q} = \text{S}$, 70%) and **8b** ($\text{Q} = \text{Se}$, 65%,). The **7b** → **8b** reaction is illustrated in Figure 5 and structures of these clusters are presented in Figure 6. An analogous reaction series leading to $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_8(\text{PET}_3)_4]$ has been described.^{15–17} Clusters **8a** and **8b** contain $[\text{W}_2\text{Fe}_6\text{S}_6\text{Q}_2]^{2+}$ cores whose identical isomer shifts of 0.61 mm/s and electron count lead to the all-ferrous formulation $\text{W}^{3+}_2\text{Fe}^{2+}_6$.

Dimerization of the $[\text{MFe}_3\text{S}_4]$ core can in principle generate six EBDC isomers of $[\text{M}_2\text{Fe}_6\text{S}_8]$, two with centro-symmetry and four others that constitute enantiomeric pairs.³¹ All EBDCs of known structure have a real or idealized centrosymmetric structure with a $\text{Fe}_2(\mu_4\text{-S})_2$ bridge rhomb and heterometal atoms in distant transoid positions (Figure 1). Cluster **8b** adheres to this regularity, having crystallographically imposed centrosymmetry with the μ_3 -Se atoms of reactant **7b** occupying the two μ_4 -Q positions of an EBDC.

(4) P^N-Type Clusters—The prototypic molybdenum cluster of this type, $[(\text{Tp})_2\text{Mo}_2\text{Fe}_6\text{S}_9(\text{SH})_2]^{3-}$, is formed by reaction 1 ($\text{Q} = \text{S}$). Given the results in Figure 1, a corresponding experiment with tungsten clusters is unnecessary inasmuch as the same outcome is entirely probable. Here we consider the reactions of the diselenide EBDC **8b** with the three equiv each of three external nucleophiles in reactions 8–10 which are illustrated in Figure 5. These reactions yield P^N-type clusters **9** (64%), **10** (59%), and **11** (51%) whose structures are found in Figure 7. Isomer shifts of **9** (0.55 mm/s), **10** (0.57 mm/s), and **11** (0.62 mm/s) indicate reduced oxidation levels. The $[\text{W}_2\text{Fe}_6\text{S}_7\text{Se}_2]^{1+}$ core of **9** and the $[\text{W}_2\text{Fe}_6\text{S}_6\text{Se}_3]^{1+}$ core of **10** are formulated as $\text{W}^{3+}_2\text{Fe}^{2+}_5\text{Fe}^{3+}$ and the $[\text{W}_2\text{Fe}_6\text{S}_6\text{Se}_2(\text{SMe})]^{1+}$ core of **11** as $\text{W}^{3+}_2\text{Fe}^{2+}_6$, consistent with the larger isomer shift of the latter. The core units are built of two distorted cubane units with a μ_6 -Se common vertex and further connected by μ_2 -Q (**9–11**) and μ_2 -SMe (**11**) bridges.

The central part consists of a Fe_4Se rectangular pyramid with a planar base. The most characteristic features are μ_6 -Se bridging atoms and large Fe–Se–Fe angles (151–160°) centered at these atoms. There was no evidence from structural data of any significant population of selenium atoms at μ_3 positions. Structural considerations of molybdenum P^N-type clusters^{15,17} largely apply to the tungsten clusters.

Cluster **9** results from hydrosulfide attack and contains a μ_6 -Se bridge and a μ_2 -Se atom disordered over the two doubly bridging positions. Mirror symmetry in acetonitrile solution is indicated by ten well-resolved Tp^* signals in the ¹H NMR spectrum.³¹ In the spectra of **9** and **10**, signals of coordinated QH^- were not located. Cluster **10** is formed with hydroselenide and incorporates one μ_6 -Se and two μ_2 -Se atoms; the remaining hydroselenides are bound in terminal positions. Cluster **11** is the result of the reaction with a nucleophile that is utterly improbable to occupy a μ_6 position. Accordingly, one μ_2 -SMe bridge is formed and is disordered over the μ_2 -Se site; two methanethiolate anions are terminally bound. Reactions 8 and 9 involve a one-electron oxidation of reactants²³ whereas reaction 10 proceeds by addition of methan-ethiolate to the core with no change in isomer shift. In this reaction, the absence of a protic source and the presence of a monoanionic bridging ligand tend to stabilize the all-ferrous core. Cluster **11** is the only P^N-type cluster isolated with a monoanionic bridge component.

5. Double Cuboidal Clusters.⁴³—Reaction of **1** with 2 equiv each of FeCl_2 and HS^- in reaction 11 yields cluster monoanion **12** (52%), which undergoes a one-electron reduction with borohydride to give dianion **13**. Isomer shifts lead to the formulations $\text{W}^{4+}_2\text{Fe}^{3+}_3\text{Fe}^{2+}$ (**12**) and $\text{W}^{4+}_2\text{Fe}^{3+}_2\text{Fe}^{2+}_2$ (**13**). Alternative formulations involving W^{III} ($\text{W}^{3+}\text{W}^{4+}\text{Fe}^{3+}_4$ for **12**, $\text{W}^{3+}\text{W}^{4+}\text{Fe}^{3+}_3\text{Fe}^{2+}$ for **13**) predict isomer shifts lower than those observed. In this interpretation, formation of **12** requires a four-electron reduction of the tungsten reactants by three equiv of FeCl_2 and hydrosulfide.

Shown in Figure 8 is the preparative scheme for these clusters. Selenium-containing **14** (32%) and **15** (43%) clusters are accessible in moderate yields by reactions 12 and 13 respectively. The isoelectronic relationship between dianions **13** and **15** is apparent from the pairs of sharp signals at 5.3–6.4 ppm. Cluster synthesis proves the existence of three oxidation states. The voltammograms of **13** and **15** in Figure 9 demonstrate the formation of two more oxidation states at <-1.9 V (Table 1), thereby defining the five-membered electron transfer series $[(\text{Tp}^*)_2\text{W}_2\text{Fe}_4\text{S}_6\text{Q}_3]^{0,1-,2-,3-,4-}$. The 0/1– step of all clusters (not shown) and the 3–/4– step of **15** are not well-defined in the DMF medium used. We interpret the 1–/2– step ($\mathbf{12} + e^- \rightleftharpoons \mathbf{13}$) as iron-based involving the configurations deduced from isomer shifts. We do not know the site of reaction of the last two steps, but raise the possibility that they are $\text{W}^{4+}/\text{W}^{3+}$ processes. The isomer shift orders $\mathbf{12} < \mathbf{13}$ and $\mathbf{14} < \mathbf{15}$ are consistent with the second member of each pair being more reduced, but the shift differences of 0.05 and 0.02 mm/s, respectively, are much smaller than the value $(0.63-0.23)/4 = 0.10$ mm/s predicted from the empirical relationship. This may be a result of electron delocalization including the WS_3 groups.

As revealed in Figure 10, cluster structures are built upon a W_2Fe_4 plane with a nearly square Fe_4 portion. The cuboidal units $\text{WFe}_2(\mu_2\text{-S})_2(\mu_3\text{-S})(\mu_4\text{-Q})$ are recognizable by connectivity and, as depicted with **12**, the placement of $\mu_2\text{-S}$ and $\mu_4\text{-Q}$ atoms on one side of the plane and $\mu_3\text{-S}$ and $\mu_2\text{-Q}$ atoms on the other. Selected metric features are summarized in Table 3; there is no systematic trend of these bond and angular values with oxidation state. The $[\text{M}_2\text{Fe}_4(\mu_2\text{-Q})_6(\mu_3\text{-Q})_2(\mu_4\text{-Q})]$ connectivity pattern was first and most frequently demonstrated with $[\text{Fe}_6\text{S}_9(\text{SR})_2]^{4-}$ ^{44–48} and also with the selenide clusters $[\text{Fe}_6\text{Se}_9(\text{SR})_2]^{4-}$ ^{49,50}. The only other heterometal clusters of this type are $[(\text{edt})_2\text{Mo}_2\text{Fe}_6\text{S}_9]^{3-,4-}$ whose cores are isoelectronic with **12** and **13** but differ by the presence of trigonal bipyramidal molybdenum sites.⁵² The isomer shift of the 4– cluster was interpreted in terms of the charge distribution $(\text{Mo}^{4+}_2\text{Fe}^{3+}_2\text{Fe}^{2+}_2)$ corresponding to that of **13**.

Selenide Cluster Incorporation

The conversion of an EBDC to a P^{N} -type cluster in reaction 1 originally provoked the issue of the fate of the attacking hydrosulfide in the formation of the $[\text{Mo}_2\text{Fe}_6\text{S}_8\text{Q}]^{1+}$ core.¹⁷ Included in Figure 11 is the result depicted in Figure 1 in which one selenide is incorporated in a $\mu_2\text{-Se}$ site of the product core. The syntheses and structures of single cubanes, EBDCs, P^{N} -type clusters, and double-cuboidal clusters reveal that selenide can function as an external nucleophilic reactant when incorporated into cluster cores or as an internal, presumably intramolecular, reactant upon conversion of one cluster core to another. The situation is summarized in Figure 11. In all cases, the X-ray structural results do not reveal significant selenium occupation of cluster sites other than those specified.

(1) Single Cubanes—The synthesis of clusters **5b–7b** provides examples of the incorporation of selenide into cubane $[\text{MFe}_3\text{S}_3\text{Q}]^{3+,2+}$ cores (Figures 2 and 5). These results are consistent with the prior formation of $[(\text{Bu}_3\text{tach})\text{MoFe}_3\text{S}_3\text{SeL}_3]^{1-,0}$ and

$[(\text{Bu}_3\text{tch})\text{WFe}_3\text{S}_3\text{SeL}_3]$ by reaction of $[(\text{Bu}_3\text{tch})\text{MS}_3]$ with FeCl_2 , Na_2Se , and $\text{L} = \text{Cl}^-$ or RS^- .⁵ These incorporations are termed *specific* inasmuch as the selenide atom is always placed in the μ_3 -Q site bridging three iron atoms; i.e. all W-S bonds are preserved in the reduction of tungsten in cluster formation (reaction 5).

(2) Edge-Bridged Double Cubanes—Reductive dimerization of single cubanes in reaction 7 produces the EBDCs **8ab**. The origin of the μ_4 -S atoms—possibly resulting from sulfide rearrangement within a cubane core upon reduction or scrambling between cores—cannot be addressed from the structure of an all-sulfide cluster. However, the reductive conversion of selenide cluster **7b** to **8b**, which has two μ_4 -Se atoms in the $[\text{W}_2\text{Fe}_6\text{S}_6\text{Q}_2]^{2+}$ core, supports a pathway involving neither of these events. This result requires that the single cubane reactants remain intact during reduction, phosphine dissociation, and dimerization, which occurs along Fe–Se edges to recover the observed transoid stereochemistry. It is further probable that the unique sulfur in the precursor cubane assumes the μ_4 -S site in the all-sulfide EBDC product.

(3) P^N-Type Clusters—Reactions of **8b** with QH^- lead to previously unknown chalcogenide atom rearrangements in the course of cluster formation. Reactions 8 and 9 involve both external and internal reactants. Reactants QH^- induce the rearrangements $2\ \mu_4\text{-Se} \rightarrow \mu_2\text{-Se} + \mu_6\text{-Se}$ in forming P^N-type cores. Thus, one of the μ_4 -Se atoms in the precursor double cubane assumes the μ_6 -Se site and the other a doubly bridging site. The external chalcogenide appears in the products **9** and **10** as a μ_2 -Q bridge. The formation of such a bridge is anticipated by the result of reaction 1 with $\text{Q} = \text{Se}$. From these observations, it is probable that a μ_4 -S atom in the EBDC precursor assumes the μ_6 -S role in the P^N-type cluster product.

(4) Double Cuboidal Clusters—The use of Na_2Se in reactions 12 and 13 places selenide in the μ_2 -Se and μ_4 -Se sites of the $[\text{W}_2\text{Fe}_4\text{S}_6\text{Q}_3]^{2+}$ core of double cuboidal **14**. The WS_3 groups are unaffected. We conclude in this reaction and the related reaction 11 the three chalcogenide atoms bridging the WFe_2S_3 fragments arise from the sulfide or selenide external reagent.

Summary

The structural roles of external and internal chalcogenide reactants are summarized in Table 4. We consider it highly probable that the positions occupied by selenide in single cubanes, EBDCs, P^N-type clusters, and double cuboidal clusters are same as those assumed by external or internal sulfide in the formation of sulfide-only clusters. The premise is that selenium is a faithful structural surrogate of sulfur in molecules with equal numbers but differing populations of chalcogenides. From this information, it is possible to conceptualize the formation of an EBDC from a single cubane and a P^N-type cluster from an EBDC, as outlined in Figure 11. However, it is not yet possible to propose detailed molecular pathways on the basis of the evidence available. The single cubane conversion to an EBDC is perhaps the simplest. Yet the order of reduction and phosphine dissociation is not known nor are the details of the dimerization reaction. The EBDC to P^N-type cluster conversion is more complicated owing to the larger number of Fe–Q bonds broken and made and the sequence of events in the process. However, any eventual mechanism must conform to the structural fate of the two μ_4 -Q atoms of the precursor.

The results with external and internal selenide support the viability of template-assisted cluster assembly. Note that in every transformation in Figure 11 (summarized in Table 4) selenide is bound only to iron; i.e., the WS_3 template group of precursor **1** remains intact. Further, every cluster contains a WFe_2S_3 fragment, which has been separately isolated in the

form of incomplete cubanes **3** and **4**. The success of the approach must depend in large part on the greater bond strength and kinetic inertness of the template group. While the bond strength order $\text{W}^{\text{III,IV}}\text{-S} > \text{Fe}^{\text{II,III}}\text{-S}$ would appear a certainty, there are no appropriate data for comparison. Given the pronounced chemical similarities between tungsten and molybdenum,⁵³ we anticipate that the results obtained in this work would extrapolate to the corresponding Mo-Fe-S/Se clusters. However, the potential template reactant $[(\text{Tp}^*)\text{MoS}_3]^{1-}$ needed to test this issue has not been prepared. Lastly, selenide substitution and associated structural results have served the additional purpose of confirming template-based cluster assembly. The complex $[(\text{Cp}^*)\text{MoS}_3]^{1-}$ ⁵⁴ may have similar templating capability although it has not been directly employed in cluster assembly leading to cubane-type MoFe_3S_4 clusters.⁵⁵

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Depiction of the conversion of the edge-bridged double cubane cluster $[(Tp)_2Mo_2Fe_6S_8(PEt_3)_4]$ to P^N -type clusters by reaction with HS^- or HSe^- in acetonitrile. Note the μ_2 position of selenide in the product cluster.

Figure 2.

Synthetic scheme for incomplete cubane (**2**, **3**, **4**) and cubane-type clusters **5ab** from template precursor **1**. Clusters **6ab** and **7ab** are obtained from **5ab** by ligand substitution reactions.

Figure 3.

Structures of the incomplete cubane clusters **2**, **3**, and **4**. In this and succeeding figures, 50% probability ellipsoids are shown. Disorder in the chloride ligands of **3** is evident. Selected dimensions (Å, deg) of **2**: W=S 2.159(1), W–S 2.292(2), Fe–S 2.255(1), W–Fe 2.724(1), S–Fe–S 102.83(3).

Figure 4. Structures of the cubane-type clusters **5b** and **6b** revealing the specific incorporation of a μ_3 -Se atom in the cores.

Figure 5.

Synthetic scheme for diselenide edge-bridged double cubane cluster **8b** by reduction of single cubane **7b** and its conversion to P^N-type clusters **9**, **10**, and **11** by reaction with sulfide or selenide nucleophiles.

Figure 6.

Structure of the cubane-type clusters **7b** and its edge-bridged double cubane reduction product **8b** (imposed centrosymmetry); note the μ_4 positions of the two selenide atoms. Ethyl groups have been omitted for clarity. Selected distances (Å): Fe...Fe 3.053(3) (bridge rhomb), Se...Se 3.832(3), W...W 8.347(5).

Figure 7.

Structures of the P^N -type clusters **9** (155.34(4)•), **10** (150.99(5)•), and **11** (159.6(4)•), each of which contains a μ_6 -Se atom. The bottom structure contains disordered Se and SMe bridges in the μ_2 positions. For clarity, a structure without disorder is depicted. The largest Fe–(μ_6 -Se)–Fe angle involving Fe atoms with terminal ligands is given for each cluster.

Figure 8. Synthetic scheme for double-cuboidal clusters **12–15** based on the reactions of FeCl_2 and sulfide or selenide with **1** or **2**.

Figure 9. Cyclic voltammograms (100 mV/s) of double-cuboidal clusters **13** and **15** in DMF at ambient temperature; peak potentials area indicated.

Figure 10.

Structures of double-cuboidal clusters **12** (monoclinic form), **13**, and **15** viewed down a real or idealized C_2 axis. The side view of **12** is normal to the W_2Fe_4 plane and shows atom displacements (Å) from that plane.

Figure 11.

Summary of sulfide and selenide incorporation in core structures of four cluster types. The core rearrangement in the lower part of the left-hand column is depicted in full in Figure 1.

$[(\text{Tp}^*)\text{WS}_3]^{1-}$	1 ²¹
$[(\text{Tp}^*)\text{WFeS}_3\text{Cl}_2]^{1-}$	2
$[(\text{Tp}^*)\text{WFe}_2\text{S}_3(\text{SEt})\text{Cl}_2]^{1-}$	3
$[(\text{Tp}^*)\text{WFe}_2\text{S}_3(\text{SEt})_3]^{1-}$	4
$[(\text{Tp}^*)\text{WFe}_3\text{S}_3\text{QCl}_3]^{1-}$	Q = S 5a , ²² Se 5b
$[(\text{Tp}^*)\text{WFe}_3\text{S}_3\text{Q}(\text{SEt})_3]^{1-}$	Q = S 6a , ²² Se 6b
$[(\text{Tp}^*)\text{WFe}_3\text{S}_3\text{Q}(\text{PEt}_3)_3]^{1+}$	Q = S 7a , Se 7b
$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_6\text{S}_6\text{Q}_2(\text{PEt}_3)_4]$	Q = S 8a , Se 8b
$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_6\text{S}_7\text{Se}_2(\text{SH})_2]^{3-}$	9
$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_6\text{S}_6\text{Se}_3(\text{SeH})_2]^{3-}$	10
$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_6\text{S}_6\text{Se}_2(\text{SMe})_3]^{3-}$	11
$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_4\text{S}_9]^{1-}$	12
$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_4\text{S}_9]^{2-}$	13
$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_4\text{S}_6\text{Se}_3]$	14
$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_4\text{S}_6\text{Se}_3]^{2-}$	15

Bu^t₃tach = 1,3,5-*tert*-butyl-1,3,5-triazacyclohexane; EBDC = edge-bridged double cubane; edt = ethane-1,2-dithiolate(2-), Q = sulfide and/or selenide; Tp = tris(pyrazolyl)hydroborate(1-); Tp* = tris(3,5-dimethylpyrazolyl)hydroborate(1-).

Chart 1.
Designation of Clusters and Abbreviations

Table 1

Zero-field Mössbauer Parameters and Redox Potentials.

cluster	δ (mm/s) ^a	ΔE_Q (mm/s)	$\Delta E_{1/2}$ (V) ^b
2	0.52	1.17	irrev
4	0.45	1.02	−0.17 (1-/2-), −1.42 (2-/3-)
5a	0.50	0.86	−0.72 (1-/2-), −1.69 (E _{pc}) ^c
5b	0.52	0.96	−0.69 (1-/2-), −1.64 (E _{pc}) ^c
6a	0.42	1.41	−1.13 (1-/2-), −2.12 (E _{pc})
6b	0.44	1.27	−1.10 (1-/2-), −1.92 (2-/3-)
7a	0.49 ^d	<i>e</i>	−0.96 (1+/0)
7b	0.51 ^d	<i>f</i>	−0.89 (1+/0)
8a,8b	0.61, 0.61	0.84, 0.84	<i>g</i>
9	0.55 ^d	<i>h</i>	−1.19 (2-/3-), −1.83 (3-/4-)
10	0.57 ^d	<i>k</i>	<i>g</i>
11	0.62	0.81	−0.85 (1-/2-), −1.39 (2-/3-)
12 ⁱ	0.37	1.21	−0.54 (1-/2-), −1.99 (2-/3-), −2.40 (3-/4-)
13 ⁱ	0.42	0.98	−0.54 (1-/2-), −1.97 (2-/3-), −2.38 (3-/4-)
14	0.41	1.21	—
15 ⁱ	0.43	1.15	−0.51 (1-/2-), −1.91 (2-/3-), −2.19 (3-/4-) ^j

^a90–120 K, vs. Fe metal at room temperature.^bV_s. SCE, 298 K, acetonitrile unless noted otherwise.^cPeak potential, irreversible.^dWeighted mean value of two overlapping doublets.^e ΔE_Q = 0.84 (71%), 2.28 (29%).^f ΔE_Q = 0.87 (72%), 1.78 (28%).^gNot determined.^h ΔE_Q = 0.77 (61%), 0.93 (39%).ⁱPotentials in DMF.^jApproximate value.^k ΔE_Q = 0.66 (71%), 1.12 (29%).

Table 2

Dimensional Comparison of Fe-Q Cluster Fragments.^a

fragment	cluster	Distances (Å)	angles (°)
9 (Q=S)	2.322(2)	—
	10 (Q=Se)	2.448(1)	—
13 (Q=S) ^c	2.23(1)	76.7(1)
	15 (Q=Se) ^c	2.364(9)	75.05(7)
	[(Tp)2Mo2Fe6S9(SH)2] ³⁻ ^d	2.225(5)	75.0(4)
	10 (Q=Se) ^e	2.375(7)	77.0(5)
5a ^f	2.259(5)	73.2(2)
	5b ^f	2.39(1)	68.9(6)
8a (Q=S) ^g	(a) 2.290(2) (b) 2.393(2)	78.22(6)
	8b (Q=Se) ^g	(a) 2.388(1) (b) 2.510(1)	77.08(3)
13 (Q=S) ^c	2.32(1) ^h	68.4(1) 73.3(6) 110(1)
	15 (Q=Se) ^c	2.461(2) ^h	64.9(4) 71.7(4) 105(1)
[(Tp)2Mo2Fe6S9(SH)2] ³⁻ ^d	2.38(2) ⁱ	70.3(5) ⁱ 68.9(5) ^j 108(2) ^j
	10 (Q=Se) ^e	2.51(3) ⁱ	65(2) ⁱ 71.7(4) ^j 104(2) ^j

^a Mean values used where possible.^b Terminal bond.^c Double-cuboidal.^d Ref. 15.^e P_N-type.^f Cubane-type.^g EBDC.^h Mean value of 4.ⁱ Mean value of 6.

j Mean value of 2.

Table 3Metric Parameters ($\text{\AA}$, deg)^a of the Double Cuboidal Clusters $[(\text{Tp}^*)_2\text{W}_2\text{Fe}_4\text{S}_6\text{Q}_3]^z$ (Q = S, Se).

	$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_4\text{S}_6\text{Se}_3]$	$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_4\text{S}_9]^{1-b}$	$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_4\text{S}_6\text{Se}_3]^{2-c}$	$[(\text{Tp}^*)_2\text{W}_2\text{Fe}_4\text{S}_9]^{2-}$
Fe-(μ_2 -S) ^d	2.209(2)	2.217(1)	2.232(2)	2.217(9)
Fe-(μ_2 -Q)	2.321(12)	2.194(1)	2.365(3)	2.226(10)
Fe-(μ_3 -S)	2.268(14)	2.266(1)	2.296(5)	2.288(10)
Fe-(μ_4 -Q)	2.444(8)	2.321(3)	2.463(4)	2.315(9)
Fe...Fe ^e	2.66(3), 2.754(6)	2.646(2), 2.686(2)	2.643(4), 2.881(4)	2.604(2), 2.763(12)
Fe-(μ_2 -Q)-Fe	72.9(2), 72.6(1)	75.5(1)	75.4(1), 74.6(1)	76.6(1), 76.8(1)
Fe-(μ_4 -Q)-Fe ^f	65.3(2), -68.7(1)	69.51(9), 70.71(9)	64.6(1) -72.2(1)	68.3(1) -73.7(1)
	102.7(1), 103.8(1)	108.3(2), 109.0(2)	104.3(1), 105.9(1)	109.4(2), 110.8(2)
$\delta(\mu_2\text{-S})^g$	1.21(1), 1.20(1)	1.267(3), 1.276(3)	1.312(6), 1.286(6)	1.269(4), 1.321(5)
	1.27(1), 1.17(1)		1.267(5), 1.351(5)	1.227(5), 1.385(4)
$\delta(\mu_2\text{-Q})^g$	0.47(1), 0.49(1)	0.712(4)	0.710(4), 0.895(4)	0.702(5), 0.845(5)
$\delta(\mu_3\text{-S})^g$	1.66(1), 1.70(1)	1.677(3)	1.707(5), 1.718(5)	1.710(4), 1.697(4)
$\delta(\mu_4\text{-Q})^g$	1.565(6)	1.334(4)	1.462(2)	1.290(4)

^aSingle values are unique or mean values.^bMonoclinic, C_2 axis; parameters for orthorhombic form very similar except for one (long) Fe...Fe distance of 2.731(1) $\text{\AA}$.^cOne of two independent clusters of nearly identical dimensions.^dBridge atom bound to W.^eLonger distance parallel to W-(μ_4 -Q)-W vector.^fLarger angles involve opposite atoms.^gPerpendicular displacement from W_2Fe_4 mean plane; μ_2 -S and μ_4 -Q on same side of W_2Fe_4 plane and μ_2 -Q and μ_3 -S on opposite side.

Table 4

Chalcogenide Reactant Summary for W-Fe-Q Cluster Synthesis (Q = S, Se).

<ul style="list-style-type: none"> Structural fate of <i>external</i> chalcogenide reactants 	
single cubanes:	$(\mu_3\text{-Q})\text{Fe}_3$
P ^N -type clusters:	$(\mu_2\text{-Q})\text{Fe}_2$
double-cuboidal clusters:	$(\mu_2\text{-Q})\text{Fe}_2 + (\mu_4\text{-Q})\text{Fe}_4$
<ul style="list-style-type: none"> Reactions of <i>internal</i> chalcogenide atoms 	
SC → EBDC	$(\mu_3\text{-Q})\text{Fe}_3 \rightarrow (\mu_4\text{-Q})\text{Fe}_4$
EBDC → P ^N -type	$(\mu_4\text{-Q})\text{Fe}_4 \rightarrow (\mu_2\text{-Q})\text{Fe}_2 + (\mu_6\text{-Q})\text{Fe}_6$
<ul style="list-style-type: none"> Because all W-S bonds are preserved in all reactions, the concept of $[(\text{Tp}^*)\text{WS}_3]^{1-}$ as a <i>template reactant</i> is validated. 	