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Structural diversity of tetranuclear tungsten sulfide clusters: syntheses and crystal structures of clusters containing raft-type $W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4$ and tetrahedral $W_4(\mu\text{-}S)_6$ cores

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Reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ **1** with 2 equivalents of $(Me_3Si)_2S$ in the presence of an excess of MeOH gave a tetranuclear tungsten sulfide cluster $[W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4(SH)_2(PMe_2Ph)_6]$ **2**. Substitution of chloride anions for the terminal SH ligands in **2** took place on reaction with 1 equivalent of $SnCl_2$, giving the isostructural W_4 cluster $[W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4Cl_2(PMe_2Ph)_6]$ **3**. Both **2** and **3** with ten skeletal electrons consist of an almost equilateral raft-type W_4 framework with five metal–metal bonds. On treatment with 2.4–3 equivalents of $AgOSO_2CF_3$, compound **3** underwent two-electron oxidation to give $[W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4Cl_2(PMe_2Ph)_6][OSO_2CF_3]_2$ **4**, which has a distorted raft-type W_4 core owing to the presence of only eight skeletal electrons. On the other hand, reduction of **3** with an excess of Na/Hg resulted in formation of the twelve-skeletal-electron cluster $[W_4(\mu\text{-}S)_6(PMe_2Ph)_4]$ **5** containing a tetrahedral W_4 core with six W−W bonds. The detailed structures of **2**–**5** were determined by single-crystal X-ray diffraction.

The chemistry of transition-metal sulfide clusters, especially those containing Group 6 and 8 metals, is progressing rapidly owing to their possible relevance to the structures and functions of metalloenzymes such as nitrogenase[1] and to industrial solid-surface catalysis including hydrodesulfurization processes.[2] Another important aspect of sulfide cluster chemistry is the structural relationship between molecular sulfide clusters and non-molecular metal sulfides exemplified by the superconducting Chevrel phases.[3] Although the flexible co-ordination ability of sulfide ligands to transition metals has led to the formation of sulfide clusters with a variety of core structures,[4] emphasis has mainly been placed on triangular clusters and tetranuclear cubane-type clusters with respect to Group 6 metal sulfide chemistry.[5]

In the course of our study on the synthesis and reactivities of multimetallic sulfur complexes,[5d,6] we have recently obtained the raft-type tetratungsten sulfide cluster $[W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4(SH)_2(PMe_2Ph)_6]$ **2** from the reaction of a dinitrogen complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ **1** with H_2S generated from $(Me_3Si)_2S$ and MeOH, and its subsequent conversion into a tetrahedral tetratungsten cluster $[W_4(\mu\text{-}S)_6(PMe_2Ph)_4]$.[7] Reactions of H_2S with low-valent metal complexes have proved to provide a versatile method for preparing sulfide clusters. However, the reactivity of **1** towards H_2S has not been investigated previously, although the reactions of a series of molybdenum and tungsten dinitrogen complexes of the type $[M(N_2)_2(PR_3)_4]$ (M = Mo or W; PR_3 = tertiary phosphine) with various thiols have extensively been studied.[8]

We now report the details of the new tetranuclear sulfide clusters containing either a raft-type or a tetrahedral tungsten framework. For homometallic tetratungsten sulfide clusters, only linear[9] and cubane-type cores[10] have been reported previously.

Experimental

All manipulations were performed under an atmosphere of nitrogen or argon using standard Schlenk techniques. Solvents were dried by refluxing over sodium–benzophenone [tetrahydrofuran (thf), toluene, benzene, diethyl ether and hexanes], P_2O_5 (dichloromethane) or $Mg(OMe)_2$ (methanol), and distilled just before use. Hexamethyldisilathiane $[(Me_3Si)_2S]$ was obtained from Fluka and used after degassing by freeze–pump–thaw cycles, while $SnCl_2$ (Nacalai Tesque) and $AgOSO_2CF_3$ (Tokyo Chemical Industry Co.) were used as recieved. Infrared spectra were recorded on a Shimadzu 8100M spectrometer, ^1H (270 MHz) and $^{31}P\text{-}\{^1H\}$ (109 MHz) NMR spectra on a JEOL EX-270 spectrometer. Elemental analyses were performed on a Perkin-Elmer 2400II CHN analyser.

Preparations

$[W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4(SH)_2(PMe_2Ph)_6]$ 2. To a toluene solution (60 cm^3) of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ **1**[11] (3.013 g, 3.80 mmol) in a two-necked round-bottomed flask (500 cm^3) was added MeOH (1.5 cm^3, 37 mmol), and the solution was allowed to cool to −196 °C. Then $(Me_3Si)_2S$ (1.6 cm^3, 7.6 mmol) was added at this temperature and the flask evacuated after all the materials inside had frozen. The mixture was then warmed to 50 °C and stirred for 4 h. The resultant green solution was evaporated *in vacuo* and the dark green oil remaining was crystallized from thf–ether (40 cm^3–110 cm^3). Dark green *microcrystals* formed were washed thoroughly with cold thf until the washings turned green and then dried *in vacuo* (751.7 mg, 43%). $\tilde{\nu}_{max}/cm^{-1}$(SH) 2512w (KBr). $\delta_H([^2H_8]thf)$ 8.12–7.06 (30 H, m, PMe_2Ph), 2.34 [12 H, d, ^2J(PH) 7.9, wingtip PMe_2Ph], 1.61, 1.35 [12 H each, br d, ^2J(PH) 6.8 Hz, hinge PMe_2Ph]; signals due to the hydrosulfido protons were not assignable. $\delta_P([^2H_8]thf)$ −17.9 [2 P, s, ^1J(WP) 175, wingtip PMe_2Ph] and −52.3 [4 P, s, ^1J(WP) 167 Hz, hinge PMe_2Ph] (Found: C, 31.7; H, 3.8. $C_{48}H_{68}P_6S_8W_4$ requires C, 31.6; H, 3.8%).

$[W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4Cl_2(PMe_2Ph)_6]$ 3. To a suspension of compound **2** (714.7 mg, 0.392 mmol) in thf (30 cm^3) was added $SnCl_2$ (82.8 mg, 0.437 mmol) and the mixture was allowed to reflux for 90 min. After cooling, it was filtered and the filtrate reduced in volume to 20 cm^3. Slow addition of ether (40 cm^3) deposited dark green *microcrystals*, which were washed with cold thf until the washings turned green and dried *in vacuo* (452.7 mg, 63%). $\delta_H([^2H_8]thf)$ 7.98–7.08 (30 H, m, PMe_2Ph), 2.15 [12 H, d, ^2J(PH) 7.9 Hz, wingtip PMe_2Ph] and 1.27 (12 H, br s, hinge PMe_2Ph); a signal ascribed to another hinge PMe_2Ph might be overlapping the signals due to the impurity in $[^2H_8]$thf at δ 1.73. $\delta_P([^2H_8]thf)$ −18.3 (2 P, br s, wingtip PMe_2Ph) and

−52.6 [4 P, s, ${}^1J$(WP) 169 Hz, hinge PMe_2Ph] (Found: C, 32.2; H, 3.9. $C_{48}H_{66}Cl_2P_6S_6W_4$ requires C, 31.55; H, 3.6%).

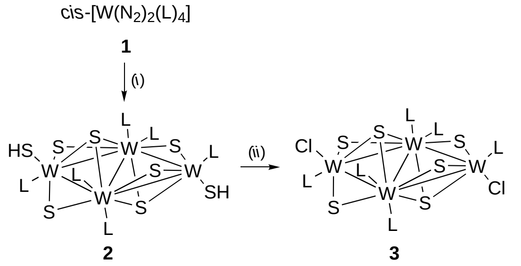
$[W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4Cl_2(PMe_2Ph)_6][OSO_2CF_3]_2$ 4. To a suspension of compound **3** (83.3 mg, 0.0456 mmol) in thf (8 cm^3) was added a solution of $AgOSO_2CF_3$ (28.0 mg, 0.109 mmol) in thf (2 cm^3) and the mixture was stirred for 2 h in the dark. After removal of the solvent *in vacuo* the resultant reddish brown oil was extracted with CH_2Cl_2 (10 cm^3). Diffusion of vaporized ether into the concentrated extract afforded dark reddish brown *crystals* (70.6 mg, 73%). $\delta_H(CD_2Cl_2)$ 8.04–6.96 (30 H, m, PMe_2*Ph*), 2.74, 1.74, 1.49 (12 H each, br s, P*Me*$_2$Ph). $\delta_P(CD_2Cl_2)$ −2.0 (2 P, br s, wingtip PMe_2Ph) and −46.2 (4 P, br s, hinge PMe_2Ph) (Found: C, 27.95; H, 3.3. $C_{50}H_{66}Cl_2F_6O_6P_6S_8W_4$ requires C, 28.25; H, 3.1%). The yield of **4** is substantially variable owing to the concurrent formation of an uncharacterizable brown solid as a by-product. The optimum yield observed in repeated runs is given here.

$[W_4(\mu\text{-}S)_6(PMe_2Ph)_4]$ 5. A suspension of compound **3** (178.9 mg, 0.0979 mmol) in thf (16 cm^3) was added to sodium amalgam (59 mg of Na in 17 g of Hg) and the mixture was stirred for 8 h at room temperature. The resulting dark brown solution was separated from mercury by decantation and dried *in vacuo*. The dark brown solid remaining was extracted with benzene (2 cm^3 × 6) and chromatographed on alumina with benzene–hexane (6:4). A purple band eluted was collected and evaporated to dryness. The residue was crystallized from thf–ether, giving **5** as purple *crystals* (14.6 mg, 10%). δ_H([${}^2H_8$]thf) 8.00–7.25 (20 H, m, PMe_2*Ph*), 2.42 [24 H, d, ${}^2J$(PH) 6.3 Hz, P*Me*$_2$Ph]. δ_P([${}^2H_8$]thf) −3.7 [s, ${}^1J$(WP) 141.0, ${}^2J$(WP) 5.7, ${}^3J$(PP) 10.4 Hz]. Recrystallization from toluene afforded the analytically pure **5** with one solvating toluene molecule (Found: C, 30.0; H, 3.4. $C_{39}H_{52}P_4S_6W_4$ requires C, 29.8; H, 3.3%).

Crystallography

Single crystals suitable for X-ray analyses were sealed in glass capillaries under an inert atmosphere and mounted on a Rigaku AFC7R four-circle diffractometer equipped with a graphite-monochromatized Mo-Kα source ($\lambda = 0.7107$ Å). Orientation matrices and unit-cell parameters were determined by least-squares treatment of 25 machine-centred reflections with $25 < 2\theta < 40°$. The data collection was performed at room temperature using the ω–2θ scan technique at a rate of 16° min^{-1} to a maximum 2θ value of 55°. The intensities of three check reflections were monitored every 150 showing no significant decay for compounds **2**, **4** and **5**, but a steady decrease in intensities for **3** during data collection (average 19.3% decrease for the three check reflections at the final stage). Intensity data were corrected for Lorentz-polarization effects and for absorption (ψ scans). A decay correction was also applied for **3**. Crystal and data collection parameters are summarized in Table 1.

Structure solution and refinements were carried out by using the TEXSAN program package.[12] The heavy-atom positions were determined by the Patterson-methods program (DIRDIF-PATTY),[13] and remaining non-hydrogen atoms were found by subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques (based on F^2) for compounds **2** and **5**, while for **3** the carbon atoms were refined only isotropically. For **4** all non-hydrogen atoms were found in the Fourier-difference map except for two fluorine atoms, which were placed at the calculated positions. Whereas the structure of the cation was refined anisotropically, for the CF_3SO_3 anion three oxygen atoms were refined isotropically and one carbon and three fluorine atoms were included in the refinement but with fixed parameters since anisotropic refinement was unsuccessful probably due to partial disorder of the triflate anion. The hydrogen atom of the hydrogensulfide ligand in **2** was found in the final Fourier-difference map, while all other hydrogen atoms were placed at calculated positions, and included in the final stages of refinements with fixed parameters.



Scheme 1 (*i*) $(Me_3Si)_2S$–MeOH, toluene, 50 °C; (*ii*) $SnCl_2$, thf, reflux ($L = PMe_2Ph$)

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/457.

Results and Discussion

Preparation of equilateral raft-type tetratungsten hexasulfide clusters 2 and 3

In spite of recent postulation that the aldehyde ferredoxin oxidoreductase from the hyperthermophilic organism *Pyrococcus furiosus* contains a W–SH group,[14] only a limited number of tungsten hydrogensulfido complexes are known.[15] We have found that treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ **1** with $(Me_3Si)_2S$ (2 equivalents) and MeOH (10 equivalents) in toluene at 50 °C afforded a tetranuclear tungsten sulfido–hydrogensulfido cluster $[W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4(SH)_2(PMe_2Ph)_6]$ **2** in moderate yield (Scheme 1); the structure of **2** has been characterized by X-ray crystallography as shown in Fig. 1 (see below). The IR spectrum of **2** shows a characteristic band at 2512 cm^{-1}, clearly indicating the presence of the hydrogensulfide ligand, although the signals assignable to the hydrogensulfido protons were not observed in its ${}^1H$ NMR spectrum. The methyl protons in the PMe_2Ph ligands appeared as one sharp doublet at δ 2.34 and two slightly broadened doublets at δ 1.61 and 1.35 with the same intensities. The former low-field resonance may be assignable to the methyl groups in the wingtip PMe_2Ph ligands, while the last two are ascribable to those in the two pairs of the hinge PMe_2Ph ligands. The broadness of the latter signals might be attributed to the inequivalence of the two methyl groups in each hinge PMe_2Ph ligand. The ${}^{31}P$-{${}^1H$} NMR spectrum exhibits two signals with the intensity ratio of 1:2, consistent with the solid-state structure of **2**. The ${}^1J$(WP) values of 167 and 175 Hz are comparable to those of, *e.g.* $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3X_3(dmpe)_3][BPh_4]$ (113.9–184.2 Hz; X = Cl or H, dmpe = $Me_2PCH_2CH_2PMe_2$).[16]

When compound **1** was treated with $(Me_3Si)_2S$ alone, no reaction occurred. This suggests that hydrogen sulfide generated *in situ* from $(Me_3Si)_2S$ and MeOH reacts with **1** to give cluster **2**. The ${}^1H$ NMR spectrum of the reaction mixture obtained by treatment of **1** with H_2S gas at 50 °C indicated the formation of **2**, although isolation of **2** in a pure form was not successful due to the concomitant production of a large amount of $Me_2PhP{=}S$.

Reactions of *cis*-$[Mo(N_2)_2(PMe_2Ph)_4]$, *trans*-$[W(N_2)_2(PMePh_2)_4]$, and *trans*-$[W(N_2)_2(dppe)_2]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) with $(Me_3Si)_2S$–MeOH or H_2S gas were also attempted. However, we could not isolate any characterizable products from these reaction mixtures. The isostructural molybdenum cluster containing PMe_3 in place of PMe_2Ph, $[Mo_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4(SH)_2(PMe_3)_6]$ **6**, was previously prepared by the reaction of a trinuclear cluster $[NH_4]_2[Mo_3(\mu_3\text{-}S)(\mu\text{-}S_2)_3(S_2)_3]$ with PMe_3 in thf–

Table 1 X-Ray crystallographic data for compounds **2**–**5**

	2	**3**	**4**	**5**
Formula	$C_{48}H_{68}P_6S_8W_4$	$C_{48}H_{66}Cl_2P_6S_6W_4$	$C_{50}H_{66}Cl_2F_6O_6P_6S_8W_4$	$C_{32}H_{44}P_4S_6W_4$
M	1822.79	1827.56	2125.69	1480.35
Crystal system	Monoclinic	Monoclinic	Triclinic	Tetragonal
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$I4_1/amd$ (no. 141)
Crystal colour	Dark green	Dark green	Dark reddish brown	Purple
Crystal dimensions/mm	0.2 × 0.2 × 0.1	0.1 × 0.2 × 0.3	0.1 × 0.3 × 0.5	0.2 × 0.2 × 0.1
a/Å	11.158(4)	13.80(1)	11.036(2)	23.160(4)
b/Å	21.408(1)	19.236(4)	12.026(2)	23.160(4)
c/Å	13.765(1)	12.807(9)	14.695(3)	9.939(4)
α/°	–	—	71.69(2)	—
β/°	113.53(1)	117.25(3)	68.98(2)	—
γ/°	—	—	89.53(2)	—
$U/Å^3$	3014(1)	3021(2)	1716.2(7)	5331(2)
Z	2	2	1	4
$D_c/g\ cm^{-3}$	2.008	2.009	2.057	1.844
F(000)	1740	1740	1016	2752
μ(Mo-Kα)/cm^{-1}	80.83	80.85	72.09	89.86
Reflections measured	$+h, +k, \pm l$	$+h, +k, \pm l$	$\pm h, -k, \pm l$	$+h, +k, +l, h \geqslant k, h + k + l = 2n$
No. unique reflections	7108	5514	7888	1759
Transmission factors	0.5732–1.0000	0.6334–1.0000	0.4354–1.0000	0.7175–1.0000
No. data used $[I > 3\sigma(I)]$	4266	2128	5700	717
No. variables	298	178	320	61
*R**	0.037	0.069	0.036	0.049
*R′**	0.026	0.043	0.031	0.047
Goodness of fit	1.35	1.98	3.20	2.89
Maximum residual/e $Å^{-3}$	1.24	2.46	1.70	1.35

* $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; $w = 1/\sigma^2(F_o)$.

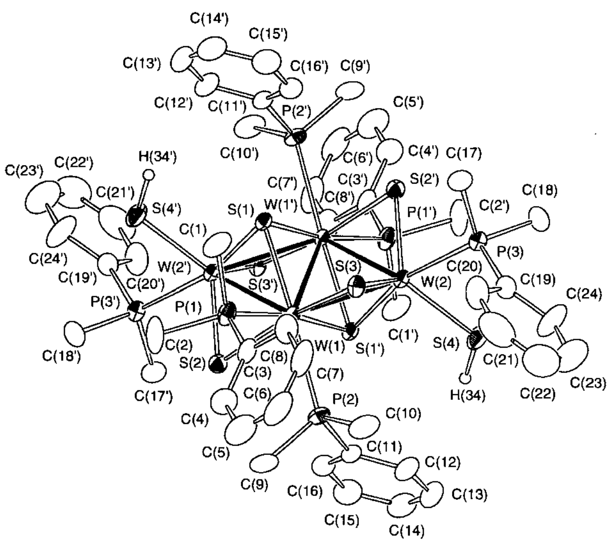


Fig. 1 Molecular structure of compound **2** with the atom numbering scheme

butylamine.[17] Interestingly, treatment of the complexes of Mo and W having PMe_3 ligands $[MH(\eta^2\text{-}CH_2PMe_2)(PMe_3)_4]$ (M = Mo or W) with H_2S gas has been shown to give not the tetranuclear clusters but the mononuclear complexes *trans*-$[MS_2(PMe_3)_4]$ as the final products.[15*n*,18]

The terminal hydrogensulfide ligands in compound **2** were readily substituted by chloride anion to give $[W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4Cl_2(PMe_2Ph)_6]$ **3** in moderate yield when **2** was heated with 1 equivalent of $SnCl_2$ in thf (Scheme 1). An X-ray analysis has shown that the structure of the W_4S_6 core in **3** is essentially identical with that of **2** (Fig. 2). Similar substitution has been already reported for the molybdenum cluster **6**, giving the corresponding molybdenum chloro cluster $[Mo_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4Cl_2(PMe_3)_6]$.[19] The IR and NMR spectral features of the chloro cluster **3** are quite similar to those of hydrogensulfido cluster **2**, except that the ν(SH) band observed in the IR spectrum of **2** disappeared in that of **3**.

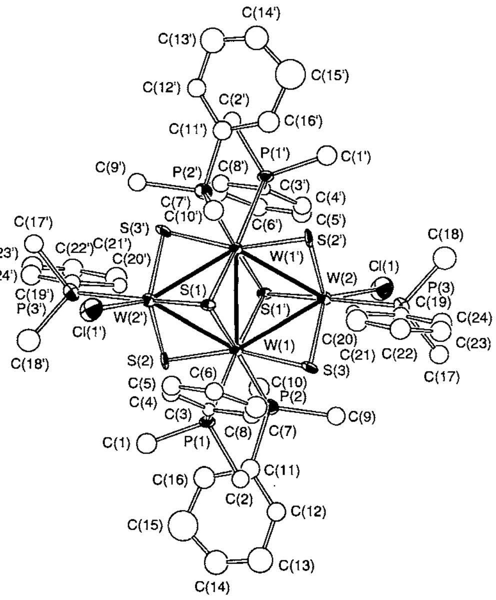


Fig. 2 Molecular structure of compound **3** with the atom numbering scheme

Crystal structures of compounds 2 and 3

The molecular structures of compounds **2** and **3** are shown in Figs. 1 and 2, and relevant crystallographic parameters are given in Tables 1 and 2.

Fig. 1 clearly indicates the tetratungsten framework arranged in an essentially equilateral raft-type geometry for compound **2**. The molecule has a crystallographically imposed inversion centre in the midpoint of the W(1)–W(1′) bond and has an approximate C_{2h} symmetry with a two-fold axis passing through the hinge tungsten atoms. The two W_3 triangles are each capped by a μ_3-sulfide ligand from mutually opposite sides of the W_4 plane and each of the four peripheral W–W edges in the raft is bridged by a μ-sulfide ligand. Thus the W_4S_6 core comprises two fused incomplete cubanes in a face-sharing manner. The coordination geometry around the hinge tungsten atom is almost

Table 2 Selected bond distances (Å) and angles (°) in compounds **2**–**4**

	2	**3**	**4**
W(1)–W(1′)	2.8373(8)	2.811(3)	2.833(1)
W(1)–W(2)	2.8114(7)	2.818(2)	2.7384(6)
W(1)–W(2′)	2.8118(6)	2.814(2)	2.9374(7)
W(1)–S(1)	2.380(2)	2.389(10)	2.373(2)
W(1)–S(1′)	2.374(2)	2.365(7)	2.391(2)
W(1)–S(2)	2.435(3)	2.422(10)	2.470(2)
W(1)–S(3)	2.435(3)	2.41(1)	2.378(3)
W(1)–P(1)	2.606(3)	2.623(7)	2.623(2)
W(1)–P(2)	2.592(2)	2.58(1)	2.609(3)
W(2)–S(1′)	2.393(2)	2.405(10)	2.405(2)
W(2)–S(2′)	2.279(2)	2.25(1)	2.225(2)
W(2)–S(3)	2.274(2)	2.228(7)	2.226(2)
W(2)–X*	2.390(2)	2.408(9)	2.339(2)
W(2)–P(3)	2.513(3)	2.51(1)	2.558(3)
W(1′)–W(1)–W(2)	59.71(2)	59.99(6)	63.61(2)
W(1′)–W(1)–W(2′)	59.69(2)	60.11(7)	56.63(2)
W(1)–W(2)–W(2′)	60.60(2)	59.90(7)	59.76(2)

* X = S(4) (**2**) or Cl(1) (**3** and **4**).

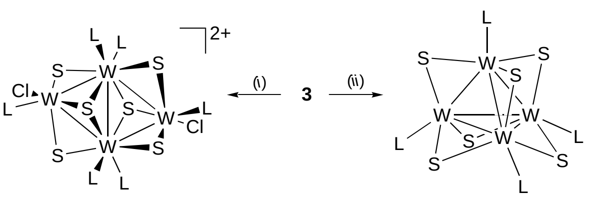
octahedral, whereas that of the wingtip tungsten atoms corresponds to a distorted trigonal bipyramid, if the W–W interactions are disregarded. The sulfur atom terminally bound to the wingtip tungsten has been characterized to be a hydrogensulfido sulfur rather than a terminal sulfide, since the final Fourier-difference map clearly showed the presence of a hydrogen atom attached to this sulfur atom [S(4)–H(34) 1.28 Å, W(2)–S(4)–H(34) 116.4°]. This assignment is also confirmed by the W(2)–S(4) distance at 2.390(2) Å, which is almost comparable to the W–SH distances so far reported (2.567–2.596 Å)[15f,†] Furthermore, this is much longer than those of the typical terminal W=S bonds (2.01–2.18 Å)[20,21] and even the exceptionally elongated W=S bonds in [$WS_2(PMe_3)_2L_2$] (2.25 Å; L = PMe_3 or CNBu^t).[15n,21]

In the $[W_4]^{14+}$ moiety of compound **2**, there are ten cluster skeletal electrons, which is consistent with the presence of the five W–W single bonds varying from 2.8114(7) to 2.8373(8) Å, although these bonds are slightly longer than the W–W distances in the $[W_3S_4]^{4+}$ incomplete cubane-type clusters (2.6728–2.784 Å).[4b,5b] Each μ-sulfide ligand bridges a hinge W and a wingtip W atom in an unsymmetrical manner: the distances to the hinge W atoms [2.435(3) Å] are considerably longer than those to the wingtip W atoms [2.274(2) and 2.279(2) Å].

The W_4S_6 core structure of compound **3** is essentially the same as that of **2**. The W–Cl bond length in **3** [2.408(9) Å] is comparable to those in [$W_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_3(L\text{–}L)_3$][$PF_6$] (2.463–2.488 Å; L–L = $R_2PCH_2CH_2PR_2$, R = Me or Et).[16,22] Raft-type metal frameworks similar to **2** and **3** have been demonstrated previously for a ten-electron niobium cluster [$Nb_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_4Cl_4(PMe_3)_6$][23] and several non-molecular compounds such as $CsNb_4Cl_{11}$,[24a] $Ba_{1.13}Mo_8O_{16}$,[24b] and $NaMo_2O_4$.[24c]

Reaction of cluster 3 with $AgOSO_2CF_3$ to give cationic cluster 4

When the chloro cluster **3** was treated with 2.4–3 equivalents of $AgOSO_2CF_3$ two-electron oxidation of **3** took place to give a cationic cluster [$W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4Cl_2(PMe_2Ph)_6$][$OSO_2CF_3$]$_2$ **4** (Scheme 2). The IR spectrum of **4** clearly shows the presence of triflate anion. The ^1H and $^{31}P\text{-}\{^1H\}$ NMR signals of **4** are significantly broadened but comparable to those of **2** and **3**. An X-ray analysis has been carried out to clarify the detailed structure of **4**; an ORTEP[25] drawing of the cationic part of **4** is depicted in Fig. 3 and selected bond distances and angles are listed in Table 2. In **4** there exists a crystallographic inversion centre in the midpoint of the W(1)–W(1′) bond. The atom connectivity in this cation is identical with that of **3**. However, the planar W_4 framework in **4** is no longer equilateral. Thus, although the backbone W(1)–W(1′) distance at 2.833(1) Å is comparable to the W–W distances in **2** and **3** [2.811(3)–2.8373(8) Å], one peripheral edge is substantially elongated [W(1)–W(2′) 2.9374(7) Å] and the other is shortened [W(1)–W(2) 2.7384(6) Å] from the W(1)–W(1′) distance, which results in dispersion of the W–W–W angles [56.63(2)–63.61(2)°] from 60°. Such deformation of the W_4 framework apparently arises from the presence of only eight skeletal electrons in **4**. Each peripheral edge is bridged unsymmetrically by a μ-sulfide ligand: the distances of W(1)–μ-S are 2.378(3) and 2.470(2) Å, while those of W(2)–μ-S are 2.225(2) and 2.226(2) Å. The W–Cl distance of 2.339(2) Å in **4** is shorter than that in **3** [2.408(9) Å].



4 **5**

Scheme 2 (*i*) $AgOSO_2CF_3$, thf, room temperature (r.t.); (*ii*) Na/Hg, thf, r.t. (L = PMe_2Ph)

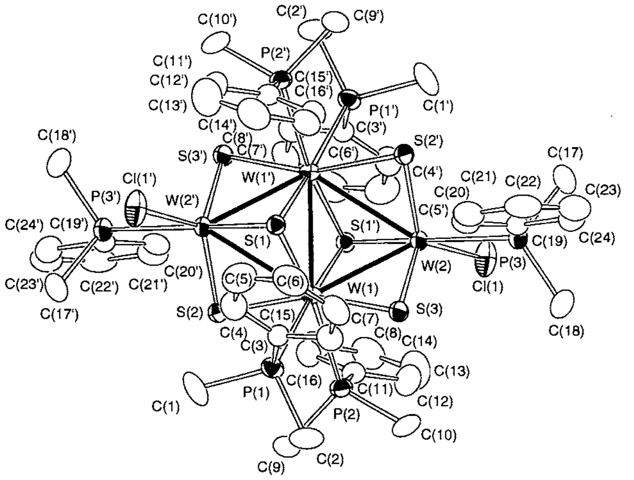


Fig. 3 Structure of the cation in compound **4**. The triflate anion is omitted for clarity

A closely related alkoxide cluster with eight skeletal electrons [$W_4(\mu_3\text{-}OEt)_2(\mu\text{-}OEt)_4(OEt)_{10}$] **7** has previously been shown to have a similarly distorted raft-type framework.[26] Cotton and Fang[27] have explained the distortion from the C_{2h} structure as the result of a second-order Jahn–Teller distortion and predicted the more regular structure (C_{2h}) for a hypothetical ten-electron cluster $[W_4(OEt)_{16}]^{2-}$, a two-electron reduced form of **7**. The present study may provide some confirmation of their theoretical prediction.

A distorted raft-type framework similar to that in compound **4** has also been found in a six-electron vanadium cluster [NEt_4]$_2$[$V_4(\mu_3\text{-}S)_2(SCH_2CH_2S)_6$][28] and a non-molecular compound $Ba_{1.13}Mo_8O_{16}$.[24b] On the other hand, in the eight-electron clusters Li_4[$Nb_4(\mu_4\text{-}S)_2(\mu\text{-}SPh)_8(SPh)_4$][29a] and [$Nb_4(\mu_4\text{-}S)_2(\mu\text{-}SPh)_8(PMe_2R)_4$] (R = Me or Ph)[29b] the regular square core has been observed.

Conversion of raft-type cluster 3 into tetrahedral cluster 5

As illustrated in Scheme 2, reduction of the chloro cluster **3** with an excess of sodium amalgam gave a novel tetratungsten hexasulfide cluster [$W_4(\mu\text{-}S)_6(PMe_2Ph)_4$] **5** in low yield. The ^1H NMR spectrum of **5** exhibits only one doublet assignable to the methyl groups in the PMe_2Ph ligands, suggesting a highly symmetrical structure for **5**. In addition, the $^{31}P\text{-}\{^1H\}$ NMR spec-

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[†] Another W–SH bond distance (2.384 Å) is also available, although the result of the X-ray analysis contains a disorder problem.[15k]

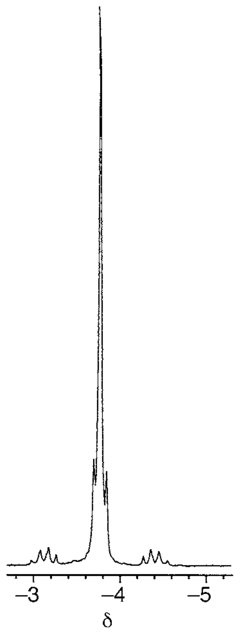

Fig. 4 The ^{31}P-{^{1}H} NMR spectrum of compound **5**

trum shows a singlet accompanied by the tungsten satellite signals (Fig. 4). This spectrum may be interpreted in terms of a superposition of the spectra derived from the spin systems of the five isotopomers: A_4 (no ^{183}W nuclei, 53.7% abundance), $A_3A'X$ (one ^{183}W, 36.1%), $A_2A'A''XX'$ (two ^{183}W, 9.1%), $AA'A''A'''XX'X''$ (three ^{183}W, 1.0%), and $AA'A''A'''XX'X''X'''$ (four ^{183}W, <0.1%),‡ although signals from isotopomers containing more than two ^{183}W nuclei were unobservable because of their low abundance and fine structures. The singlet due to the A_4 isotopomer defines the chemical shift, and the fine structure from the $A_3A'X$ isotopomer consisting of a pair of outer quartets and a pair of inner doublets overlapped by the central singlet in part shows the nuclearity of the symmetrical structure. The ^1J(WP) value of 141.0 Hz falls in the range reported for trinuclear complexes [$W_3(\mu_3\text{-}S)(\mu\text{-}S)_3X_3(dmpe)_3$][$BPh_4$] (113.9–184.2 Hz, X = Cl or H),[16] while the ^2J(WP) value (5.7 Hz) is substantially smaller than those for these trinuclear complexes (41.6 and 49.1 Hz).[16] For **5** the ^3J(PP) coupling of 10.4 Hz is also resolved.

The tetranuclear nature of cluster **5** inferred from the ^{31}P-{^{1}H} NMR spectrum has unambiguously been established by X-ray crystallography; an ORTEP drawing is depicted in Fig. 5 and selected bond distances and angles are listed in Table 3. The molecule has a crystallographically imposed S_4 axis passing through S(1$^{\text{I}}$) and S(1$^{\text{II}}$). The structure consists of an almost regular tetrahedron of tungsten atoms with each edge bridged by a μ-sulfide ligand. Each tungsten atom is bound to a dimethylphenylphosphine and thus the $W_4S_6P_4$ core has approximate T_d symmetry. The W–W distance in **5** [2.634(3) Å] is substantially shorter than those in **2** and **3** [2.811(3)–2.8373(8) Å], although it is still close to the range found in $[W_3S_4]^{4+}$ incomplete cubane-type clusters (2.6728–2.784 Å).[4b,5b] As a consequence of the reduction there are twelve cluster skeletal electrons in **5**, which form six W–W bonds.

The adamantane-like atom connectivity of the W_4S_6 core in cluster **5** is found in the cubic metal sulfide lattice known as the sphalerite or zinc blende structure, although the co-ordination geometry around the W atom is fairly distorted from an ideal tetrahedral environment [S–W–P 89.2, S–W–S 120.0° (mean)] due to the presence of W–W interactions. It is to be emphasized that most of the tetrametallic sulfide clusters containing a tetrahedral metal framework are of the cubane-type[4,5] and, to our knowledge, the adamantane-like core in **5** is unprecedented for transition-metal sulfide clusters. Among some post-transition-metal sulfide compounds including $[NMe_4]_4[M_{10}(\mu_3\text{-}S)_4(\mu\text{-}SPh)_{12}(SPh)_4]$ (M = Zn or Cd),[31a] $[Zn_{10}(\mu_3\text{-}S)_4(\mu\text{-}SEt)_{12}(NC_5H_3Me_2\text{-}3,5)_4]$,[31b] and $[Ge_4(\mu\text{-}S)_6X_4]$ (X = Br or I)[31c] as well as transition-metal oxo compounds such as $[NEt_4]_4[Ta_4(\mu\text{-}O)_6F_{12}]$,[32a] $[M_4(\eta^5\text{-}C_5Me_5)_4(\mu\text{-}O)_6]$ (M = Ti[32b] or V[32c]) and $[Mn_4(C_6H_{15}N_3)_4(\mu\text{-}O)_6]Br_{3.5}[OH]_{0.5}\cdot 6H_2O$,[32d] the adamantanoid core has been demonstrated. Tetratungsten and tetramolybdenum clusters with twelve skeletal electrons having a different metal framework are also known, which include a metallacyclobutadiene-type cluster $[W_4(\mu\text{-}OPr^i)_4(OPr^i)_8]$,[33] a square-planar cluster $[Mo_4(\mu\text{-}OPr^i)_8Cl_4]$,[34] and a butterfly-type cluster $[Mo_4(\mu_3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_4(OPr^i)_2Br_4]$.[34]

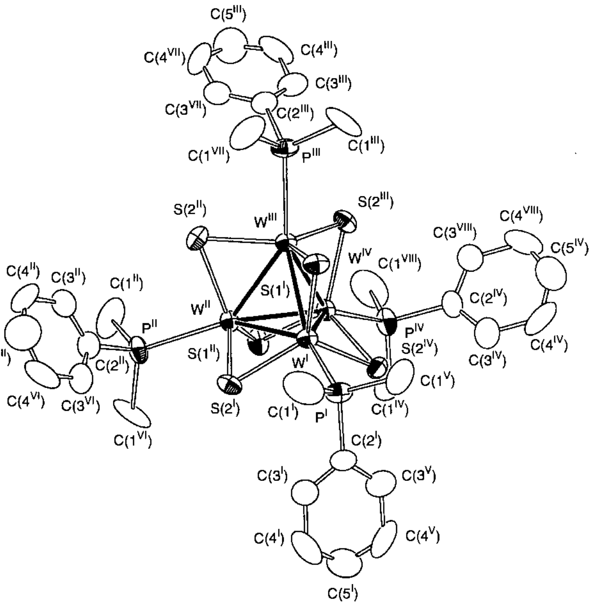

Fig. 5 Molecular structure of compound **5** with the atom numbering scheme

Table 3 Selected bond distances (Å) and angles (°) in compound **5**

W$^{\text{I}}$–W$^{\text{II}}$	2.634(2)	W$^{\text{I}}$–S(1$^{\text{I}}$)	2.32(1)
W$^{\text{I}}$–W$^{\text{III}}$	2.634(3)	W$^{\text{I}}$–S(2$^{\text{I}}$)	2.323(7)
W$^{\text{I}}$–P$^{\text{I}}$	2.533(10)		
W$^{\text{II}}$–W$^{\text{I}}$–W$^{\text{III}}$	60.00(3)	S(2$^{\text{I}}$)–W$^{\text{I}}$–S(2$^{\text{IV}}$)	119.99(6)
W$^{\text{II}}$–W$^{\text{I}}$–W$^{\text{IV}}$	60.00(6)	S(1$^{\text{I}}$)–W$^{\text{I}}$–P$^{\text{I}}$	88.8(3)
S(1$^{\text{I}}$)–W$^{\text{I}}$–S(2$^{\text{I}}$)	119.98(3)	S(2$^{\text{I}}$)–W$^{\text{I}}$–P$^{\text{I}}$	89.5(2)

Symmetry transformations used to generate equivalent atoms: II $-x, y, -z$; III $-x, -y, z$; IV $x, -y, z$.

The redox behaviour of sulfide clusters has been attracting much interest in relation to the electron-transfer and redox reactions occurring in biological systems. Previous studies have shown that the oxidation or reduction of the metal clusters leads to either slight deformation of the cluster core or distinct core transformation accompanied by apparent metal–metal bond formation or breaking. As described above, oxidation of compound **3** corresponds to the former type of reactions. Similar transformations have been observed previously in the series $[Mo_6(\mu_3\text{-}S)_8(PEt_3)_6]^{n-}$ (n = 0 or 1)[35] and $[\{Mo(\eta^5\text{-}C_5H_4Pr^i)\}_4(\mu_3\text{-}S)_4]^{n+}$ (n = 0–2).[36] On the other hand, the redox reactions of the latter type include the reductive dimerization of the molybdenum sulfide chloride cluster $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3Cl_4L_5]$ (L = PEt$_3$ or thf), which affords a raft-type hexamolybdenum cluster $[Mo_6(\mu_3\text{-}S)_4(\mu\text{-}S)_4(\mu\text{-}Cl)_2Cl_4(PEt_3)_6]$[37] or an octahedral cluster

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‡ A similar spectral feature has been observed for $[Pt_4(\mu\text{-}CO)_5(PR_3)_4]$ (R_3 = Et$_3$, Me$_2$Ph, MePh$_2$ or Et$_2$Bu^t), in which the four platinum atoms are postulated to be equivalent and form a regular tetrahedron on the NMR time-scale.[30]

$[\mathrm{Mo_6(\mu_3\text{-}S)_8(PEt_3)_6}]$[35] depending upon the reaction conditions. Interestingly, the present study has shown that the reduction of **3** leads to conversion of the raft-type core into the tetrahedral framework through an intramolecular reductive condensation. Core rearrangement from a raft type to a tetrahedron induced by ligand dissociation has been reported previously: a butterfly cluster $[\mathrm{Os_4(\mu_3\text{-}S)(CO)_{13}}]$ (62 valence electrons) loses one carbonyl ligand to give a tetrahedral cluster $[\mathrm{Os_4(\mu_3\text{-}S)(CO)_{12}}]$ (60 valence electrons) upon heating.[38]

In summary, we have found that the raft-type tetratungsten cluster **2** can be prepared by a self-assembly approach. It has also been demonstrated that the raft-type cluster **3** derived from **2** readily undergoes two-electron oxidation and reduction, the former of which results in formation of the distorted raft-type cluster of **4**, while the latter leads to conversion of the raft-type core into the tetrahedral framework in **5**.

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