Pentacoordinate Bridging Sulfido Ligand in a Square-Pyramidal Geometry. The Synthesis and Crystal and Molecular Structure of $Os_5(CO)_{15}(\mu_5\text{-}S)[W(CO)_4(PPh_3)]$

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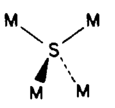
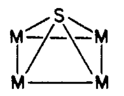
Bridging sulfido ligands have been shown to be among the most effective of all of the main-group element ligands in the stabilization of polynuclear transition-metal complexes.[1] This stems from the strong "affinity" of sulfur for the transition elements and from its great diversity of stable coordination forms. A variety of doubly, triply, and quadruply bridging structural forms have been characterized in recent years. The most common quadruply bridging forms are the tetrahedron A[2] and square pyramid B.[1b,3]



A



B

In the form A the sulfido ligand serves as a six-electron donor while in the form B it is believed to serve as a four-electron donor. Thus, in the latter case it should contain a lone pair of electrons, and, accordingly, the type B ligand should be capable of serving as a Lewis donor. However, we are unaware of any examples where this character has been demonstrated in a transition-metal complex.[4]

We have recently synthesized and structurally characterized the sulfido osmium cluster compound $Os_5(CO)_{15}(\mu_4\text{-}S)$ (**1**) and have shown that it contains a quadruply bridging sulfido ligand of the type B which bridges the square base of a square-pyramidal cluster of five osmium atoms.[3] We now wish to report that **1** reacts with $W(CO)_5PPh_3$ when subjected to UV irradiation to form the new complex $Os_5(CO)_{15}(\mu_5\text{-}S)[W(CO)_4(PPh_3)]$ (**2**) in which the quadruply bridging sulfido ligand is bonded to the tungsten atom through the formation of a S→W donor–acceptor bond.

1, 30 mg (0.021 mmol) was dissolved in 100 mL of hexane solvent at 25 °C. $W(CO)_5(PPh_3)$, 25 mg (0.043 mmol), was added and the solution was irradiated (UV) for 3 h. After this period the solvent was removed in vacuo and the residue was chromatographed by TLC on silica gel with 20/80, v/v, CH_2Cl_2/hexane solvent. Orange and red bands were eluted. The first band was **1** unreacted (8 mg). The second band was the product **2** (10.5 mg, 35% yield, based on the amount of **1** consumed).[6] Compound **2** was characterized by a single-crystal X-ray diffraction analysis. It crystallizes in the monoclinic crystal system in the space group $P2_1/c$. The unit cell was found to contain two independent molecules in the asymmetric crystal unit.[7,8] Both molecules are structurally similar, and an ORTEP diagram of one of these is shown in Figure 1.[9] The molecule consists of a square-pyramidal cluster of five osmium atoms with each metal atom containing three carbonyl ligands.[10] The base of the square pyramid is bridged by a sulfido ligand. The osmium–sulfur distances range from 2.43 (2) to 2.50 (2) Å over both molecules and are very similar to those observed in **1** which range from 2.418 (9) to 2.502 (10) Å.[3]

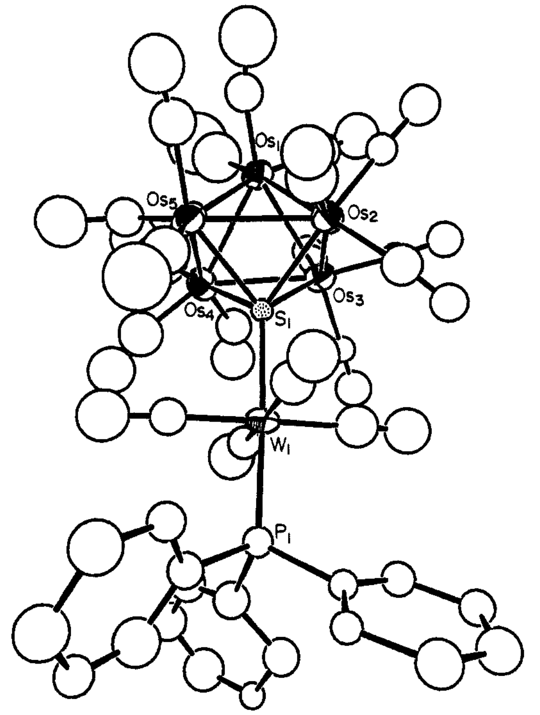


Figure 1. ORTEP diagram of one of the two crystallographically independent molecules of $Os_5(CO)_{15}(\mu_5\text{-}S)[W(CO)_4(PPh_3)]$ (**2**) showing 50% probability thermal ellipsoids. The drawing was prepared for the molecule labeled B (see supplementary material).

A $W(CO)_4PPh_3$ group is linked to the cluster by a S→W donor–acceptor bond, W(1A)–S(1A) = 2.52 (2) Å, W(1B)–S(1B) = 2.52 (2) Å. The tungsten–sulfur bond lengths are very similar to those found in the compounds $Os_3(CO)_9(\mu_3\text{-}S)(\mu_4\text{-}S)[W(CO)_5]$, 2.522 (8) Å,[11] and $Fe_3(CO)_9(\mu_3\text{-}P\text{-}t\text{-}Bu)(\mu_4\text{-}S)[W(CO)_5]$, 2.547 (6) Å,[12] which contain a $W(CO)_5$ grouping attached to a trinuclear cluster through the formation of a donor–acceptor bond with a triply bridging sulfido ligand. The PPh_3 ligand is positioned trans to the sulfido ligand in **2** in order to minimize the steric interactions between the phosphine ligand and the cluster. Four linear carbonyl ligands lie in a plane that completes the coordination sphere around the tungsten atom. The sulfido ligand lies 1.42 (1) Å [1.43 (1) Å] from the Os_4 base of the cluster. The distance is the same as that found in **1** (1.42 (1) Å) and shows that the attachment

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(1) (a) Vahrenkamp, H. *Angew. Chem., Int. Ed.* Engl. **1975**, *14*, 322. (b) Adams, R. D. *Polyhedron* **1985**, *4*, 2003.

(2) Adams, R. D.; Foust, D. F. *Organometallics* **1983**, *2*, 323.

(3) Adams, R. D.; Horvāth, I. T.; Segmuller, B. E.; Yang, L. W. *Organometallics* **1983**, *2*, 1301.

(4) A square-pyramidal structural form for sulfur has been observed in the naturally occurring minerals pentlandite and argentian pentlandite.[5]

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(6) IR spectra were recorded in hexane solvent (νCO, cm^{-1}) 2105 vw, 2091 w, 2067 vs, 2056 m, 2045 m, 2031 s, 2013 m, 2002 w, 1996 wv, sh, 1899 m. Satisfactory elemental analyses have been obtained.

(7) Red crystals of **2** were obtained only after repeated efforts by cooling solutions in CH_2Cl_2/hexane solvent to −20 °C. The crystals belong to the monoclinic crystal system. Space group: $P2_1/c$, a = 19.839 (9) Å, b = 16.461 (6) Å, c = 27.407 (10) Å, β = 92.94 (3) °, Z = 8, ρ_{calcd} = 2.92 g/cm³.

(8) Intensity data were collected on an Enraf Nonius CAD4 X-ray diffractometer by using Mo K$\bar{\alpha}$ radiation at the Molecular Structure Corp., College Station, TX. Structure solutions and refinements were performed on a Digital Equipment Corp. VAX 11/782 computer at the University of South Carolina by using the Enraf-Nonius program library SDP-PLUS. The data were corrected for the effects of absorption. The structure was solved by a combination of direct methods (MULTAN) and difference Fourier syntheses and was refined by using 3354 reflections ($F^2 \geq 5.0\sigma(F^2)$) to the final values for the residuals R = 0.0469 and R_w = 0.0552.

(9) Selected interatomic distances (Å) and angles (deg) for **2** are as follows. The quantities in brackets are for the second independent molecule (A) in the asymmetric crystal unit. Os(1B)–Os(2B) = 2.847 (3) [2.831 (3)], Os(1B)–Os(3B) = 2.822 (3) [2.869 (3)], Os(1B)–Os(4B) = 2.895 (3) [2.868 (3)], Os(1B)–Os(5B) = 2.845 (3) [2.844 (3)], Os(2B)–Os(3B) = 2.831(3) [2.863 (3)], Os(2B)–Os(5B) = 2.846 (3) [2.844 (3)], Os(3B)–Os(4B) = 2.822 (3) [2.823 (3)], Os(4B)–Os(5B) = 2.842 (3) [2.822 (3)], Os(2B)–S(1B) = 2.43 (2) [2.46 (1)], Os(3B)–S(1B) = 2.50 (2) [2.45 (2)], Os(4B)–S(1B) = 2.44 (2) [2.48 (2)], Os(5B)–S(1B) = 2.49 (2) [2.44 (2)], W(1B)–S(1B) = 2.52 (2) [2.52 (2)], Os(2B)–S(1B)–Os(3B) = 70.1 (3) [71.3 (3)], Os(3B)–S(1B)–Os(4B) = 69.7 (3) [69.8 (3)], Os(4B)–S(1B)–Os(5B) = 70.5 (3) [69.9 (3)], Os(2B)–S(1B)–Os(5B) = 70.7 (3) [70.9 (3)], Os(2B)–S(1B)–W(1B) = 125.7 (4) [125.6 (4)], Os(3B)–S(1B)–W(1B) = 128.2 (4) [121.6 (4)], Os(4B)–S(1B)–W(1B) = 124.3 (4) [125.2 (4)], Os(5B)–S(1B)–W(1B) = 124.0 (4) [128.8 (4)].

(10) The four carbonyl ligands that lie approximately in the Os_4 plane have adopted semibridging character in varying degrees. For example, Os(3B)···C(11B) = 2.78(6) Å, Os(4B)···C(13B) = 2.73 (5) Å. The IR absorption at 1899 cm^{-1} indicates that this character also exists in solution.

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of the $W(CO)_4(PPh_3)$ moiety does not pull the sulfur away from the cluster any farther. The geometry about the sulfido ligand approximates very closely that of a square pyramid, but slight differences in the Os–S distances and W–S–Os angles remove a rigorous C_{4v} symmetry.[9]

The question of the orbital hybridization at the pentacoordinate sulfido ligand is one that cannot be answered in detail at this time, but a significant contribution from the sulfur d-orbital set would seem to be very likely.

The existence of the tungsten–sulfur coordinate bond in **2** strongly suggests the existence of a lone pair of electrons on the quadruply bridging sulfido ligand in **1**. The pentacoordinate structural form of the sulfido ligand observed in **2** further extends the range of its known coordination forms and further demonstrates its versatility as a ligand.[1] It is believed that these factors can play key roles in the use of sulfido ligands to stabilize cluster complexes and to facilitate their synthesis by serving as sites for metal agglomeration.[1,13,14]

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Supplementary Material Available: Tables of fractional atomic coordinates and thermal parameters, interatomic distances, selected interatomic angles and structure factor amplitudes (53 pages). Ordering information is given on any current masthead page.

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Demonstration of Alternative Spin States in Clusters Containing the Biologically Relevant $[Fe_4S_4]^{1+}$ Core

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The clusters $[Fe_4S_4(SR)_4]^{3-}$,[1-6] containing the cubane-type odd-electron $[Fe_4S_4]^{1+}$ core, are analogues of reduced clusters in ferredoxins and other Fe–S proteins and enzymes.[7,8] Standard biological clusters of this type have spin-doublet ground states, characteristic EPR spectra centered around $g \sim 1.94$ which integrate to ca. one spin per cluster, and consistent Mössbauer spectral features. Evidence is accumulating that one or more varieties of nonstandard clusters exist, whose unconventional nature is evidenced in EPR and Mössbauer spectral properties and sometimes in redox potentials. Examples include "P-clusters" of the FeMo protein of nitrogenase[9] and the clusters in *B. subtilis* glutamine phosphoribosylpyrophosphate amidotransferase,[10] Se-reconstituted clostridial ferredoxin,[11] and the Fe protein of nitrogenase.[9,12,13] Indeed, in the crystalline state, analogue clusters $[Fe_4S_4(SR)_4]^{3-}$ do not possess uniform core structures[1,5,6] or electronic properties,[3,4] suggesting possibly similar behavior by biological clusters. One particularly arresting aspect of certain analogues is their magnetic behavior, which indicates population of low-lying states of a spin manifold with $S > {}^1/_2$,[14] a matter reexamined here.[15]

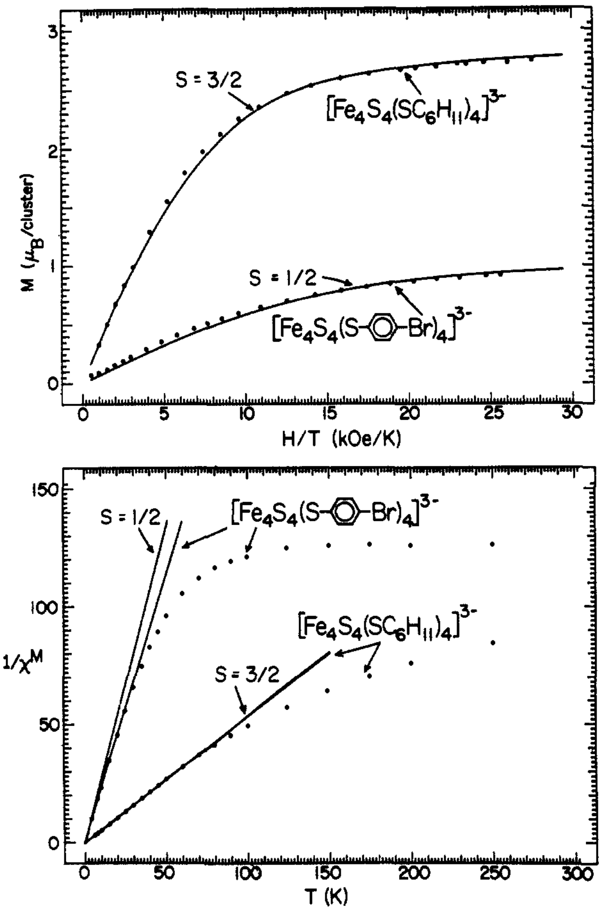

Figure 1. Magnetic properties of $(Et_4N)_3[Fe_4S_4(S\text{-}p\text{-}C_6H_4Br)_4]$ and $(Et_4N)_3[Fe_4S_4(SC_6H_{11})_4]\cdot 4MeCN$. Upper: magnetization behavior at H_0 = 50 kOe and T = 1.8–100 K. Lower: temperature dependence of the reciprocal molar susceptibility at H_0 = 5 kOe; the behaviors of $S = {}^1/_2$ and ${}^3/_2$ Curie paramagnets are indicated. Solid lines are theoretical fits[16] to the magnetization data.

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