Inorganic Synthesis in Supercritical Amines: Synthesis of [W$_4$S$_8$(H$_2$NCH$_2$CH$_2$NH$_2$)$_4$]S, Containing an Isolated Sulfide Ion

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Our research group has found that a wide variety of novel main group polyanionic clusters can be prepared quite easily in supercritical ethylenediamine (en).[1] Zintl compounds are often soluble and stable in basic amine solvents,[2] and we have been able to exploit this to prepare previously unknown phases in en between 300 and 400 °C.[1b] This thermal regime is currently receiving a great deal of attention because it is cool enough to inhibit formation of the thermodynamically stable, dense phases which form at higher temperatures. Thus chemical reactions performed in this intermediate regime produce kinetically stabilized solids. Molten fluxes have been most commonly used for these purposes,[3] but recent results have demonstrated that superheated solvents and supercritical fluids have at least as much promise for the synthesis of novel solid-state compounds.[4] Supercritical fluids are especially attractive because they are excellent media for the crystal growth of intractable solids.[5]

Recently we turned our efforts to the preparation of new ternary and quaternary solids containing early and middle transition elements. However, use of transition metal powders has met with only limited success. Previous work in our group has shown that metal carbonyls can be completely oxidatively decarbonylated by polychalcogenide anions.[6] Thus we have been investigating their use as precursors to new metal-containing solids in supercritical amines. In this communication we report the isolation of an unusual new entended solid from the reaction of K$_2$S$_4$ and W(CO)$_6$ in supercritical en.

It was found that if K$_2$S$_4$ is reacted with W(CO)$_6$ in supercritical ethylenediamine at 300 °C and autogenous pressure (approximately 3500 psi) for several days, only a bright yellow solution is obtained, which is presumably due to WS$_4$$^{2-}$. This reaction is entirely analogous to that carried out in DMF under normal conditions.[6a] However, if the reaction was carried out for a considerably shorter period of time (10 h), a mass of lustrous black/red cubes could be isolated in 31% yield.[7] These red crystals were analyzed by SEM and found to contain only tungsten and sulfur as heavy elements. They were then characterized by complete elemental analysis, IR and far-IR spectroscopy,[7] magnetic measurements on a SQUID, and single-crystal X-ray diffraction.[8]

The structure of the solid was shown to consist of a tetrahedron of tungsten atoms with each face bridged by a μ_3-sulfur atom (see Figure 1). The W–W distances range from 2.801 (2) to 2.878 (2) Å, clearly within bonding distance for tungsten sulfide clusters,[9] and the W–μ_3-S distances range from 2.36 (1) to 2.409 (9) Å, also typical for these types of compounds.[9] The net result is a highly distorted cubane having no symmetry elements. Each tungsten is also bonded by a terminal sulfide, with an average W=S distance of 2.54 (1) Å, and a chelating ethylenediamine, creating a pseudooctahedral coordination environment around each metal. This W=S distance is quite long for a terminal sulfide, and we attribute this to the steric congestion around the metal centers. In addition to these clusters, the lattice also contains *lone sulfide atoms stabilized only by hydrogen bonding to chelated ethylenediamine molecules.* To our knowledge this is the first example of a truly lone sulfide dianion not stabilized by highly ionic lattice interactions, as in BaS or Na$_2$S for example.[10] The IR clearly shows bands assignable to en, but there are no bands in the region between 2300 and 2600 cm^{-1} which could be assigned to S–H stretches. The far-IR has a series of strong bands from 635 to 253 cm^{-1}, which can be assigned to combinations of W–S and W–N stretches, as well as some broad bands at low wavenumber (150–80 cm^{-1}) probably due to W–W stretches.[11]

The lone sulfide atom is stabilized by four hydrogen bonds from four different coordinated nitrogen atoms on three different

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(7) According to the method of Rabenau,[5c] a $^1/_4$-in. tube 10 cm in length was charged with 170 mg (0.48 mmol) of W(CO)$_6$ and 100 mg (0.49 mmol) of K$_2$S$_4$, 0.7 mL of ethylenediamine (50% fill) was added, and the tube was sealed under vacuum. The tube was transferred to a Parr 4740 autoclave, counterpressured with 2000 psi of argon, and heated at 300 °C in a tube furnace for 10 h. After cooling and depressurizing, the tube was frozen in liquid N$_2$ and opened. (*Caution: tubes can build up internal pressure and should be opened behind a blast shield!*) The solution was decanted, and the product was washed with en (3 × 1 mL) and THF (3 × 1 mL) and dried. Yield: 47 mg, 31%. Anal. Calcd for C$_8$H$_{32}$N$_8$S$_9$W$_4$: C, 7.6; H, 2.6; N, 8.9; S, 22.8; W, 58.2. Found: C, 8.1; H, 2.9; N, 8.9; S, 22.7; W, 55.8. IR (Nujol mull), cm^{-1}: 1553 (s), 1321 (m), 1286 (m), 1173 (s), 1047 (vs), 1012 (m), 526 (m), 461 (m), 432 (m), 268 (s), 253 (s), 150–80 (m, br).
(8) Crystal data for [W$_4$S$_8$(H$_2$NCH$_2$CH$_2$NH$_2$)$_4$]S, monoclinic, *P*2$_1$/*c*, *Z* = 1, *a* = 13.771 (3) Å, *b* = 19.209 (4) Å, *c* = 13.771 (3) Å, *β* = 109.64 (3)°, *V* = 2850.9 (9) Å^3 at 294 K, λ = 0.710 73 Å, μ = 36.0 cm^{-1}, f_{000} = 1680.00, 4028 reflections measured to 2θ(Mo Kα$_1$) = 45°, 3711 unique (R_{int} = 0.090), ψ-scan absorption correction (transmission factors 0.56–1.00), *R* = 0.0552, R_w = 0.0630 for 2282 reflections having $F_o^2 > 3σ$-(F_o^2); tungsten and sulfur atoms refined anisotropically, carbon and nitrogen isotropically.
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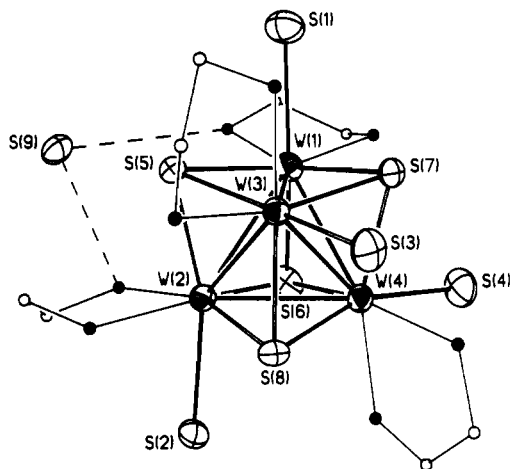(11) Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1986; p 331.

Figure 1. ORTEP plot (35% probability ellipsoids for W and S atoms) of [W$_4$S$_8$(H$_2$NCH$_2$CH$_2$NH$_2$)$_4$]S. Some significant distances in angstroms: W(1)–W(2), 2.878 (2); W(1)–W(3), 2.808 (2); W(1)–W(4), 2.802 (2); W(1)–S(1), 2.549 (8); W(1)–S(5), 2.395 (9); W(1)–S(6), 2.403 (7); W(1)–S(7), 2.381 (8); W(1)–N(1), 2.292 (36); W(1)–N(2), 2.239 (33); S(9)–N(1), 3.420; S(9)–N(3), 3.308; S(9)–N(5), 3.390; S(9)–N(6), 3.404. Some significant angles in degrees: S(1)–W(1)–S(6), 163.7-(3); S(1)–W(1)–S(7), 86.9 (3); S(5)–W(1)–S(6), 102.1 (3); S(5)–W(1)–S(7), 106.0 (3); N(1)–W(1)–N(2), 76.7 (13).
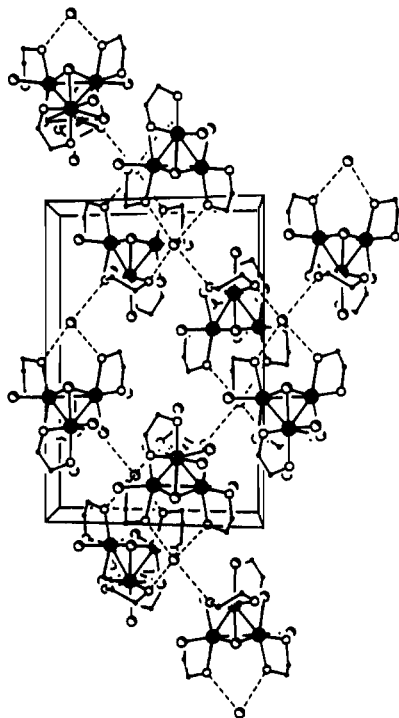

Figure 2. Unit cell of [W$_4$S$_8$(H$_2$NCH$_2$CH$_2$NH$_2$)$_4$]S, showing how the structure is built up through N–S hydrogen bonding to the lone sulfide atom. The open structure is clearly visible.

clusters. The hydrogen-bonding environment around the sulfide atoms is four-coordinate with N⋯S(9) distances ranging from 3.34 to 3.42 Å. The overall effect is the formation of a lattice held together by the extensive hydrogen-bonding network. As with many hydrogen-bonded compounds, the lattice has a fairly open structure, with moderately sized gaps in the unit cell (Figure 2). Since sulfides are less basic than first-row anions, observable hydrogen bonding is rare. However, the observed distances are comparable to those previously reported in (N$_2$H$_5$)(SH) and thiourea.[12] The solid is completely insoluble in DMF or water

and the crystals are stable in air for an indefinite period of time at room temperature.

Magnetic susceptibility data were recorded in the range 6–400 K at 2 kOe on a superconducting SQUID susceptometer using procedures reported elsewhere.[13] The data are plotted in Figure S1 (supplementary material). Although there are some deviations from the Curie–Weiss law, a least-squares fit of the data to the expression $\chi = C(T - \Theta)$ gives a Weiss constant of $\Theta = -4.6$ K and $C = 0.569$ emu K/mol. The Curie–Weiss fit is illustrated in the figure as the smooth line drawn through the point of inverse susceptibility plotted as a function of temperature (see inset). At 400 K, the magnetic moment is 2.67 μ_B per molecule, slightly less than the 2.83 μ_B expected for the $S = 1$ spin-only moment and consistent with the presence of two unpaired electrons per cluster. Therefore the data can be interpreted as localized moments with minimal interaction between the cubanes. The Θ term is small and may be due to a small amount of zero-field splitting of the $S = 1$ state, consistent with slight antiferromagnetic interactions between the different W$_4$S$_8$ fragments.

The presence of a sulfide dianion imparts a 2+ charge on the cubane cluster. In the presence of eight-coordinated sulfides, the metal core should consist of two W(IV) and two W(V) formal oxidation states. This leaves six metal valence electrons delocalized in metal–metal-bonding orbitals. Harris has shown that for octahedrally coordinated metal–sulfur cubanes, the predominantly metal core bonding orbitals consist of six low-lying metal-centered orbitals, which can be broken up into a$_1$, e, and t$_2$ states.[14] The a$_1$ is generally considered to be far below the other two states, followed by the e and the t$_2$. However, it is possible for the t$_2$ state to be lower in energy than the e state.[15] This would result in four electrons delocalized in three degenerate states, accounting for the observed paramagnetic behavior. Despite the large number of metal sulfide cubanes, there are relatively few tungsten cubanes to fully explore this postulate.[14]

The unusual nature of a lone sulfide led us to consider other possibilities, such as the presence of trace adventitious chloride or potassium ions, but this is clearly ruled out by SEM results, independent elemental analysis, and the high yield and reproducibility of the reaction. The possibility of SH$^-$ is also ruled out by the four-coordinate hydrogen-bonding environment around the sulfide, the lack of any S–H stretch in the IR, and the magnetic susceptibility data. To confirm that formation of the product is not due to any unusual contribution of potassium ion, the reaction was also performed successfully by starting with only elemental sulfur rather than any premade polysulfide, and the product was shown to be identical by IR, far-IR, and unit cell determination. We also considered the possibility that the long bonds on the terminal sulfides on the metal cubane are actually due the presence of coordinated SH groups. However, the lack of S–H stretches in the region of 2500 cm^{-1} in the IR and the fact that SH groups coordinated to a dication would probably be deprotonated by either S^{2-} or en make this unlikely. There is no obvious way to test this, as S–H stretches are often weak in the IR and the magnetic data could also be fitted for a 10-electron cluster if the e state drops below the t$_2$ state.

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