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Frederick D. Lewis,[20a]* Charles E. Hoyle[20b]

Department of Chemistry, Northwestern University
Evanston, Illinois 60201

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Synthesis of Ternary Metal Sulfide Arrays

Sir:

Metal-sulfur aggregates are currently of interest because of their unusual structural and bonding features,[1] and because of possible relevance to biological electron transfer processes[2-4] and fixation of atmospheric gases.[5,6] We report here the synthesis, by a novel deoxygenation reaction of dithiotungstates, $WO_2S_2^{2-}$, of a new class of neutral ternary metal sulfur arrays containing tungsten and a group 1b metal and the structural characterization of a representative member of this class, $(Ph_2PCH_3)_2Au_2WS_4$.

Formerly,[7] it was thought that reactions of transition metal ions with MoS_4^{2-} or WS_2^{2-} in water led to MoS_2 or WS_2 and metal sulfide. Müller and co-workers[8] showed that, by careful attention to reaction conditions, anionic complexes of the type $M(M'S_4)_2^{2-}$ (M = Co, Ni, Zn; M′ = Mo, W) could be prepared and we[9] found that similar reactions involving $WO_2S_2^{2-}$ and rare earth ions produced metal tungstates by hydrolysis processes. To extend our previous work, metathetic reactions of $WO_2S_2^{2-}$ in nonaqueous solvents were carried out.

In certain cases, such reactions proceeded cleanly to give the expected product. Thus, orange (diphos)$NiWO_2S_2$ (**1**) was prepared in 42% yield from (diphos)$NiCl_2$ and $(Ph_3PCH_3)_2WO_2S_2$ (**2**) in dichloromethane.[10] The infrared spectrum of **1** showed ν_{WO} at 928, 918, 910, and 890 cm^{-1} and ν_{WS} at 457(sh) and 452 cm^{-1}; it may be a mixture of isomers. In systems containing labile, nonchelating phosphines, however, deoxygenation of $WO_2S_2^{2-}$ occurred. Reation of **2,** copper(I) chloride, and diphenylmethylphosphine in dichloromethane at room temperature afforded, after chromatography on silica gel, a 22% yield (based on tungsten) of diamagnetic, yellow crystalline $[(Ph_2PCH_3)_2Cu]_2WS_4$ (**3**):[11] mp 175–176°, ν_{WS} 451, 438 cm^{-1}, $\Delta\nu$ (Raman) 470, 458, 246 cm^{-1}, $\lambda_{\max}$ (1,2-$C_2H_4Cl_2$, log ϵ) 410 (3.42), $\delta\,^{31}P$ 129.3 ppm,[12] $\delta\,^1H - 1.70$ (d, $^2J_{PCH} = 4.2$ Hz), $\chi_g - 0.38 \times 10^6$ cgs. A similar synthesis employing silver hexafluorophosphate produced yellow $[(Ph_2PCH_3)_2Ag]_2WS_4$[11] (**4**) in 25% yield: mp 145–146° dec, ν_{WS} 463, 447, $\lambda_{\max}$ 392 (3.04), $\delta\,^{31}P$ 134.0, $\delta\,^1H - 1.85$ ppm (d, 3.5), Λ_M 7.57 ohm^{-1} cm^2 mol^{-1} (CH_3NO_2). The absence of ^{31}P-$^{107,109}Ag$ coupling at ambient temperatures indicates the occurrence of rapid ligand exchange.[13] This has been substantiated by molecular weight determinations: calcd, 1328; found, 502 ($CHCl_3$), 676 (C_6H_6).

Solutions of **4** in donor solvents such as acetone or acetonitrile were unstable and deposited large orange crystals of $[(Ph_2PCH_3)Ag]_2WS_4$ (**5**) on standing at room temperature:[11] mp 149° dec; ν_{WS} 447, 432 cm^{-1}; $\lambda_{\max}$ 383 (3.16); $\delta\,^1H - 1.98$ (d,6), along with diphenylmethylphosphine. An analogous gold complex,[11] **6,** $[(Ph_2PCH_3)Au]_2WS_4$, was synthesized from **2** and $(Ph_2PCH_3)AuCl$: mp 175° dec; ν_{WS} 445, 438 cm^{-1}; $\Delta\nu$ 460(s), 449, 441, 272 cm^{-1}; $\lambda_{\max}$ 402 (3.76); $\delta\,^{31}P$ 88.0 ppm; $\chi_g - 0.38 \times 10^6$ cgs. Associative ligand exchange in **6** was observed. The ^1H NMR spectrum in acetone-d_6 contained a doublet at −2.57 ppm which collapsed to a singlet upon addition of excess diphenylmethylphosphine.

Crystals of the gold–tungsten sulfide **6** were grown from dichloromethane–cyclohexane. They are monoclinic, $P2_1$ (No. 4, C_2^2) with $a = 16.542$ (7) Å, $b = 13.504$ (4) Å, $c = 6.647$ (2) Å, $\beta = 96.18$ (2)° $d_{\text{calcd}} = 2.494$ g cm^{-3} for $z = 2$, and d_{found} (flotation) = 2.51. Data were collected at −160 °C on a diffractometer equipped with a highly oriented graphite monochromator and molybdenum tube source and using a standard θ–2θ scan technique. A total of 2709 unique intensities were collected, corrected for absorption, and reduced in the usual manner. The metal atoms were located by direct methods and Patterson techniques, and all remaining nonhydrogen atoms were located in three successive Fourier syntheses. Full matrix anisotropic least-squares refinement converged at $R(F) = 0.0265$. The structure shown in Figure 1, consists of a tetrahedral WS_4 core with S–W–S angles ranging from 108.54 to 111.55° and $d(W–S)_{av} = 2.22$ Å. The gold atoms are bound to opposite pairs of sulfur atoms with $d(Au–S)_{av} = 2.53$ Å, $\angle S–Au–S_{av} = 98°$, and $\angle W–S–Au$ (av) = 75.15°. The phosphorus lies in the S–Au–S plane with $d(Au–P)_{av} = 2.27$ Å and $\angle P–Au–S = 131°_{av}$.

Structurally characterized materials containing trigonally coordinated Au(I) are rare, but the geometry about gold in **6** approximates that found in the salt $[(Ph_3P)_3Au]B_9H_{12}S$.[14] The tungsten–sulfur bond distance is 0.05 Å greater than in $(NH_4)_2WS_4$,[15] indicating the expected decrease in W–S bond order. A singular feature of the structure is the sharply acute Au–S–W angles. The 2.84 Å gold–tungsten distance is 0.06 Å longer than the sum of the atomic radii for these two metals. More significantly, the observed distortion of the $AuWS_2$ rhombus may imply a direct, transannular gold–tungsten bonding interaction[16] and, indeed, the importance in less constrained systems of the angles about bridging atoms as a measure of interactions between the atoms being bridged has been pointed out many times.[19-21] Metal-metal bonding might appear to be a logical consequence of placing two metals of

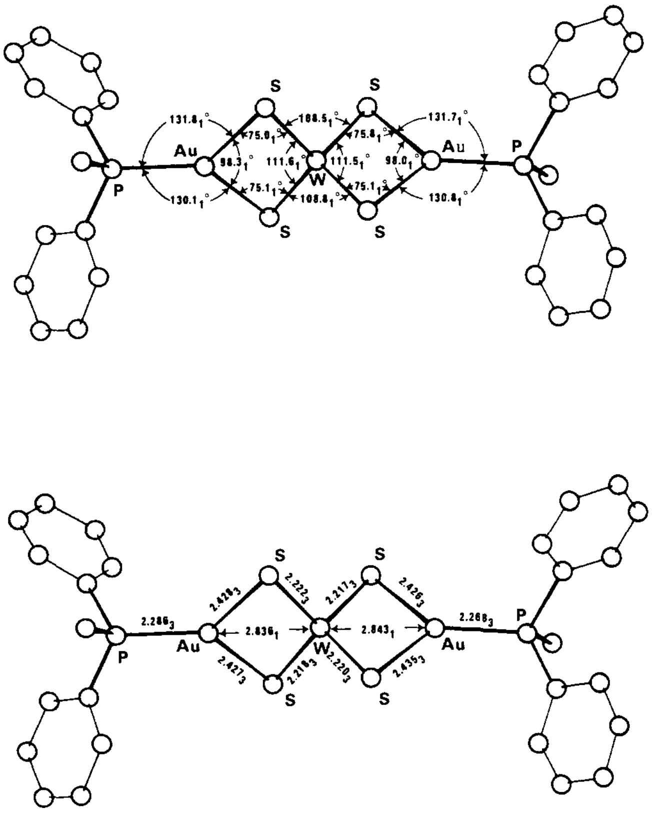

Figure 1. Molecular structure of $(Ph_2PCH_3)_2Au_2WS_4$.

greatly different formal oxidation states, Au(I) and W(VI), in close proximity as they are in **6**.[22]

Additional experiments have revealed that a like deoxygenation with tertiary phosphines cannot be applied to $MoO_2S_2{}^{2-}$ but the molybdenum analogues of **3** and **6** are readily obtained from $(Ph_3PCH_3)_2MoS_4$.

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(23) Certain commercial services have been identified in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the services identified are necessarily the best available for the purpose.

J. C. Huffman
Department of Chemistry, Indiana University
Bloomington, Indiana 47401

R. S. Roth, A. R. Siedle*
Institute for Materials Research
National Bureau of Standards
Washington, D.C. 20234

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Heavy-Ion Radiolysis of Solid Glycine[1]

Sir:

The increasing interest[2] in the effects of heavy-ion beams on biological systems emphasizes the need for detailed information on the effects of linear energy transfer (LET) in the radiation chemistry of biochemical compounds. Henriksen[3] has examined the effects of LET on the ESR spectra of free radicals formed in solid amino acids and peptides by heavy-ion beams, but no detailed radiation chemical studies of such systems have appeared to date.

We have chosen solid glycine for initial investigation because the mechanism of the γ-radiolysis of this biochemical compound has been formulated in detail,[4,5] i.e.

$$NH_3{}^+CH_2COO^- \rightsquigarrow (NH_3{}^+CH_2COO^-)^+ + e^- \quad (1)$$

followed by

$$(NH_3{}^+CH_2COO^-)^+ \rightarrow NH_3{}^+\dot{C}HCOO^- + H^+ \quad (1a)$$

$$e^- + NH_3{}^+CH_2COO^- \rightarrow NH_3 + \dot{C}H_2COO^- \quad (2)$$

where $NH_3{}^+\dot{C}HCOO^-$ and $\dot{C}H_2COO^-$ represent the long-lived free radicals oserved at room temperature by ESR spectroscopy.[6] On dissolution of the irradiated solid in O_2-free water, these radicals are removed essentially quantitatively through the reaction

$$NH_3{}^+\dot{C}HCOO^- + \dot{C}H_2COO^- \rightarrow NH_2{}^+{=}CHCOO^- + CH_3COO^- \quad (3)$$

The imino acetic, $NH_2{}^+{=}CHCOO^-$, is labile and hydrolyzes spontaneously

$$H_2O + NH_2{}^+{=}CHCOO^- \rightarrow NH_4{}^+ + CHOCOO^- \quad (4)$$

The overall stoichiometry with γ-rays corresponds to $G(NH_3) \simeq 5$, $G(CH_3COOH) \simeq G(CHOCOOH) \simeq 2.5$.

We now have measured the yields of these reactions as a function of LET using beams of H^+, He^{2+}, Be^{4+}, C^{6+}, and Ne^{10+} at energies of ~10 MeV/nucleon. Some physical parameters of these beams are summarized in Table I.

A modification of the standard beam optics of the LBL 88-in. cyclotron[7] was employed so that dosages and dose rates are comparable to those employed in earlier γ-ray studies. Details of the irradiation procedures have been fully described in a recent publication.[8] The analytical techniques and procedures used in the present work were developed in our earlier studies.[5,9,10]